

ADVANCES IN ELECTROMETALLURGY

2, 2006

Quarterly

English translation of the quarterly «Sovremennaya Elektrometallurgiya» journal published in Russian since January 1985

Founders: E.O. Paton Electric Welding Institute of the NASU
International Association «Welding»

Publisher: International Association «Welding»

Editor-in-Chief B.E. Paton

Editorial Board:

D. I. Dyachenko
exec. secr. (Ukraine)
J. Foc (France)
Ö. El Gammäl (Germany)
I. I. Gasik (Ukraine)
G. I. Grigorenko
vice-chief ed. (Ukraine)
B. Eorouhich (Slovenia)
V. I. Lakomsky (Ukraine)
V. É. Lebedev (Ukraine)
S. F. I edina (Spain)
L. B. I ädivär (Ukraine)
Ä. I itchel (Canada)
B. Ä. I vchan (Ukraine)
Ä. N. Petrunko (Ukraine)
V. Ramakrishna Rao (India)
Ts. V. Râshâv (Bulgaria)
N. P. Örigub (Ukraine)
A. A. Troyansky (Ukraine)
I. L. Zhadkevich (Ukraine)

Executive director

A. T. Zelnichenko

Translator

V. F. Örets

Editor

N. A. Dmitrieva

Electron galley

I. S. Batasheva,

T. Yu. Snegiryova

Editorial and advertising offices

are located at PWI:
International Association «Welding»,
E.O. Paton Electric

Welding Institute of the NASU,
11, Bozhenko str., 03680,
Kiev, Ukraine

Tel.: (38044) 287 67 57,
529 26 23,

Fax: (38044) 528 04 86

E-mail: journal@paton.kiev.ua

http://www.nas.gov.ua/pwj

Subscriptions:

4 issue per year;

184\$ — regular, **150\$** — for subscription
agencies, **100\$** — for students;
postage and packaging included.
Back issues available.

All rights reserved.

This publication and each of the articles
contained herein are protected
by copyright.

Permission to reproduce material
contained in this journal must be obtained
in writing from the Publisher.

Copies of individual articles may be
obtained from the Publisher.

CONTENTS

Towards the 90 birthday anniversary of Prof. B.I. Medovar

**Paton B.E., Medovar L.B., Saenko V.Ya., Tsykulenko A.K.,
Fedorovsky B.B., Us V.I. and Shevchenko N.T.** On welding,
metals science and metallurgy in the scientist heritage or on present
status and future of special electrometallurgy 2

ELECTROSLAG TECHNOLOGY

Eryomin E.N. and Zherebtsov S.N. Centrifugal electroslag casting
of tractor bushings of turning hinge 5

ELECTRON BEAM PROCESSES

**Grechanyuk N.I., Osokin V.A., Grechanyuk I.N., Kucherenko
P.P., Minakova R.V., Golovkova M.E. and Kopylova G.E.**
Composite materials on base of copper and molybdenum,
condensed from vapor phase, for electric contacts. Structure,
properties, technology. Part 2. Fundamentals of electron beam
technology for producing materials for electric contacts 8

PLASMA-ARC TECHNOLOGY

**Zhadkevich M.L., Shapovalov V.A., Melnik G.A., Zhirov D.M.,
Zhdanovsky A.A., Tsykulenko K.A. and Prikhodko M.S.** Plasma
liquid-phase reduction of iron from its oxides using gaseous reducers 18

GENERAL PROBLEMS OF METALLURGY

**Borisova A.L., Borisov Yu.S., Adeeva L.I., Tunik A.Yu., Karpets
M.V. and Doroshenko L.K.** Effect of alloying on composition,
structure and properties of powders of alloy AlCuFe, containing
quasi-crystalline phase 22

**Firstov S.A., Zamkov V.N., Brodnikovsky N.P., Topolsky V.F.,
Kotko A.V., Samelyuk A.V. and Golovash A.V.** Investigation of
structure and mechanical properties of
Ti-7.2Al-2.9Mo-2.7W-3Nb-2.3Zr-0.4Si alloy 30

ELECTROMETALLURGY OF STEEL AND FERROALLOYS

**Novikov N.V., Kapran I.I., Sokolov K.D., Gasik M.I. and
Ovcharuk A.N.** Innovation technological processes of electric
furnace ferronickel refining by progressive industrial methods.
Information 2. Thermodynamic investigations of processes and
technology of ladle desulfuration of electric furnace ferronickel by
sodium carbonate 36
Sojfer V.M. The Danieli metallurgical equipment 42

ENERGY AND RESOURCE SAVING

Petrov B.F. and Lakomsky V.I. To issue on specific electric
resistance of thermoanthracite 46
Matveev V.V. Economic efficiency of railway wheel profile renovation
by surfacing of worn treads 49
**Petrov S.V., Marinsky G.S., Chernets A.V., Korzhik V.N. and
Mazunin V.M.** Application of steam-plasma process for pyrolysis of
organic wastes including medical and other hazardous ones 55

NEW MATERIALS

Lakomsky V.I. New functional material — oxide cathode of welding
electric arc. Information 2 60

INFORMATION

Theses for a scientific degree 64
Developed at PWI 7, 41

ON WELDING, METALS SCIENCE AND METALLURGY IN THE SCIENTIST HERITAGE OR ON PRESENT STATUS AND FUTURE OF SPECIAL ELECTROMETALLURGY*

B.E. PATON, L.B. MEDOVAR, V.Ya. SAENKO, A.K. TSYKULENKO, B.B. FEDOROVSKY,
V.I. US and N.T. SHEVCHENKO

E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

On 29th of March 2006 uncommon man and prominent welder-scientist, metal scientist and metallurgist, academician of the NAS of Ukraine Boris I. Medovar (1916–2000) would have been 90. Bibliographic publication, issued in 1986 to his 70th anniversary, rather fully represents life and creativity of the scientist**. Last 14 years of his life the scientist continued to work selflessly, first of all over the main topic of all his scientific activity — ESR. ESR and the whole range of scientific and practical problems connected with his favorite work remained till the end of life of B.I. Medovar the backbone of his scientific interests. Despite idle talks that ESR is not needed by state-of-the-art metallurgy, he continued purposeful investigations in this field, because he understood well both world trends in development of special electrometallurgy and place of ESR in production of steels and alloys for so called «critical application».

In the ocean of steel, which is annually produced by mankind, share of the electroslag metal makes up only 800 ths t. In other words, a little bit less than 0.1 %. But the fact that without this seemingly negligibly small volume, a drop in the ocean of metal, state-of-the-art engineering, first of all power engineering, is impossible, was understood by the scientist as far back as in early 1970s of the previous century. Already at that time B.I. Medovar publicly stated that ESR had great prospects, because only ESR ensured the highest local rate of solidification in comparison with other processes of special electrometallurgy and, as a result, higher hot plasticity of super-alloys — alloys, which determined progress in power engineering and the whole life activity of people.

Really, after short-term reduction of volumes of production and investments, caused by termination of cold war, stable growth in special electrometallurgy

(including ESR) has been continued for 10 years. In particular, production of metals using remelting processes has been annually increased within this period on average by 4–5 %. This growth is achieved due to maximally efficient use of available capacities and construction of new furnaces.

So, according to different sources, within these 10 years more than 10 ESR furnaces were built in industrially developed countries, first of all furnaces of chamber type, designed for production of super-alloys and high-alloy steels of «energy designation». Moreover, Austrian colleagues were able to implement on commercial scale developed in PWI under guidance of B.I. Medovar process called by him ESR DC (ESR with double-circuit scheme of power supply) in which one power supply circuit is a traditional chain represented by the transformer–short circuit–consumable electrode–slag pool–metal pool–ingot–bottom plate–short circuit–transformer, and second power supply circuit is represented by the second transformer–short circuit–current carrying mould–slag pool–metal pool—... and than may be implemented one of numerous versions of a circuit closure both on the mould proper, on an ingot–bottom plate–transformer and using any other physically possible method.

In Figure 1, *a* the most tested by now scheme of ESR DC implementation is presented.

Peculiar feature of the ESR DC process is break of rigid ratio between supplied to the metal being re-melted power and rate of the ingot build-up. So, implementation of ESR DC allows performing melting of alloys, which are especially sensitive to various kinds of segregation processes, first of all super-alloys, under much more favorable conditions than in classical processes of remelting.

In Figure 1, *b* longitudinal section of an ingot molten from practically flat form of bi-phase zone is

*In continuation and development of the article published to jubilee of B.I. Medovar in journal «Avtomaticheskaya Svarka», 2006, No. 3.

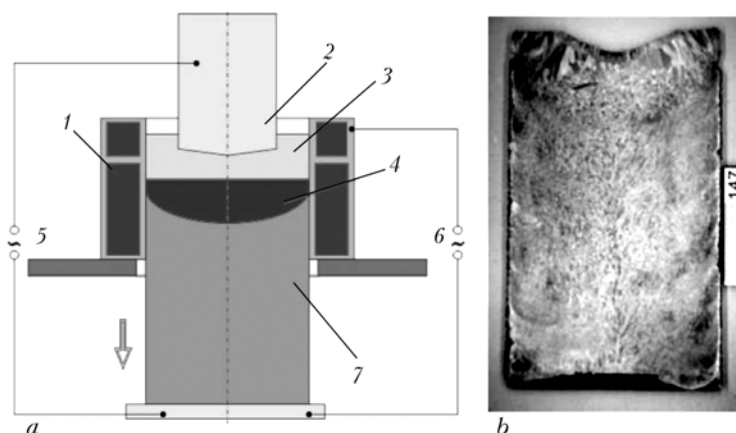


Figure 1. Electroslag remelting according to double-circuit scheme ESR DC: 1 — water-cooled current conducting mould; 2 — consumable electrode; 3 — slag pool; 4 — metal pool; 5, 6 — power sources; 7 — ingot

presented as example of ESR DC possibilities. We assume that exactly these works of B.I. Medovar have nowadays principal significance for power engineering industry and energy safety of the country. Because, as showed course of science and technology development, nowadays and in near future power plant engineering industry will need big forged pieces from high-alloy steels and alloys for rotors and disks of steam and gas turbines. In particular, for heat-electric generation plants of Ukraine and CIS countries temperature of live steam 540–550 °C is characteristic as before, while developed countries transfer their heat power stations at working temperatures 625–650 °C. For using such temperatures steels with base composition 12 % Cr–1.5 % W are needed. Rotors of steam turbines from such steels are manufactured nowadays only from ESR ingots of 100 t and higher mass. Moreover, flat solidification front, ensured by ESR DC, allows implementing old ideas of developing a rotor of changeable over its length chemical composition.

But steam turbines are just a part of state-of-the-art power engineering industry, in which gas power engineering turbines acquire ever growing significance. Metal for gas turbines is also mainly the metal produced by the methods of special electrometallurgy. What is special electrometallurgy (SEM) nowadays? In which form is it and will be connected with power engineering in near future? In Figure 2* interconnection of main SEM technological processes and principal possibilities of enterprises of Ukraine in production of billets of rotors and state-of-the-art turbine disks are shown.

Production of steels and alloys for power engineering industry is based on triple or double remelting according to the scheme VIM–ESR–VAR or VIM–ESR or ESR of the open melting metal and out-of-furnace treatment, including vacuum one. Metallurgic basis of existing power engineering industry of Ukraine and majority of industrially developed countries was formed more than 30 years ago. The basis of power engineering metallurgy in the USSR and

Ukraine had to become and became Kramatorsk Machine-Building Center — pride of national machine-building industry Novo-Kramatorsk Machine-Building Works and Plant of Castings and Forged Pieces (LIP), which is called nowadays «Energomashspetsstal». Unfortunately, it is impossible to start at present in Ukraine (or any CIS country) production of state-of-the-art steam and gas turbines from the national metal, because the metallurgists lack respective equipment. But in the works of our institute carried out under guidance of B.I. Medovar during last years of his life and proposed after his death scientific basis of ESR of steels and alloys for state-of-the-art power engineering industry was developed. Moreover, taking into account application in power engineering industry of more and more sensitive to zonal segregation alloys, in this works bases for the electroslag enlargement of ingots, practically to any needed by the power engineering industry workers size, was laid with a margin for future.

There are several especially favorite objects of investigation on long creative way of the academician.

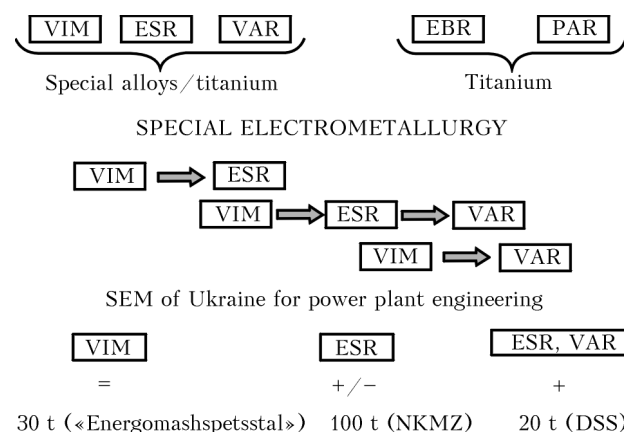


Figure 2. Special electrometallurgy and its possibilities in Ukraine: VIM — vacuum-induction melting; VAR — vacuum arc remelting; ESR — electroslag remelting; EBR — electron beam remelting; PAR — plasma-arc remelting (EBR and PAR on cold bottom is mainly used for melting titanium ingots); NKMZ — Novo-Kramatorsk Machine-Building Works; DSS — «Dneprospetsstal»

*Krylov, V. (2006) On energy safety of the country, Ukrainian metallurgical science and ... life! *Metally*, 3, pp. 50–51.



Figure 3. Discussion in workshop of IA «Zhdanovtyazhmash» (at present «Azovmash», Mariupol, Ukraine), 1983. From left to right: Prof. A.D. Chepurnoj, Dr. G.P. Klimenko, Academician of NASU B.I. Medovar, Dr. P.S. Nefyodov, Academician B.E. Paton, Dr. D.P. Nagaevsky

Rather many of them are connected with welding, especially with welding of pipes of big diameter and welding of high-temperature austenite steels and alloys. But his approach to the metals science was based not just on deep theoretical knowledge, but also on real knowledge of the industry and understanding of its needs and trends of development. Having combined in one person experience and knowledge of a metals scientist, a welder and a metallurgist, talent of a researcher-experimenter, and sharp-sighted eye of an engineer, the academician dealt for the whole his life with the most acute problems in his field of science and engineering, being even not at the «spearhead», but ahead of the «spearhead» of the main attack.

Indefatigable thirst of new, constant interest to new tasks, ability to infect colleagues with his vision of problems and ways of their solution attracted to the scientist not just his employees, but also colleagues from other SRI and industrial enterprises (Figure 3). They joked sometimes in PWI that B.I. Medovar made the whole institute to work for him. It is quite evident that it is impossible to implement in the research institute this kind of fruitful joined efforts by administrative measures. People, who try to work creatively, are united only by common ideas. And he was always rich in ideas and was not afraid to share them. In addition, the academician had good capacity for teaching and was able to find and target at the research work capable youth. It is not without reason that among his disciples there are about one hundred candidates and more than two dozen doctors of sciences. His fantastic work capacity charged with energy his colleagues who worked side by side with him.

There are many examples, which show how bravely the scientist went against settled concepts. Perhaps the most striking of them is refusal from ESR of conventional structural low- and medium-alloyed steels. Before eyes of his disciples and numerous national and foreign «ESRists» B.I. Medovar clearly formulated and substantiated the need of using ESR not for refining steels and alloys from harmful impurities, but for «refining the metal structure» and control of shape, size, and distribution of metal and non-metal structures in the metal. Ideas, connected with control of solidification of steels and alloys, constantly worried restless and inquisitive mind of the researcher. Exactly on this way various technologies of the electroslag casting and even new class of metal materials with assigned anisotropy of structure (AAS) and properties were born — AAS-reinforced quasi-monolithic and quasi-lamellar steels.

Wonderful vision of the metals science problems of metallurgy allowed B.I. Medovar implementing interesting technical solutions not just on the basis of numerous experiments and deep studies, but also, it would seem «on the tip of a pen». In this way low-carbon armor plate and such at present ordinary method as hardening of low-alloy steels of 09G2S type or controlled rolling of conventional carbon steels were born. The list could be continued, but following style of the scientist we shall note only one thing: at present one may state with confidence that ESR and the whole range of the electroslag technologies born in our institute with direct participation of B.I. Medovar dynamically develop, and his long work is continued by his disciples and followers.



CENTRIFUGAL ELECTROSLAG CASTING OF TRACTOR BUSHINGS OF TURNING HINGE

E.N. ERYOMIN and S.N. ZHEREBTSOV

Omsk State Technical University, Omsk, RF

Technology and equipment of a bay for centrifugal casting of thin-wall bushings of the K-700 tractor turning hinge are described. Results of the cast metal tests and advantages of the metal are shown.

Key words: centrifugal electroslag casting, cast bushings, chill mould, mechanical properties

Steel special-purpose parts having shape of bodies of revolution with through cavities of various diameters are often used in machine building industry. To the items of such type relate bushings of the K-700 tractor turning hinge from steel 40Kh with external diameter 306 and internal diameter 285 mm. They are manufactured by machining of forged pieces or stamped parts, which causes high material and labor expenses.

Application of various methods of hot conversion is a forced measure, which is resorted to because of low quality of casting. That's why production of hol-

low cast billets, shape and size of which maximally approach those of ready items and quality of which would not be inferior to that of the deformed items, is an actual task.

Centrifugal electroslag casting (CESC) has great potential for solution of this problem [1]. Essence of the process consists in electroslag remelting of metal in a melting unit, which ensures accumulation of liquid metal and slag in necessary amounts and their subsequent pouring into a revolving mould. Consumable electrodes of any shape and section may be used as a remelted metal. This very process was used for manufacturing billets of hinge bushings.

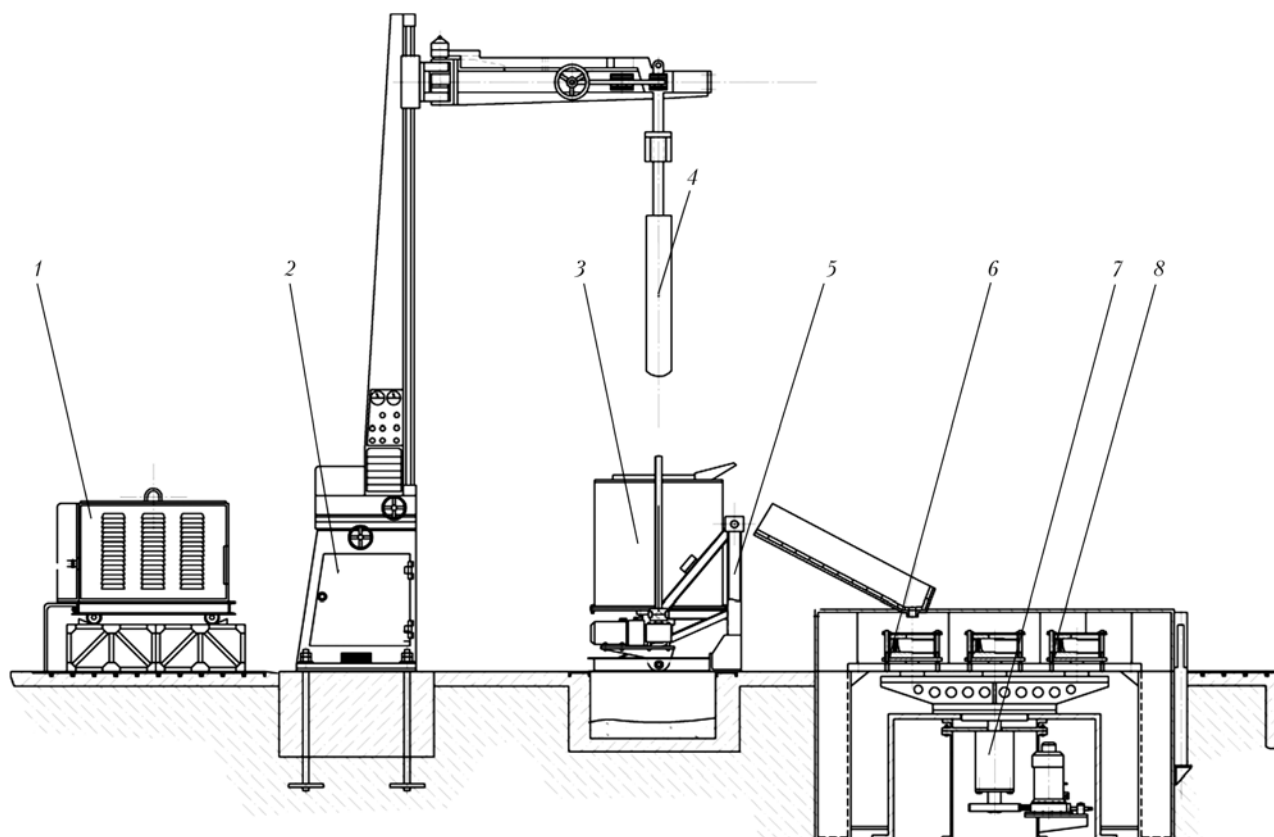


Figure 1. Set of equipment of CESC bay: 1 — transformer TShS-3000-1; 2 — installation A-550U; 3 — melting unit; 4 — consumable electrode; 5 — mechanism for turning over melting unit; 6 — item being cast; 7 — centrifugal machine; 8 — cast mould

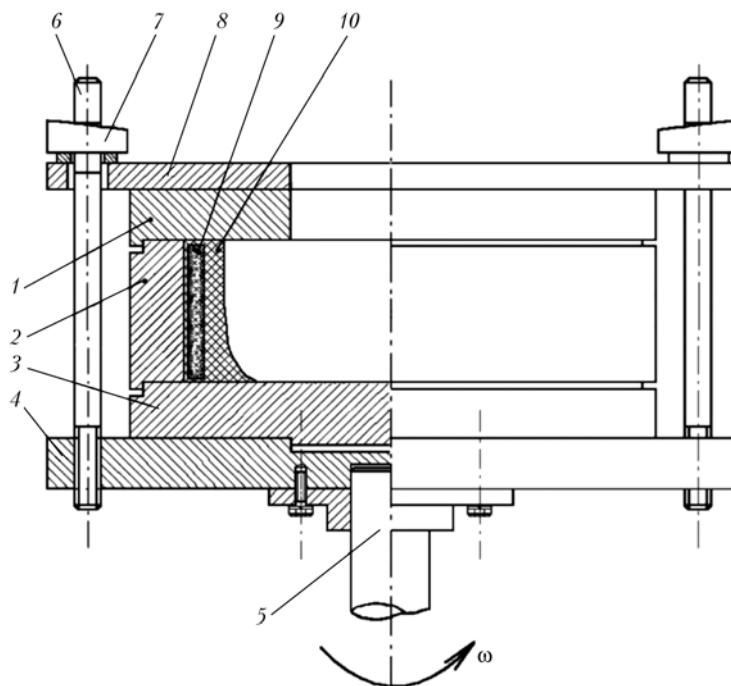


Figure 2. Principle scheme of chill mould for bushing CESC: 1 — cover; 2 — side ring; 3 — bottom; 4 — faceplate; 5 — centrifugal machine shaft; 6 — stud; 7 — wedge; 8 — pressure plate; 9 — casting; 10 — slag skull

Remelting of the consumable electrode was performed under the flux represented by a mixture of fluoric calcium, alundum, magnesite, silica, and manganese oxide. Such flux ensures refining and cleaning of liquid metal in the melting unit from sulfur and phosphorus and protection against harmful action of environment and significant yield at high cooling rate [2].

A set of equipment for performing mentioned process includes serial installation A-550U, a melting unit, a centrifugal machine with vertical axis of rotation, and a power source — transformer of TShS-3000-1 type (Figure 1).

Melting process was performed under the following conditions: working current was 2800–2900 A; voltage during the whole remelting process was constant and equaled 40 V; mass of a remelted electrode was 14 kg; duration of the remelting process was 7 min; mass of used flux equaled 6 kg. Remelting of the consumable electrode in the melting unit began from liquid start.



Figure 3. General view of chill mould with casting in skull

Accuracy of a produced casting is determined by a casting mould. That's why a built-up metal chill mould was used, which was manufactured by turning of annular billets, each of which repeated a portion of external configuration of a cast item (Figure 2). The chill mould consisted of a bottom 3, on which an intermediate side ring 2 was installed that formed external cylindrical part of a bushing, and a cover 1 of the cast mould. All these parts were fixed on faceplate 4 of the centrifugal machine. Then a plate 8 is installed, which pressed by means of studs 6 and wedges 7 all parts of the chill mould to the faceplate.

During pouring of slag-metal jet through the pouring hole it divides under action of centrifugal forces into flux and liquid metal, which forms body of the casting. Flux prevents sticking (welding) of a casting to the casting mould walls due to its arrangement in thin even layer over surface of the mould.

Speed of the centrifugal machine rotation is 400 rpm and duration of the pouring process is 5 s. By means of general reduction of the metal and the slag temperature slag skull forms on surface of the

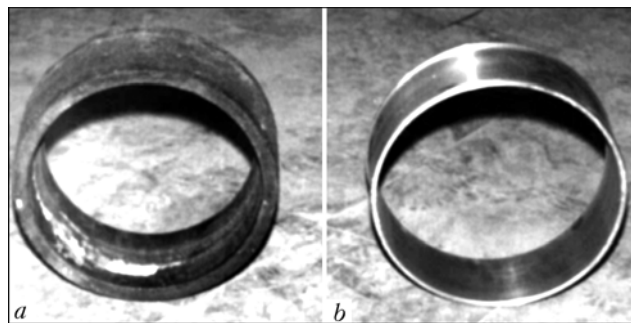


Figure 4. General view of casting cleaned of skull (a) and ready bushing (b)

**Table 1.** Chemical composition of steel 40Kh

Metal type	Share of elements, wt. %						
	C	Mn	Si	Cr	Ni	S	P
Standard	0.36–0.44	0.50–0.80	0.17–0.37	0.80–1.10	≤ 0.30	≤ 0.035	≤ 0.035
Electrode	0.42	0.61	0.24	0.93	0.12	0.019	0.017
CESC	0.41	0.59	0.25	0.91	0.12	0.009	0.015

Table 2. Mechanical characteristics of steel 40 Kh

Metal type	σ_t , MPa	σ_y , MPa	δ , %	ψ , %	KCU_{+20} , J / cm ²
Standard on forged piece	≥ 570	≥ 315	≥ 12	≥ 25	≥ 40
CESC	932	794	14.2	49.6	62

cast, which is separated from the billet only after it is removed from the mould.

In Figure 3 general view of the chill mould with the casting in skull is shown. Billets produced using this process meet all requirements established for the manufactured products (geometric accuracy of a casting and high values of the metal properties). So, allowance for machining of external side is 2–3 mm, for height — 3–4 mm, and for internal diameter — 5–8 mm. Metal utilization factor achieves 0.7 that significantly reduces metal consumption of the item and power consumption needed for its manufacture. General view of the casting cleaned of the skull and the bushing are shown in Figure 4.

Results of analysis of chemical composition and mechanical properties of steel 40Kh after CESC, in comparison with a forged metal, are given in Tables 1 and 2.

As one can see from Table 1, in CESC takes place significant reduction of the content of harmful impurities, which is explained by reduction and refining processes proceeding in the slag pool.

Ultrasonic testing and magnetic flaw detection of CESC castings showed dense cast structure and absence of micro-cracks or any defects. As a whole properties of the electroslag metal meet requirements of GOST 8479–70 established for forged metal of standard melting, which allows using cast electroslag billets instead of forged pieces. In addition, such process ensures high efficiency of producing items of different nomenclature and standard sizes.

1. Paton, B.E., Medovar, B.I. (1988) *Electroslag crucible melting and pouring of metal*. Kiev: Naukova Dumka.
2. Medovar, B.I., Tsykulenko, A.K., Shevtsov, V.L. et al. (1986) *Metallurgy of electroslag process*. Kiev: Naukova Dumka.

NEW METHOD OF QUANTITATIVE DETERMINATION OF SUSCEPTIBILITY OF STRUCTURAL STEELS TO HYDROGEN EMBRITTLEMENT

The method is based on use of a physically-grounded quantitative criterion of hydrogen effect. Smooth cylindrical samples (without notch), which are deformed by a uniaxial tension in the preset interval of temperatures, are used in a realization of this method. Criterion of embrittlement is defined as a ratio of values of a mean stress of metal fracture in hydrogen-induced and initial states with account for a ratio of deformation in sample and curvature of a neck at the moment of fracture. There is a positive decision of Patent Agency of Russia of 28.09.92 on Application No.5040067 «Method of Quantitative Determination of Degree of Hydrogen Embrittlement of Structural Steels and Welds» Int. Cl. Go1n 17.00.

Purpose. Method is designed for determination of degree of embrittlement effect of hydrogen, absorbed by metal in steel melting, in manufacture of welded structures and in the process of service of steel products under the conditions of hydrogenation from surrounding or technological environment.

Application. This method can be used in metallurgy, welding industry, in the development of challenging welding consumables, service and repair of steel products.

Contacts: Prof. Pokhodnya I.K.
E-mail: pokhod@paton.kiev.ua



COMPOSITE MATERIALS ON BASE OF COPPER AND MOLYBDENUM, CONDENSED FROM VAPOR PHASE, FOR ELECTRIC CONTACTS.

STRUCTURE, PROPERTIES, TECHNOLOGY

Part 2. Fundamentals of electron beam technology for producing materials for electric contacts

N.I. GRECHANYUK, V.A. OSOKIN, I.N. GRECHANYUK, P.P. KUCHERENKO, R.V. MINAKOVA, M.E. GOLOVKOVA and G.E. KOPYLOVA

Scientific-Industrial Enterprise «Gekont», Vinnitsa, Ukraine

Design peculiarities of the installation for performing high-rate electron beam evaporation-condensation are presented. Peculiarities of copper-base phase composition and structure of solidified pool (melt) are studied. Assumption is made about interrelation between structural-phase condition of the melt and rate of evaporation-condensation. Peculiarities of surface structure and condensate volume in various sections (before and after etching) are investigated. Technological defects and their influence on strength and ductility of the condensate during tensile test are considered. Interrelation between temperature dependence of strain activation energy, peculiarities of condensate failure, and technological defects of its structure of different origin are studied.

Keywords: installation for vacuum condensation, technology of electron beam evaporation, condensate, structure, properties

In [1] scientific, technical, and economic premises are stated for producing materials for electric contacts by the method of high-rate EB evaporation of metals and subsequent condensation of vapor flow in vacuum on a preliminary heated substrate.

In this article results of development of EB technology fundamentals for production of composite materials (CM) for electric contacts, which don't contain noble materials, and investigation of their structure and properties are presented.

Technological peculiarities of manufacturing condensed CM. For producing electric contact materials, condensed from vapor phase, commercial EB installation UE-189, designed in the E.O. Paton Elec-

tric Welding Institute and modified in SIE «Gekont», was used. Appearance of the installation is shown in Figure 1. Its principle scheme is shown in Figure 2. The installation has a working chamber 1, which is at the same time a technological chamber. To the side part of this chamber gun chamber 2 is joined, in which EB heaters 3–6 are located.

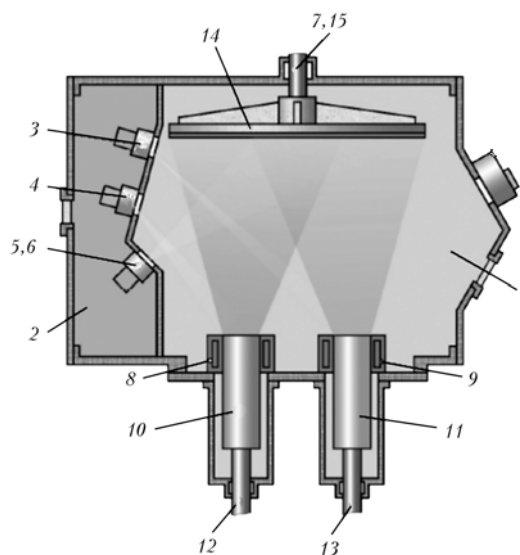


Figure 2. Principal scheme of EB installation: 1 — working chamber; 2 — gun chamber; 3–6 — EB heaters; 7 — substrate rotation rod; 8, 9 — crucibles for evaporation of copper and molybdenum, respectively; 10, 11 — ingots for evaporation; 12, 13 — mechanisms for feeding ingots into evaporation zone; 14 — substrate; 15 — substrate rotation mechanism



Figure 1. Appearance of installation UE-189



The vacuum system is designed for creating dynamic vacuum in chambers of the UE-189 installation for the purpose of ensuring process of evaporation and condensation of initial materials. The technological chamber and the gun chamber have separate vacuum pump-out systems, which ensure stability of EB heater operation.

The vacuum system consists of two roughing-down pumps AVZ-125, two booster pumps NVBM-05, and two high-vacuum units AVP-400 (one per the gun chamber and the technological chamber). Design of the vacuum system ensures emergency shut-off of pipelines by vacuum valves KMU-63 in case of a sudden de-energizing.

On upper flange of the technological chamber 1 substrate 14 rotation mechanism 15, designed and manufactured in «Gekont», is installed [2]. Peculiar feature of the design of this mechanism is possibility of its long operation (10–12 months) without violation of vacuum when rotating a substrate of up to 50 kg mass at speed up to 40 rpm at the temperature $(600 \pm 50)^\circ\text{C}$.

Heating of the substrate (fixed on the rotation rod 7) up to the mentioned temperature [3] is performed by EB heaters PE-112 5, 6 of 40 kW power. Heating of the initial material for evaporation is performed by means of EB heaters PE-104 3, 4 of 100 kW power. All heaters have independent filament of cathodes and control of EBs. Service life of cathodes of the PE-112 guns achieves 50 h, PE-104 guns — 30 h.

Evaporation unit consists of two crucibles of 100 and 70 mm in diameter (8 and 9, respectively), designed for evaporation of copper 10 and molybdenum 11, and mechanisms 12 and 13, which ensure their feeding into the evaporation zone.

Initial (being evaporated) materials. For producing condensed electric contact materials copper, molybdenum, and alloying elements (yttrium and zirconium) were used as initial elements. Calcium fluoride was used for creation of a separating layer on the substrate. Chemical composition of mentioned materials corresponded to the requirements established for copper of grades M0-M3 in GOST 859–78; pure molybdenum of vacuum remelting (PMVR) in TU 48-19-247–87; zirconium in TU 5-20-069–85; yttrium ITM1, ITM2 in TU 48-4-208–72; fluorine calcium of grade Ch in GOST 7167–77.

For production of copper ingots it was allowed to use the waste (condensate deposited on the chamber walls) and initial copper at the ratio 50:50.

Substrates for deposition of 800–1000 mm in diameter and (20 ± 2) mm thick were manufactured from steel St3. Surface of the substrate, on which deposition was performed, was subjected to milling and grinding till roughness not less than $R_a = 0.63$ (GOST 2769–73) was achieved.

Preparation of ingots for evaporation. Copper ingots were turned and drilled for placement of alloying element weights. These ingots and turned ingots of molybdenum were subjected to cleaning, de-

greasing, and weighing. Alloying elements were used in the form of degreased and dried chips of zirconium and yttrium. Weights of mentioned metals at the ratio 7:3 in amount (100 ± 3) g per 10 kg of copper were placed into special channels, drilled in copper ingot being evaporated, and on surface of the latter. For creation of a separating layer a weight of fluorine calcium (2.0 ± 0.3) g was placed on the surface being heated of the molybdenum ingot.

After charging of the substrate and initial materials to be evaporated the installation was vacuumized. After vacuum $1 \cdot 10^{-2}$ Pa was achieved, EB heaters were switched on and technological process of vacuum deposition was started.

Deposition of the separating layer CaF_2 was performed in vacuum not less than $1 \cdot 10^{-2}$ Pa after heating of the rotating substrate up to the temperature (873 ± 50) K. Duration of the separating layer application was 120–180 s.

After termination of the separating layer deposition process, alloyed pool was formed on the copper ingot face. At the same time molybdenum ingot was heated. The conditions were considered achieved when evaporation currents of copper equaled 3.0–3.4 A, molybdenum — 1.2–16 A at acceleration voltage of 20 kV. Change of the beam power in evaporation of molybdenum in different experiments allowed producing electric contact CM Cu–Mo–Zr–Y of three grades (MDK-1, MDK-2, MDK-3) with molybdenum concentration equal to 2.5–5.0, 5.1–8.0, 8.0–12.0 wt.%, respectively [4].

In [1] experimental data and existing ideas concerning selection of base and alloying elements for development of CM of electric contact designation, which don't contain silver, are presented. One of the main issues in development of EB technology, which requires for solution, is the issue of increasing intensity of the metal evaporation process.

Evaporator, rate of evaporation, composition, structure. When selecting methods of copper evaporation intensity change, we proceeded, first of all, from the known data on existing methods of such regulation. Most frequently rate of evaporation is increased by increasing size of the evaporator and power of EB [5–7]. However, when 50 kW power and specific rate of copper evaporation from the water-cooled crucible $4 \cdot 10^{-3}$ g / (cm²·s) is exceeded, stability of the pool is violated: splattering of metal from the crucible takes place. Outburst of the metal may be partially avoided by introduction of alloying additives and arrangement of a multi-component pool on surface of the melt being evaporated (an intermediate pool) [8, 9].

In [10] the intermediate pool is called melt of the additive-metal, which restrictedly interacts with the base metal, occupies $\approx 10\%$ of the whole melt volume, and preserves on its surface. The main requirement to the additive-metal is lower density than in the metal-base, and pressure of its vapors within technological range of temperatures should be lower than that of the metal-base. From chosen by us alloying

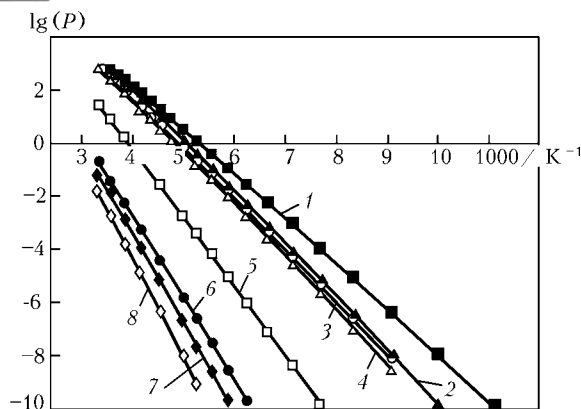


Figure 3. Dependence of vapor pressure of some metals on inverse temperature [11]: 1 — molybdenum; 2 — zirconium; 3 — niobium; 4 — vanadium; 5 — yttrium; 6 — iron; 7 — copper; 8 — chromium

elements [1], zirconium completely and yttrium partially met these requirements. Density values of zirconium — $6.49 \cdot 10^{-3}$ and yttrium — $4.55 \cdot 10^{-3}$ are lower than those of copper — $8.92 \cdot 10^{-3}$ kg / m³. As far as pressure of vapors is concerned, for copper and zirconium required difference is preserved, while for copper and yttrium it is not so significant (Figure 3) [11]. However, according to [10], zirconium and yttrium increase specific rate of copper evaporation. From analysis of Figure 4, presented in [10], one can see that alloying elements in copper melt accelerate evaporation of copper: zirconium — 2 times, vanadium — almost 6 times. There is no satisfactory explanation of evaporation rate increase in case of using an intermediate pool. It is assumed that increase of evaporation rate may be caused by surface tension and heat conductivity of the melt being evaporated, which change during alloying [12]. However, peculiarities of phase equilibria in binary systems Cu–Zr, Cu–Y, Cu–Nb, Cu–Fe and Cu–V may influence specific rate of the melt evaporation.

Four intermetallic compounds (YCu_6 , YCu_4 , YCu_2 , YCu) were detected in binary system Cu–Y, three of which melt congruently within temperature range of (935 ± 15) – (985 ± 15) °C. In the system Cu–Y also four eutectic transformations were registered, which proceeded within temperature range (890 ± 10) – (760 ± 15) °C and yttrium concentrations 12.5–74 wt.% [13].

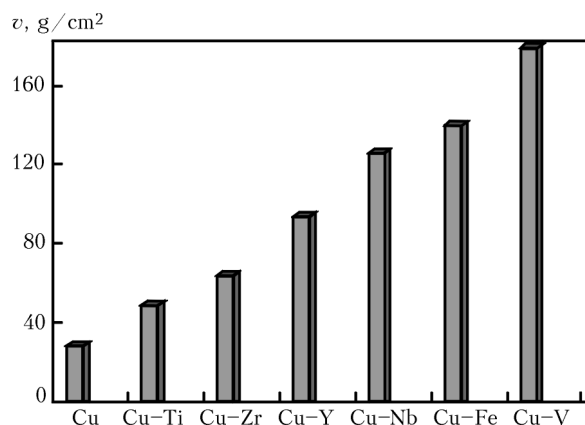


Figure 4. Change of specific copper evaporation rate v during alloying depending upon melt composition

There are six intermetallic compounds in binary system Cu–Zr, four of which melt congruently. All compounds participate in eutectic reactions within concentration range of zirconium content 8.85–55 wt.% and temperature range 971–885 °C [13].

So, during interaction of elements in each mentioned binary system exists within wide range of concentrations probability of formation of eutectic type melts with significantly lower melting point than that of initial metals.

For binary systems Cu–V, Cu–Nb and Cu–Fe presence of areas of immiscibility and lamination (with the maximum, approximately, in equimolar area) is characteristic, and monotectic reaction, for example, in system Cu–V at temperature 1530 °C, and in system Cu–Nb at temperature 1550 °C [13]. This allows assuming possibility of morphology change of structural components of the system and properties of its capillarity and increase of evaporation rate at the temperature, which significantly exceeds copper melting temperature, which does not contradict data of [10] that prove increase of copper melt evaporation rate in presence of vanadium, niobium and iron additives.

In the process of development of technology for manufacturing massive Cu–Mo–Zr–Y condensed materials samples of three alloyed pools were investigated, which ensured three rates of condensation that made up 16–20, 8–10, 4–5 μ m / min, respectively. For investigation of pool materials optic and electron scanning microscopy, X-ray spectral microanalysis, and method of microhardness were used. Despite different values of density of alloying elements of yttrium and base metal (copper), lamination of components in the pool was not detected.

Active interaction of these elements with copper, each other, and interstitial impurities was noted. Phase composition of the pools after solidification corresponded mainly to twin diagram Cu–Zr, according to which in equilibrium with copper-base solid solution exists intermetallide $ZrCu_5$, which forms due to peritectic reaction, and intermetallide $ZrCu_4$, which represents a congruently melting compound. Different mass shares of zirconium in these phases (in $ZrCu_5$ approximately 22 %, in $ZrCu_4$ — 26 %) and morphology of the latter (Figure 5) allow assuming that crystals of intermetallide $ZrCu_4$ of various shape form during solidification of the pool. Intermetallide $ZrCu_5$ in the form of thin fibers precipitates in solid solution at the temperature below solidus, i.e. as a result of aging. In solidified pool 1, which ensures maximum rate of copper evaporation, big anisotropic particles prevailed (Figure 6, a) with sizes sometimes equal to the pool depth (approximately 12 mm). It proves the fact that alloyed melt occupies the whole volume of the pool. In pool 2, where average rate of copper evaporation was 8–10 μ m / min, mainly anisotropic particles of intermetallide $ZrCu_4$ were registered having a shape of somewhat elongated hexahedron (Figure 6, b). In pool 3, for which minimum rate of copper evaporation is characteristic (4–



5 μm / min), size of isotropic particles in dominant areas sharply reduced (Figure 7, *a*). Structure of the pool was inhomogeneous. Near surface of the pool accumulation of anisotropic particles ZrCu_4 was detected, as well as porosity (Figure 7, *b*) and slag inclusions in system Zr-Y-O (Figure 7, *c*). Disperse (anisotropic or isotropic) phase ZrCu_5 (Figure 5) was present in investigated pools between particles of intermetallide ZrCu_4 . In the near-bottom zone this very phase formed branched structure (Figure 8).

So, it was experimentally established that content and distribution of elements in the alloy Cu-Zr-Y with high rate of evaporation during solidification ensure formation of anisotropic structure, which is stipulated by directed growth of intermetallide ZrCu_5 . Absence of sufficient knowledge about mechanism of melting and solidification does not allow authentic judging of the nature of detected interrelation. However, data of [14, 15] prove that the melt has to be considered as a crystal dispersed into clusters of 0.5–3.0 nm size. That's why one may assume existence of hereditary connection between structures of copper-base alloys in liquid and solid state and influence of ordering on the melt evaporation rate.

On the basis of established peculiarities of the structure, phase, and chemical compositions of the pools one may draw conclusion that phase equilibriums in copper-, zirconium- and yttrium-base systems, complicated by presence of impurities in commercially clean materials, have to be considered as some of the

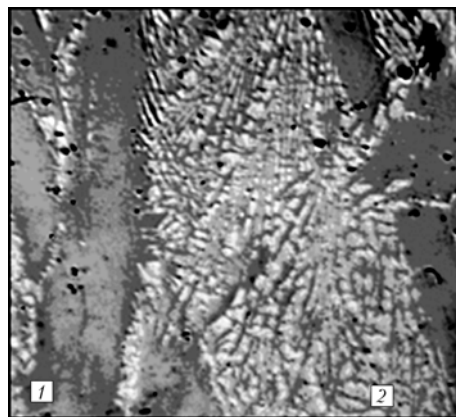


Figure 5. Morphology peculiarities of phases ZrCu_4 (1) and ZrCu_5 (2) ($\times 200$)

main factors which control rate of evaporation-condensation.

Efficiency of alloying elements is, probably, stipulated by their ability to change structure of the melt and its capillary properties. This assumption fits established in [10] two-fold increase of the copper-base melt evaporation rate in presence of zirconium and yttrium, which form intermetallic compounds and low-melting eutectics in correspondence with similar equilibrium diagrams.

Evidently the same analogy of equilibrium diagrams in systems Cu-Fe and Cu-V (presence of areas of immiscibility in liquid state and possibility of monotectic reaction proceeding at reduced tempera-

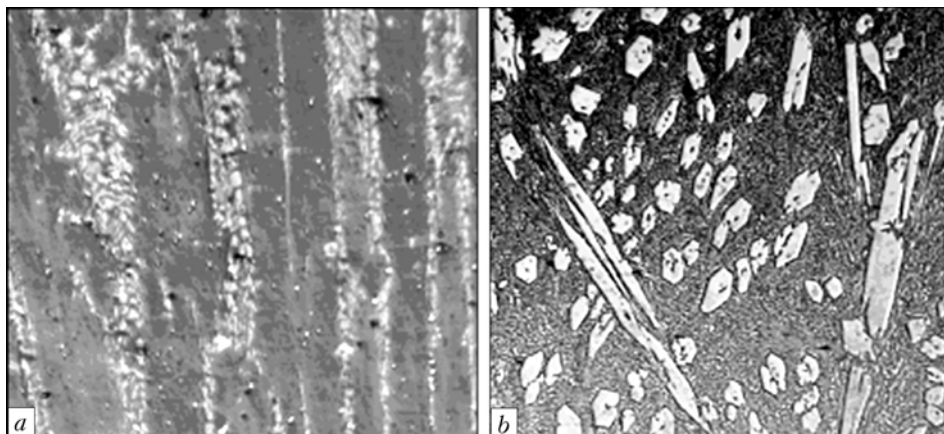


Figure 6. Melt structure of pools 1 (*a* — $\times 100$) and 2 (*b* — $\times 50$) after cooling

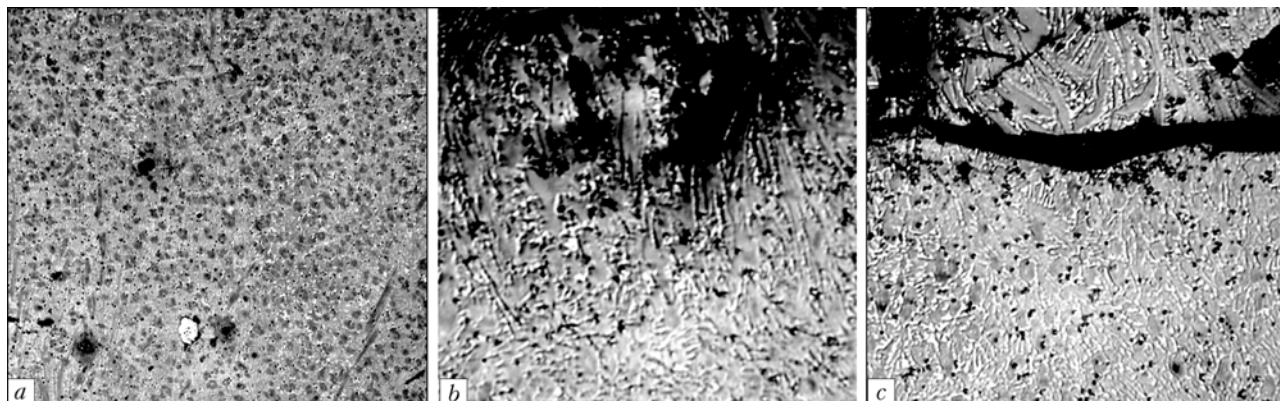


Figure 7. Pool 3 (*a*), structure inhomogeneity (*b*) and slag inclusions (*c*) near its surface ($\times 200$)

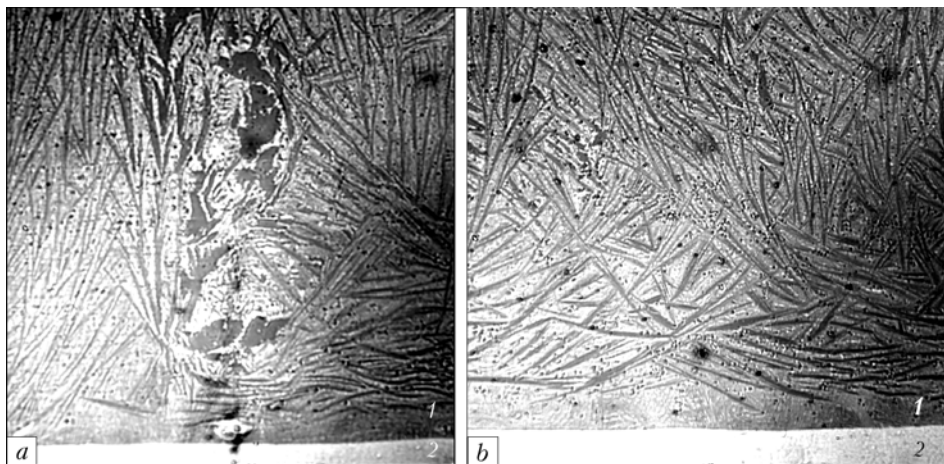


Figure 8. Structure of solidified melt (1) near boundary with copper ingot (2) irrespective of pool structure ($\times 100$): *a* — high; *b* — medium rate of evaporation

ture of the ingot, which determine structure of the melt) allows achieving even higher (4–6-fold) increase of evaporation rate in the presence of additives of iron and vanadium.

Condensate, its composition, structure and properties. Ratio of values of pressure of metal vapors at various temperatures, composition and structure of the pool melt determine peculiarities of the condensate mass transfer and chemical composition. As follows from presented data and results of mass-spectral analysis of copper condensate, containing alloying elements zirconium and yttrium used during its production, zirconium is mainly accumulated in the melt, while yttrium participates more actively in mass transfer. According to the results of this analysis, weight share of alloying elements varies in zirconium within 0.01–0.08 and in yttrium within 0.02–0.012 %.

The parameter, which allows qualitative estimating possibility of increasing intensity of the alloying element mass transfer, may be the temperature, at which pressure of saturated vapor 133.3 Pa is achieved [16]. For example, for iron, yttrium and zirconium it increases at 1923, 2128, and 2883 K. In the same sequence reduces content of elements in condensates Cu–Fe, Cu–Y, Cu–Zr (6.08–9.43; 0.13–0.18; 0.02–0.08 wt.%, respectively) [10]. These data don't contradict peculiarities of temperature dependence of vapor pressure of iron, yttrium, and zirconium (see Figure 3) [11].

When alloying elements get from the melt being evaporated into condensate, they notably affect its mechanical properties (Table 1) [10]. Morphology of

an additive and its content affect properties of the initial condensate and intensity of its loss of strength at the temperature 573 K. Maximum worsening of properties was registered when copper condensate was alloyed with iron. Tensile strength of the condensate reduces by 63 % and relative elongation δ — by 24 %. The lowest reduction of property parameters — by 40 and 11 % — takes place, when the condensate is alloyed by zirconium, whereby it should be noted that tensile strength and ductility of pure copper reduce at 573 K by 48 and 47 %, respectively, in comparison with room temperature.

Taking into account structural sensitivity of mechanical properties, one may assume that strength reduction is stipulated by the processes of recovery and ability of alloying elements to hinder these processes by means of action on phase composition, morphology, and dispersibility of new phases. However, mechanical properties are affected, in addition to mentioned factors, by other factors as well. They are stipulated by application in technological processes of commercially pure initial materials and residual mediums.

In this work influence of impurities on structure and properties was investigated on samples of CM Cu–Mo–Zr–Y proceeding from the need of increasing the level, reproducibility of the condensate properties, and optimization of technological conditions of their manufacturing. Samples of copper- and molybdenum-base materials of grades MDK-1 and MDK-3 of various lots corresponding to TU U 201134.001–98 and containing up to 12 wt.% Mo and not more than 0.08 wt.% Zr and Y (each), the rest being copper, were used as objects of investigation [4]. Samples were cut out from condensate sheets of 800 mm diameter. Size of samples allowed sequential performing macrostructural analysis of the surface, measuring thickness, density, electric resistance, hardness, and determining tensile mechanical properties.

Surface and sections of the samples parallel and perpendicular to the vapor flow (before and after etching), and fractures were subjected to microstructural investigations [17]. Thickness measurement of the samples showed that condensate, formed during

Table 1. Influence of alloying elements on mechanical properties of copper-base condensate

Material	Mechanical properties of condensates at T , °C			
	20		300	
	δ_t , MPa	δ , %	δ_t , MPa	δ , %
Cu	188	62	98	33
Cu–Y	213	53	79	34
Cu–Zr	192	56	115	50
Cu–Fe	318	33	118	25

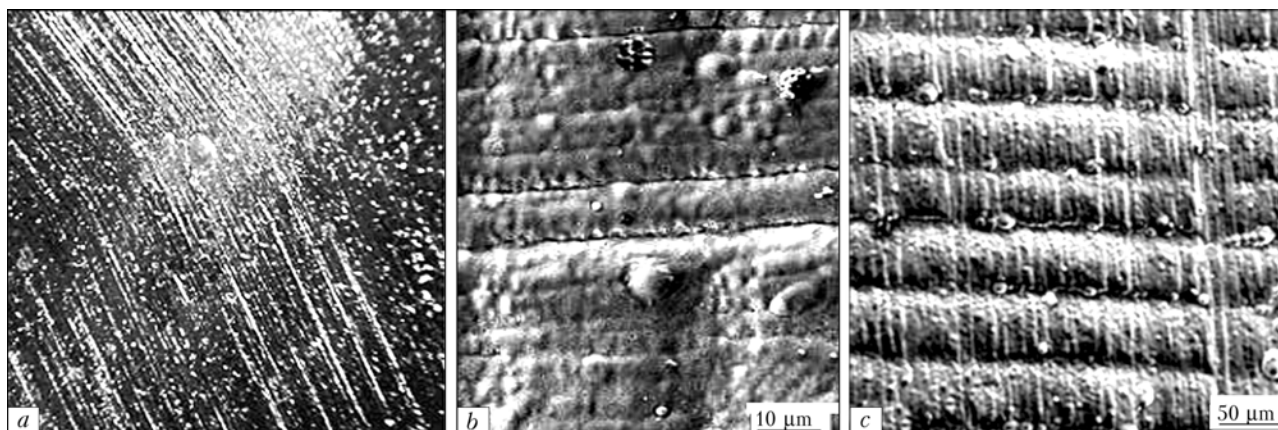


Figure 9. Block character of surface with arbitrary striation (*a*, *b* — $\times 32$) and surface of condensate with periodic striation and period of strip repeatability (150 ± 3 μm) (*c*)

rotation of the substrate, may be represented in the form of a truncated toroid. Cuneiform shape is characteristic of the periphery. Here thickness, in comparison with maximum for the toroid, reduces by (45 ± 3) %.

Surface of the samples is of block character (Figure 9). For each block periodic or arbitrary striation is characteristic. Investigation of condensates of different lots allowed establishing that in case of periodic striation width of strips and dispersion may differ by more than one order — from (35 ± 3) to (564 ± 32) μm . One of the reasons of occurrence of such macro- and microstructure (striation) may be, evidently, peculiarity of the substrate roughness caused in the course of processing by a number of factors [18] (single- or multi-tooth milling, rectilinear or circular forming edge, error in location of the forming edge, error in the shape of the calibration edge, static rigidity of the technological system, in case of reduction of which self-excited oscillation develops in this system accompanied by abrupt increase of roughness and undulation) [10].

For the whole surface presence of solidified drops of thrown out from the metal pool and pimples is characteristic. Number of the latter ones varies depending upon the lot and may achieve $1 \cdot 10^{-2}$ per 1 cm^2 . Formation of pimples is connected with throwing out and transfer on the substrate of liquid and solid phase drops at different stages of the evaporation-condensation process.

In Figure 10 surface with periodic striation and technological defects (micro-drops) is shown.

In perpendicular to the surface condensate section laminar structure was detected, which had macrolayers of different thickness ($0.1\text{--}1.5$ μm) with wide «interfaces» (Figure 11). Probably such interfaces correspond to a microlayer, which forms in case of a sudden cutout of high voltage, cessation of vapor flow delivery, adsorption of impurities from the residual atmosphere and oil vapors in working chamber of the installation. This assumption is confirmed by results of Auger-spectral analysis of boundaries of macrolayers brought out into the area of incision during preparation of the samples and destroyed in the microscope

column. For this type of boundaries presence on their surface of carbon in graphite and carbide form, molybdenum, sulfur, chlorine, nitrogen, zinc, tin, etc. is characteristic [17].

Microstructural analysis of the condensate section perpendicular to the surface (after etching) proves inhomogeneous character of macrolayers and inhomogeneity of their structure, whereby in the section, perpendicular to the surface and the strips, mentioned layers are, like strips on the surface, of undulated character, inherited from roughness of the substrate. In section perpendicular to the surface, but parallel to the strips, undulated character of structure was not registered (Figure 12). Ion etching of section, perpendicular to the surface, allowed establishing that disperse-strengthened contact copper (MDK) consists, as a gradient material, from microlayers of different composition and morphology (Figure 13).

For the layers, enriched with molybdenum, anisotropic (columnar) structure is characteristic (Figure 13, *a*), which, according to [19], forms as a result of connection of atoms from a volumetric diffusion field (VDF) of the condensed flow with 2D insular layers by diffusion coalescence. Different thickness of the layers occurs in this case as a result of formation of more efficient VDF and increase of rate and time of condensation of the fed vapors.

For layers enriched with copper mainly isotropic structure is characteristic, which consists either of

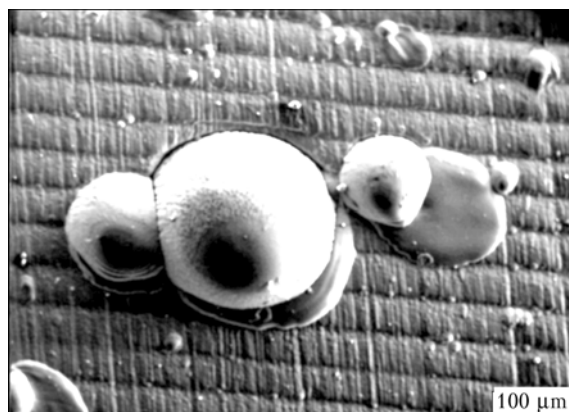


Figure 10. Technological defects on condensate surface

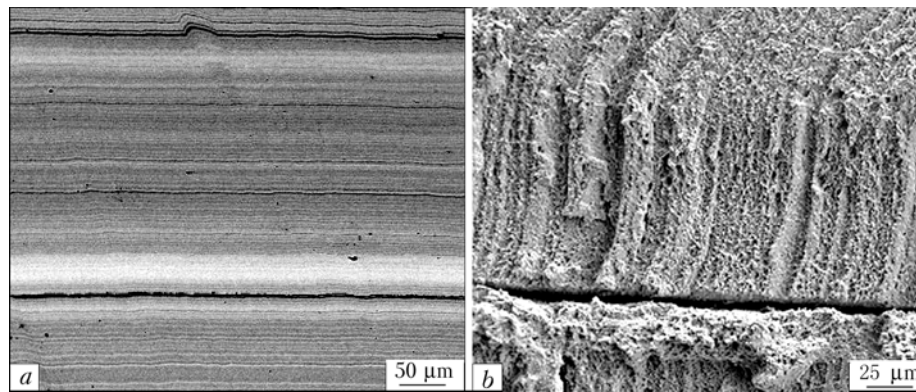


Figure 11. Boundaries of macrolayer on microsection (a) and in fracture (b)

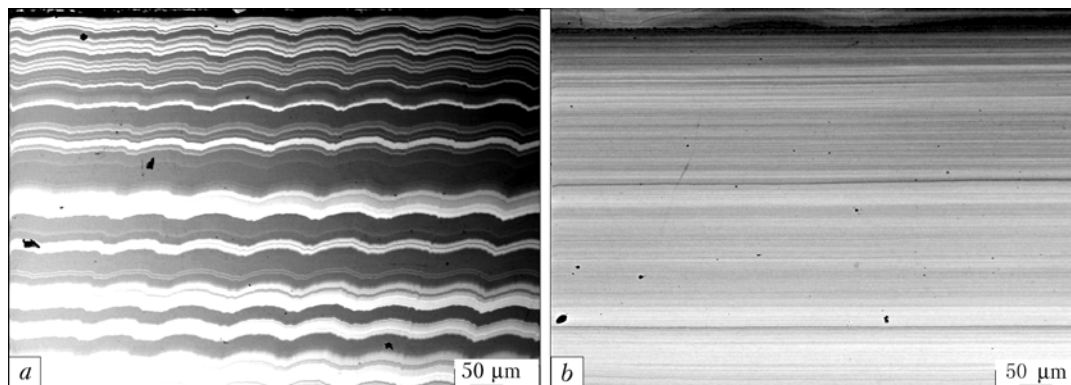


Figure 12. Microstructure of condensate sample with periodic striation in sections: a — perpendicular to surface and direction of strips; b — perpendicular to surface and parallel to direction of strips

disoriented polygonal grains (Figure 13, b), or from particles of spherical and (or) lenticular form dispersed in the matrix (Figures 13, c and 14, a).

Such analysis of sections of these condensate samples allows assuming that correct spherical shape of particles and respective morphology of layers are connected with aggregated transformation in copper in the direction vapor → liquid phase. Lenticular shape of particles forms, evidently, as a result of coalescence of solid-liquid clusters of CM Cu–Mo and origination of spherical particles during their approach to the substrate and deformation of these particles during their collision with the substrate and under action of the next portions of the «drop» vapor. This is proved by the shape of particles in Figure 14, a and b.

Turbulence of vapor flow may be the reason of formation of different forms of conglomerates during consolidation of particles in microlayers (Figure 14, c). Chemical etching of the section perpendicular to

the condensate surface proves that in case of lower content of molybdenum in MDK-1, refractory component forms separated grains with $d \ll 1 \mu\text{m}$ and conglomerates of these grains in the copper-base matrix (Figure 15). When content of molybdenum in MDK-3 increases, chains of grains and anisotropic colonies form in the matrix.

Change of structure and chemical composition of microlayers fits peculiarities of the microhardness change. Microhardness increases together with increase of the share of columnar structure and molybdenum content in the layers.

In the process of mechanical tensile tests of condensed CM dependence of sample properties upon molybdenum content was also detected (Table 2). In case of annealing of the samples (1173 K, 3 h, vacuum), their strength reduces, ductility increases, but mean value of dispersion does not reduce. Ductility of samples, which correspond to periphery of the

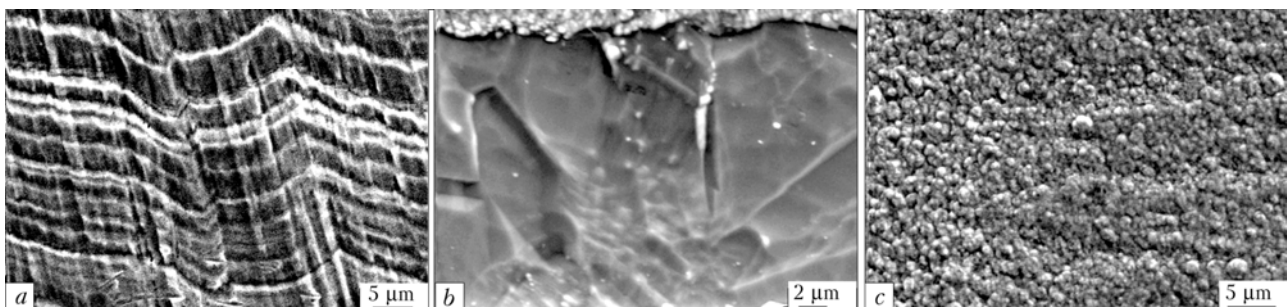


Figure 13. Condensate layers with columnar (a), polygonal (b) and spherical (c) shape of particles

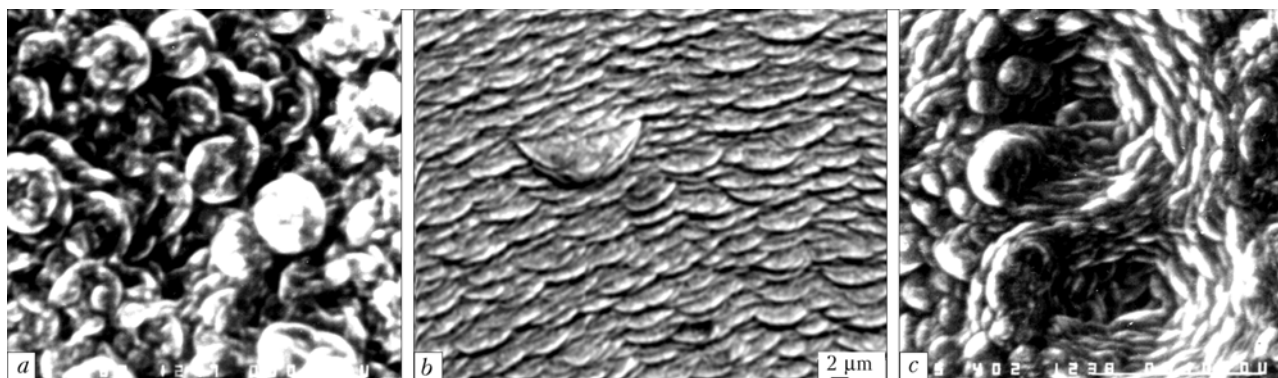


Figure 14. Mixed (a) and lenticular (b) structures of condensate and conglomerate from these particles (c) of this shape

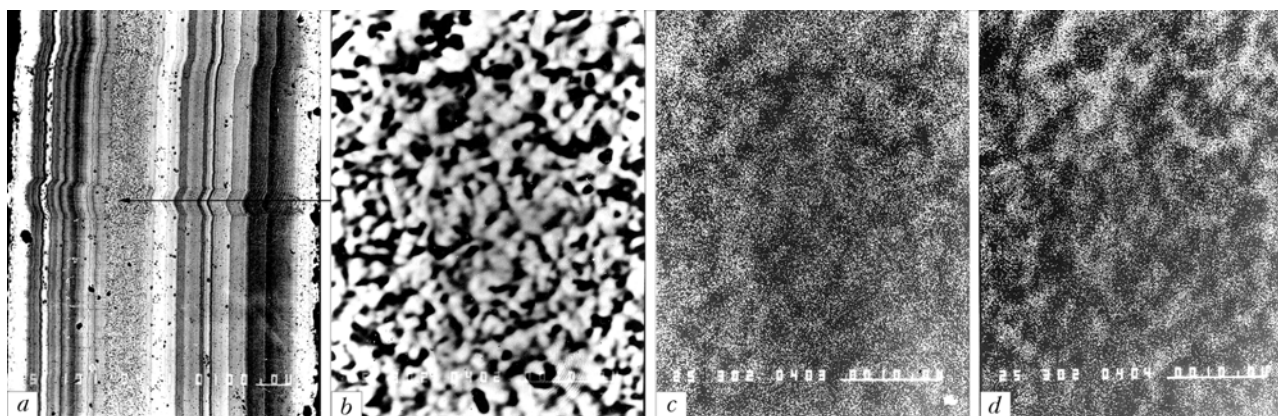


Figure 15. Distribution of refractory component in layer detected after chemical etching of sample: a — in secondary electrons; b — in compo mode; c — XR_{Cu} ; d — XR_{Mo}

sheet, reduces because of lamination first of all along boundaries of macrolayers enriched with carbon and other impurities.

An important part in formation of structure and properties of condensates play defects, which formed as a result of outburst from molten pool and transfer of liquid and solid phases. Such outbursts of the melt differ from each other by composition, adhesion to previous layer of the condensate, ability to spread over it, shape, gas content, etc. For example, spheroids, which form during solidification of metal micro-drops, contain in addition to the base elements (molybdenum, yttrium, zirconium) carbon, oxygen, nitrogen, and fluorine. The most frequent forms of solidified drops are spheroid and spherical ones. Spheroids, being retained by the previous layer, cause distortion of subsequent solidification front. Convexity, which forms on these spheroids, is transferred to each subsequent layer up to the condensate surface and forms pimples on it (Figure 16, a), whereby in the condensate volume formations of cylindrical or conical form were detected, which were conditionally called «rods».

Formation of «rod» boundaries, registered on microsections and fractures (Figure 16), is, evidently, connected with precipitation and redistribution of impurities during solidification of micro-drops, thrown away from the molten pool. As far as outburst and transfer of liquid and solid phases occurs during the whole process of evaporation-condensation, the «rods» either penetrate through the whole condensate

thickness or only part thereof. Results of analysis of peculiarities of the condensate destruction in mechanical tensile tests showed that presence of the «rods» is characteristic of, approximately, 95 % of fractures. As far as interfaces of the «rods» with the condensate base metal are the places of plastic strain localization and formation of cracks, we compared mechanical properties of condensed CM with size and number of the «rods» registered on surface of a fracture.

It was established that presence of the «rods» in a fracture is accompanied by reduction of strength and ductility, degree of which depends upon significance of length, diameter and number of the «rods» in a section. If formation of a «rod» is stipulated by outburst of liquid phase at the final stage of condensation, reduction of ductility is not detected (Table 3) [17].

Failure of a sample may occur as a result of origination and development of a crack and near the notch on the surface, along boundaries of macro- and microlayers, «rods», elements of columnar structure or other defects (Figure 17). However, significant improvement of the condensate properties was registered

Table 2. Influence of annealing on mechanical properties of condensates MDK-1 and MDK-3

Alloy grade	Initial state of CM		Annealing of CM at 900 °C for 3 h	
	δ_t , MPa	δ , %	δ_t , MPa	δ , %
MDK-1	518 ± 118	0.69 ± 0.53	543.0 ± 60.9	2.4 ± 1.1
MDK-3	659 ± 106	0	629.3 ± 61.3	0.79 ± 0.57

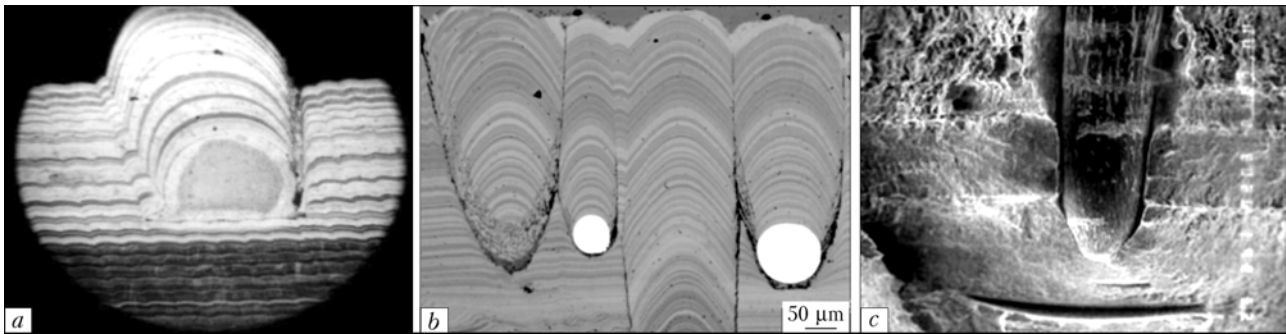


Figure 16. Peculiarities of structure of «rods» and their boundaries with surface and volume of condensate on microsections (a, b) and in fracture (c)

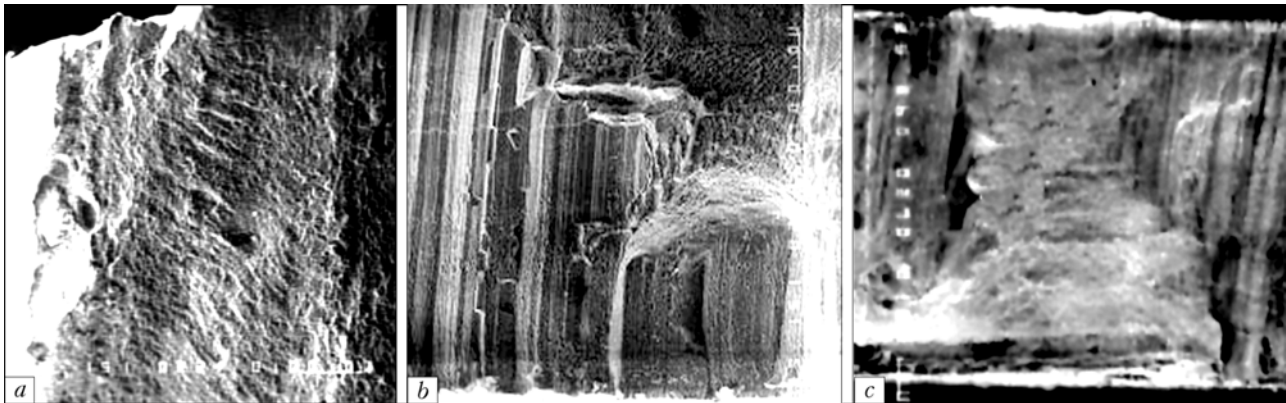


Figure 17. Origination and development of crack: a — from notch on surface; b — near boundary of columnar structure; c — in presence of difference sources

only when a fracture did not contain «rods» and in micro-volumes of the fracture increased part of fracture toughness due to formation and coalescence of pores (in presence of micro-particles of the refractory phase). Such character of failure was detected in MDK samples after annealing and at increased temperature of tests.

So, in condensed CM in system Cu–Mo–Zr–Y form, in addition to structural-dimensional hierarchy of main components, hierarchy of defects of this structure, provided commercially clean initial materials and residual medium are used. With hierarchy of defects localization of plastic strain in tensile tests and origination and development of cracks are connected.

Temperature dependence of mechanical properties of condensed CM of grade MDK-3 was studied (tests were performed in the Institute for Problems of Strength of the NAS of Ukraine by V.V. Bukhanovsky and N.P. Rudnitsky). Processing of the test results

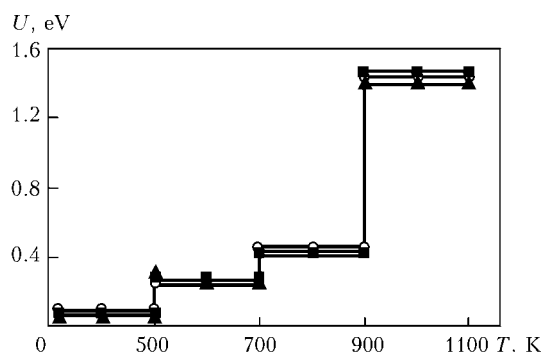


Figure 18. Temperature dependence of strain activation energy of MDK-3 samples in tensile tests

according to methodology of [20], which was carried out by us with determination of gross errors (blunders) in small samplings, allowed establishing step-wise character of strain activation energy change (Figure 18). Comparative analysis of these data and peculiarities of fracture of samples of two lots allow assuming that strain activation energy is minimal and makes up 0.061–0.062 eV within temperature range 300–500 K and corresponds to strain localization near the notches on the surface. Maximum strain activation energy 1.467–1.462 eV within temperature range 900–1100 K for the same lots is connected with fracture toughness of the material with isotropic and columnar structure (Figure 19). Within temperature range 500–900 K, evidently, takes place joint influence of weakened by impurities interfaces (macro-, micro-layers, columns in them, condensate, «rods», etc.) on processes of deformation and failure.

Table 3. Influence of size of «rods» on mechanical properties of condensate MDK-1

Sample No.	Size of defects, mm		Mechanical properties	
	d	l	σ_t , MPa	δ , %
17	0.415	1.00	602	N / D
24	0.46	0.63	628	0.95
	0.32	0.53		
18'	0.54	1.06	575	N / D
20'	0.25	1.14	634	0.3
	0.25	1.15		
22'	N / D		666	2.6
30'	Same		686	2.1

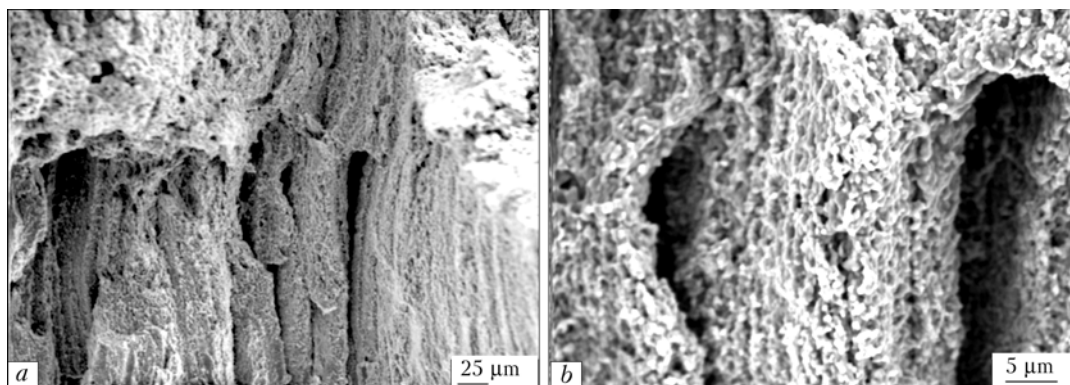


Figure 19. Influence of internal defects on character of condensed composite failure in tensile test and at temperature 1100 K: *a* — intergrain defects; *b* — micropores

The results obtained don't contradict assumption made in [20] about change of strain mechanisms (dislocation slippage for dislocation creepage) during tensile tests of copper within the same temperature range. Data of fractographic studies expand our idea about peculiarities and role of structure defects of condensed CM as places of localization of plastic strain, origination and development of cracks, and failure.

CONCLUSIONS

1. Main technological factors (combination of conditions — preparation of a substrate, its rotation, alloying of the pool, conditions of the pool heating, etc.) which affect process of evaporation and structure formation of condensed composite materials are established.

2. It is shown that in case of copper alloying by the elements, which may affect rate of the melt evaporation, peculiarities of phase transformations in binary and more complex systems and possibility of morphology control of structural components and capillarity of a system in liquid-solid state have to be taken into account.

3. It is established that condensate surface at the condensation front is of block character with periodic and arbitrary striation according to roughness of the substrate. Behind condensation front lamellar structure with hierarchy of layers was detected, which had columnar, polygonal disoriented, composite (with spherical, lenticular or mixed shape) structure, varieties of which corresponded to the condensation mechanisms.

4. It is determined that peculiarities of formation of technological defects are connected with outburst of the pool material in solid and liquid phases and segregation of impurities on interfaces of structural components.

5. It is shown that in tensile tests of copper- and molybdenum-base condensates, which contained defects of structure, reduction and instability of mechanical properties were registered stipulated by combined or separate influence of defects on peculiarities of deformation and failure. In case of the tensile test temperature increase and change of the nature of structure defects, which determine localization of plastic strain, origina-

tion, development of cracks and failure match well stepwise change of strain activation energy.

1. Grechanyuk, N.I., Osokin, V.A., Grechanyuk, I.N. et al. (2005) Composite materials on base of copper and molybdenum, condensed from vapor phase, for electric contacts. Structure, properties, technology. Part 1. State-of-the-art and prospects of application of technology of electron beam high-rate evaporation-condensation for producing materials of electric contacts. *Advances in Electrometallurgy*, **2**, 24–30.
2. Grechanyuk, M.I., Osokin, V.O., Afanasiev, I.B. et al. *Composite material for electric contacts and method of its producing*. Pat. 34875 Ukraine. Int. Cl. C23C/20. Publ. 30.12.2002.
3. Grechanyuk, N.I., Osokin, V.A., Afanasiev, I.B. et al. (1998) Electron beam technology of producing of materials for electric contacts. In: *Transact. on Electric Contacts and Electrodes*. Kiev: IMP NANU.
4. *TU U 201/3410.001.98*: Dispersion-hardened materials for electric contacts. Introd. 01.05.98.
5. Movchan, B.A., Malashenko, I.S. (1983) *Vacuum deposited heat-resistant coatings*. Kiev: Naukova Dumka.
6. Badilenko, G.F., Osokin, V.A., Krivasov, A.K. (1989) Electron beam evaporation and condensation of binary alloys. *Problemy Spets. Elektrometallurgii*, **1**.
7. Zuev, I.V. (1998) *Treatment of materials by concentrated energy flows*. Moscow: MEI.
8. d'A Hunt, C. *Prevention of splattering during vaporization processing*. Pat. 3356487 USA. Int. Cl. 1C3C23C. Publ. 05.12.67.
9. Cock, H.G., Zavrar, P.A., Hollen, R.L. *Source de vapeur et procede de depot sous vide*. Pat. 2156005 France. Int. Cl. 1C3C23C 13/00 HOIJ 19/00. Publ. 27.09.72.
10. Movchan, B.A., Osokin, V.A., Pushechnikova, L.V. et al. (1991) Electron beam evaporation and condensation of copper through intermediate pool. *Problemy Spets. Elektrometallurgii*, **3**, 58–61.
11. Nesmeyanov, A.N. (1961) *Vapor pressure of chemical elements*. Moscow: AN SSSR.
12. Nizhenko, V.I., Floka, L.I. (1981) *Surface tension of liquid metals and alloys*. Moscow: Metallurgiya.
13. (1979) *Binary and multicomponent systems on the copper base*. Refer. Book. Ed. by N.Kh. Abrikosov. Moscow: Nauka.
14. Majboroda, V.P., Shpak, A.P., Kunitsky, Yu.A. (2002) *Structural aspects of fusion and solidification theory*. Kiev: Akademperiodika.
15. Shpak, A.P., Melnik, B.A., Kralya, V.D. et al. (1996) Determination of solution microregions in liquid alloys. *Protsessy Litia*, **1**, 20–23.
16. (1977) *Technology of thin films*. Refer. Book. Ed. by L. Mayssen, R. Gleng. Moscow: Sov. Radio.
17. Minakova, R.V., Osokin, V.O., Grechanyuk, M.I. et al. (2001) About structure aspects of formation and fracture of condensed composite copper-base materials. In: *Transact. of IPM NANU on Electron Microscopy and Strength of Materials*. Kiev.
18. (1991) *Science and technological advance. Technological peculiarities of tool machining of polycrystalline superhard materials*. Ed. by G.R. Korzh. Kiev: Naukova Dumka.
19. Pereplyotov, V.I., Kosminskaya, D.A., Kravchenko, S.A. (2003) Principles of structure formation on low-supersaturated vapor condensates of Cu, Ti, Al and Cr. In: *Transact. of IMF NANU*, **25(6)**, 725–735.
20. Krashchenko, V.P., Stetsenko, V.E. (1981) Influence of temperature and deformation rate on main processes controlling the copper strength. *Problemy Prochnosti*, **4**, 78–83.



PLASMA LIQUID-PHASE REDUCTION OF IRON FROM ITS OXIDES USING GASEOUS REDUCERS

M.L. ZHADKEVICH, V.A. SHAPOVALOV, G.A. MELNIK, D.M. ZHIROV, A.A. ZHDANOVSKY,
K.A. TSYKULENKO and M.S. PRIKHODKO

E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

It was established that rate and completeness of the process of liquid-phase reduction of iron from its oxides using gaseous reducers are mostly influenced by temperature in the reaction space, flow and composition of the reducer, and slag basicity. Equipment and methodology for investigation of the process, in which plasma heating is used for ensuring necessary temperature and activation of the reducer, are described. Influence of the gaseous reducer flow and composition on efficiency of its use, rate, and completeness of the reduction reaction proceeding, effect of the slag basicity on completeness of iron reduction and content of sulfur and phosphorus in it in case of using plasma heat sources are determined.

Key words: gaseous reducer, completeness of the reducer use, degree of iron reduction, activity of wustite, basicity of slag, sulfur, phosphorus, pilot installation

Process of liquid-phase reduction of iron from its oxides is studied insufficiently, because the most distributed method in industry is melting of cast iron in the blast furnace. The furnace stack is conditionally divided into zones with different values of temperature of charge materials and processes, which proceed in them. However, in the course of almost all processes the materials being reduced are in solid state, that's why exactly solid-phase reduction is studied better.

Deficiency of coke used in the blast furnace stipulated the need of developing a new technology with application of a less deficient reducer, in which by-products of the production would be harmless for the environment.

Application of coal as a reducer causes contamination of metal with sulfur and phosphorus. That's why for direct production of high-purity metal it is advisable to use gaseous reducers, which do not contain these harmful impurities.

Increased degree of iron reduction and rate of the reaction proceeding enables temperature increase, which is the most efficiently ensured, when plasma heat sources are used [1, 2].

So, we investigated process of plasma liquid-phase reduction of iron from oxides with application of gaseous reducers.

In the monograph [3] system Fe-C-H-O is considered. One of important characteristics of complex gaseous mixtures is their theoretical work capacity in relation to oxygen (mass of oxygen absorbed or released by 1 m³ of initial system in its transition into equilibrium state with condensed phases, containing oxygen), i.e. function of difference between equilibrium and actual degrees of oxidation, where degree of the latter is a ratio of the number of oxygen moles in a complex gas mixture to the number of oxygen moles in it in case of complete oxidation of all its components up to H₂O and CO₂.

In practice hydrocarbons prior to their application as a reducer are subjected to the conversion: steam-and-water, oxygen, carbon dioxide or a combined one [3]. However, in this case actual degree of oxidation of the gas increases and reduces its theoretical work capacity. That's why it is advisable at the first stage of investigations to determine reduction potential of the carbon black-hydrogen mixture, produced by pyrolysis of hydrocarbons in plasma.

According to [4], carbon black-hydrogen mixture is the heterophase one: in hydrogen volume pure finely dispersed carbon, not containing ash and sulfur and having size of particles about $1 \cdot 10^{-6}$ m, is uniformly distributed. Black carbon has high reaction capacity due to big specific surface (about $1 \cdot 10^{-5}$ m² per 1 kg of carbon). Gas part of the mixture is highly pure and active. Carbon is well wetted by the melt of iron oxides that ensures its good assimilation and high efficiency of use. This peculiarity of black carbon-hydrogen mixture imparts it with such properties, which do not have conventional gaseous reducers.

Decrease of concentration of wustite FeO in the melt in the course of the reduction process causes decrease of iron monoxide activity and, as a result, complication of the metal reduction from it and increase of the reducer consumption [5]. So, in application of carbon monoxide for reduction of wustite at temperature 1600 °C not more than 16 % CO transform into carbon dioxide, while at FeO activity of 0.5 — not more than 6 % (Figure 1) [5]. Application of hydrogen under the same conditions gives 51 and 26 % at FeO activity 1.0 and 0.5, respectively.

Content of silica SiO₂ in the melt significantly influences activity of wustite. So, at silicon dioxide concentration 12 % not more than 8 % CO is used for reduction [5]. The reason of this is binding of iron oxide by silicon dioxide with formation of iron meta-(FeO·SiO₂) or orthosilicate (2FeO·SiO₂) [6]. According to [5], reduction of iron from such melts can not be full. Depending upon content of SiO₂, maximum degree of reduction constitutes 86–97 %. As concentration of wustite decreases, lamination of the

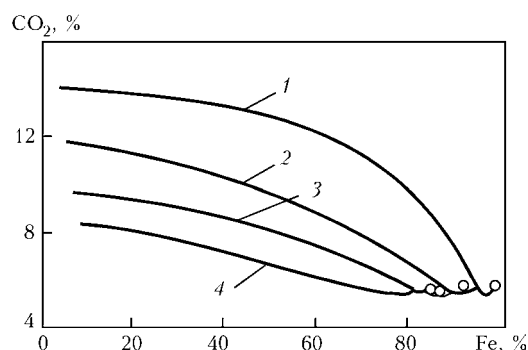


Figure 1. Dependence of CO_2 yield upon degree of iron reduction from melt FeO-SiO_2 at 1600°C with different initial concentrations of silica, %: 1 — 2; 2 — 5; 3 — 8; 4 — 12

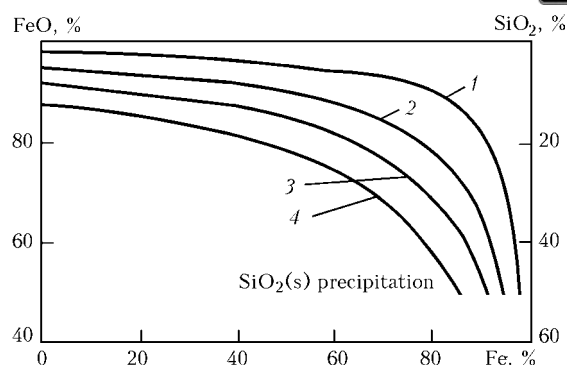


Figure 2. Change of composition of melt FeO-SiO_2 depending upon degree of iron reduction at different initial concentrations of silica (1–4 are the same as in Figure 1)

melt is possible with precipitation of solid silica SiO_2 at the temperature $1600\text{--}1700^\circ\text{C}$ (Figure 2) [5]. It is advisable to improve reduction of iron by means of the slag basicity increase. Iron silicates may be destroyed in case of addition into the slag of calcium oxide, which binds SiO_2 into calcium meta- or ortho-silicates (CaO-SiO_2 or 2CaO-SiO_2) and thus increases activity of FeO [7]. Maximum activity coefficient iron oxides achieve at slag basicity of 1.8–2.0, although at further increase of the latter and concentration of FeO about 100 % activity coefficient is close to one, i.e. the melt gets under Raoult's law.

Temperature exerts significant influence on rate and completeness of the reduction reaction proceeding. In Figure 3 [3, 8] dependence of the degree of reduction of a solid particle or a drop of the melt of wustite upon time at different temperatures is shown.

In reduction of iron by solid carbon from molten oxides, rate and completeness of reduction are positively influenced by temperature increase in the melting space, reduction of CO and CO_2 pressure, and mixing of the melt [3, 8].

In production of cast iron in the blast furnace distribution of sulfur between the slag and the metal is affected, first of all, by basicity of the slag: as basicity increases less sulfur transits into the metal. However, increase of basicity enables increase of the slag amount and consumption of coke [9]. Optimum basicity of the blast furnace slag is considered 1.0–1.3 [10]. Phosphorus transits in blast furnace melting almost completely from the charge into cast iron [9].

The investigations were carried out on developed in the E.O. Paton EWI of NASU pilot installation (Figure 4).

The installation was powered by single-phase alternative current from transformer OP 108 through regulator A1474. Current was adjusted within 500–2200 A, open-circuit voltage was 380 V, arc voltage drop was 30–180 V, maximum power was 400 kW.

Before beginning of the process, a hollow electrode was short-circuited on the metal ingot with known mass and chemical composition in the lower part of the mould. Into space between the electrode of 80 mm diameter and the mould wall with internal diameter 200 mm iron ore pellets of the following composition were poured, wt.%: 9.18 SiO_2 ; 0.32 Al_2O_3 ; 0.87 CaO ; 0.37 MgO ; 0.039 S; 0.007 P; 0.062 C; Fe_2O_3 — the base (Figure 5).

Melting chamber was blown by argon, which was supplied through the electrode cavity. After switching of the power source, electric arc was excited by lifting the electrode above the ingot. As iron ore feedstock melted, the electrode was lifted above surface of the melt with preservation of distance from end of the electrode to surface of the melt.

After complete melting of the feedstock hydrocarbons were fed into the cavity and supply of argon was stopped. In plasma of the arc in reduction zone pyrolysis of hydrocarbons took place. Produced hydrogen and carbon interacted with oxides and reduced the metal, which mixed with molten layer of the ingot and accumulated above it. Formed water vapor, carbon mono- and dioxide, and unreacted hydrogen and pyrocarbon were withdrawn from the melting space.

After termination of the process the melting chamber was blown by argon, which was supplied through the electrode cavity. In the course of plasma liquid-phase reduction of iron from oxides, flow of supplied through the electrode cavity reduction gas, length of the arc, and electric parameters of the arc burning were controlled. Then material balance was calculated and chemical analysis of produced metal and slag was made.

A series of experiments was carried out for determining influence of composition and flow of the gaseous reducer on rate and completeness of proceeding of plasma liquid-phase reduction reaction.

Comparison of experimental data in use of methane CH_4 and propane-butane mixture $\text{C}_3\text{H}_8\text{--CH}_4\text{H}_{10}$ (6 % of butane) proves that ratio of the amount of metal,

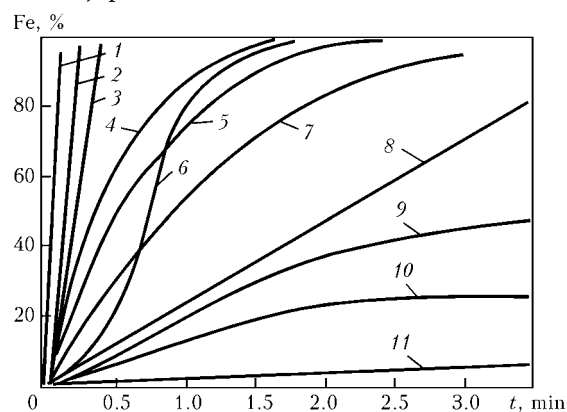


Figure 3. Change of iron reduction degree in time at different temperatures, $^\circ\text{C}$: 1 — 1600; 2 — 1560; 3 — 1540; 4 — 1480; 5 — 1450; 6 — 1380; 7 — 1370; 8 — 1420; 9 — 1350; 10 — 1200; 11 — 900

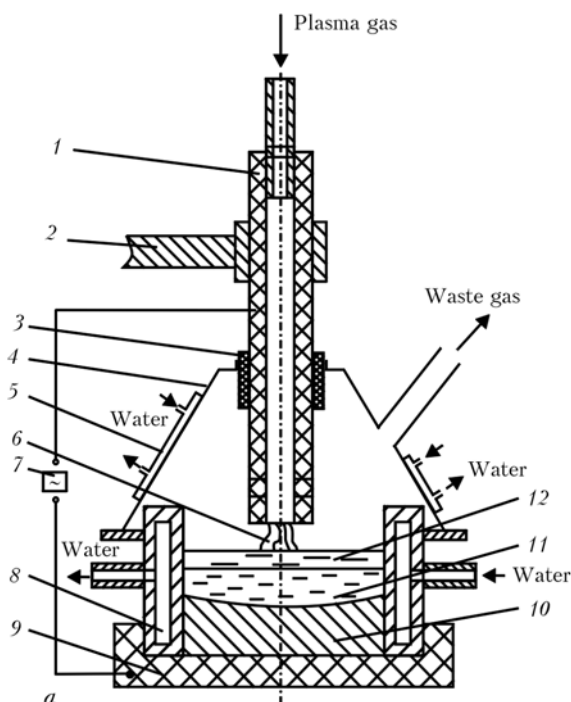


Figure 4. Scheme (a) and general view (b) of pilot installation: 1 — hollow electrode; 2 — mechanism for displacement of electrode; 3 — insulator; 4 — side panel; 5 — side panel cooling; 6 — plasma; 7 — power source; 8 — copper water-cooled mould; 9 — graphite crucible; 10 — metal ingot; 11 — molten metal; 12 — molten slag

produced with application of each of the reducers under the same conditions, as a whole is close to the ratio of their theoretical work capacities in relation to oxygen. So, one may draw conclusion that results of the experiments with application of one kind of a reducer may be transferred on other reducers, taking into account their theoretical work capacities in relation to oxygen and ratio of content in them of carbon and hydrogen.

A series of experiments was carried out, in which at the same flow of the propane-butane mixture (35 and 15 l/min) and basicity (0.1) duration of the gaseous reducer supply and duration of reduction varied.

Dependences of the degree of iron reduction upon duration of gas supply and its volume are presented in Figure 6.

Presented dependences make it possible to track thermodynamics and kinetics of the process. During the first minutes transition $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ takes place, which is proved by absence of a renewed metal. Further amount of produced iron quickly in-

creases, but then reduction process decelerates, which may be caused by reduction of wustite activity.

It should be noted that at the beginning of the process reduction rate insignificantly depends upon flow of the reducer, i.e. 35 l/min flow is excessive. But at a lower flow the process decelerates earlier because of decrease of iron oxide activity and increased need in the reducer.

So, for full recovery of the metal, saving of the reducer, and acceleration of the process it is necessary to increase flow of gaseous reducer in the course of the process.

For increasing activity of iron oxide, basicity of the slag melt was increased by addition of CaO. Basicity of the melt was determined by formula

$$B = \frac{(\text{CaO}) + 1.5(\text{MgO})}{(\text{SiO}_2) + 0.6(\text{Al}_2\text{O}_3)},$$

where (CaO), (MgO), (SiO_2), and (Al_2O_3) are the contents of respective oxides in the slag, wt.%.

In Figure 7 dependences of the metal reduction degree and content of iron oxide in the slag upon basicity in case of flow of propane-butane mixture 35 l/min and duration of its supply 14 min are given.

As it follows from the data of Figure 7, increase of basicity from 0.1 to 1.2 enables completeness of iron reduction.

Concentration of carbon in the metal is low — approximately 0.02 wt.%. Content of sulfur in the produced metal is 0.007 %, which is 5.5 times lower than in the charge, and does not depend upon basicity within the range 0.1–1.2 because of insufficiently high basicity or impossibility of producing metal with lower content of sulfur according to the proposed method. Contents of phosphorus in the metal and in

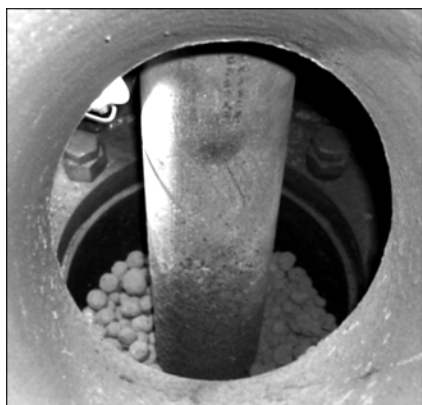


Figure 5. Pellets in mould

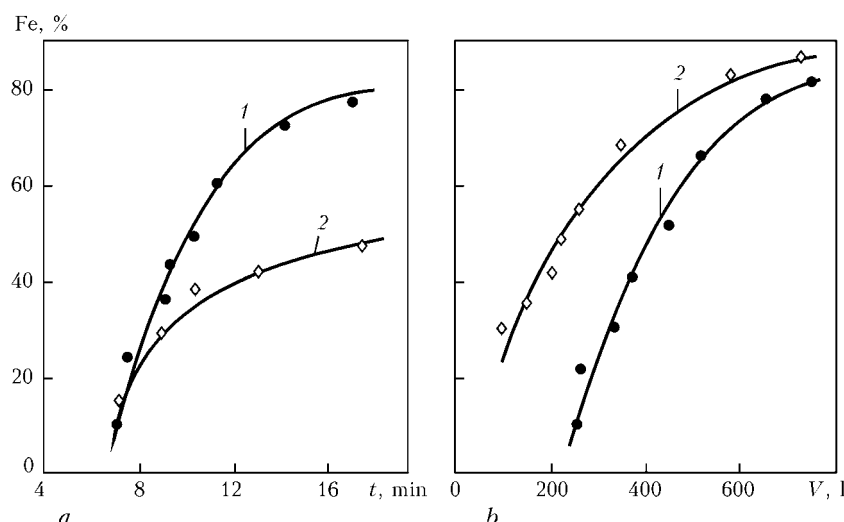


Figure 6. Dependences of iron reduction degree upon duration of reduction t (a) and volume of supplied gaseous reducer V (b) at following flows of propane-butane mixture, l/min: 1 — 35; 2 — 15

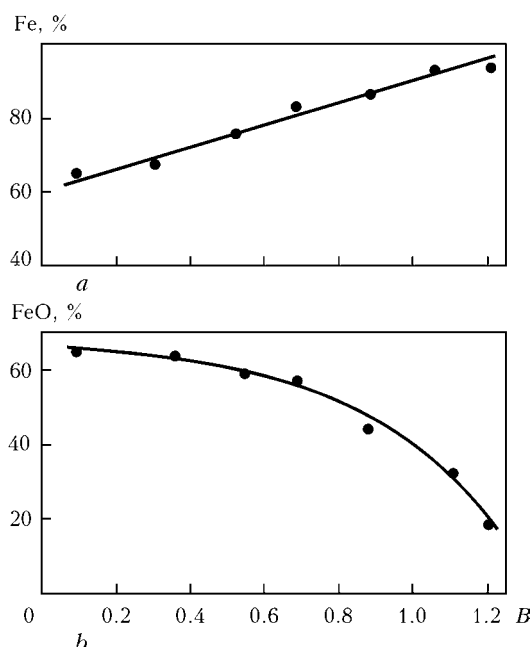


Figure 7. Dependences of iron reduction degree (a) and iron oxide content in slag (b) upon basicity B

the charge do not differ (about 0.007 wt.%) and do not depend upon basicity within mentioned range. Iron is not contaminated by impurities from the reducer, their content is rather insignificant and meets requirements established for majority of steels.

Content of nitrogen in the produced metal is about 0.0075, hydrogen — 0.0005 wt.%, which corresponds to their usual content in steel; content of oxygen is 0.075 wt.%, like in a rimming steel.

In determination of the reducer use degree actual level of oxidation of the reaction products was taken into account. In Figure 8 dependence of completeness of use upon duration of gas supply at $B = 0.1$ is shown.

Presented dependence allows tracking kinetics of the process and confirms analysis data of Figure 6. Use of the gaseous reducer approaches 30 % at the flow of 15 l/min, which is close to its use in solid-phase reduction. Optimization of the process should enable more complete use of the reducer.

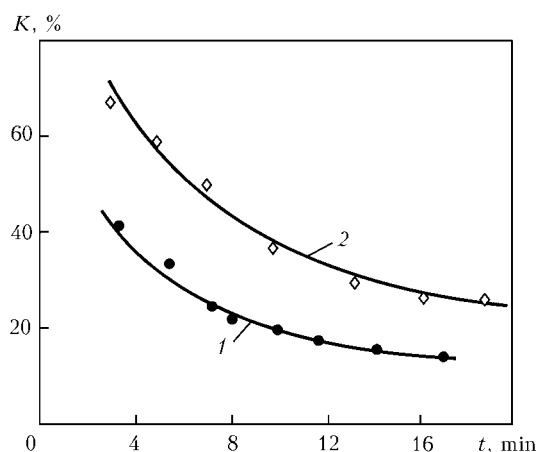


Figure 8. Dependence of degree of reduction gas use, K , upon duration of its supply (curves 1, 2 are the same as in Figure 6)

CONCLUSIONS

1. It is established that process of plasma liquid-phase iron reduction with application of gaseous reducers ensures production of a high-purity metal.

2. Main regularities of influence of flow and composition of gaseous reducer and basicity of slag on degree of iron reduction and use of the reducer are determined.

1. Dembovsky, V. (1981) *Plasma metallurgy*. Moscow: Metallurgiya.
2. Lakomsky, V.I. (1974) *Plasma-arc remelting*. Ed. by B.E. Paton. Kiev: Tekhnika.
3. Bondarenko, B.I., Shapovalov, V.A., Garmash, N.I. (2003) *Theory and technology of coke-free metallurgy*. Kiev: Naukova Dumka.
4. Kartavtsev, S.V. (2000) *Natural gas in reduction melting: Monography*. Magnitogorsk: MGTU.
5. Kozhevnikov, I.Yu. (1970) *Coke-free metallurgy of iron*. Moscow: Metallurgiya.
6. Ajzatulov, R.S., Kharlashin, P.S., Protopopov, E.V. et al. (2002) *Theoretical principles of steel-making processes: Tutorial for institutes of higher education*. Moscow: MISiS.
7. (1965) *Thermodynamical properties of inorganic materials: Refer. Book*. Moscow: Atomizdat.
8. Yusfin, Yu.S., Gimmelfarb, A.A., Pashkov, N.F. (1994) *New processes of metal producing (iron metallurgy): Manual for institutes of higher education*. Moscow: Metallurgiya.
9. Tovarovsky, I.G., Lyalyuk, V.P. (2001) *Evolution of blast furnace melting: Monography*. Dnepropetrovsk: Porogi.
10. Kurunov, I.F., Savchuk, N.A. (2002) *State-of-the-art and prospects of blast-furnace-free metallurgy of iron*. Moscow: Chernetinformatsiya.



EFFECT OF ALLOYING ON COMPOSITION, STRUCTURE AND PROPERTIES OF POWDERS OF ALLOY AlCuFe, CONTAINING QUASI-CRYSTALLINE PHASE

A.L. BORISOVA, Yu.S. BORISOV, L.I. ADEEVA, A.Yu. TUNIK, M.V. KARPETS and L.K. DOROSHENKO
E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Results of investigation of effect of scandium and chromium on structure, phase composition and technological properties of powders of alloy AlCuFe, designed for producing thermal coatings, containing quasi-crystalline phase, are presented. Behavior of powders in heating was studied using method of differential thermal analysis, which allows predicting phase transformation processes that proceed under conditions of thermal spraying of coatings.

Key words: powders for thermal spraying, quasi-crystalline phase, doped alloy AlCuFe, structure, properties, thermal analysis

One of the methods of improving quality of materials and coatings, which contain quasi-crystalline phase, including alloys of system Al–Cu–Fe, is their alloying by one or a complex of elements. At present there are about a dozen of foreign patents, in which various schemes of alloying powders of the alloy AlCuFe are proposed, depending upon functional designation of produced from them coatings.

For increasing resistance of coatings from alloy AlCuFe to oxidation composition is proposed, containing up to 6 at.% Cr. Thermal coating from powder $\text{Al}_{65.5}\text{Cu}_{18.5}\text{Fe}_8\text{Cr}_6$ is used as a sublayer in making heat-protection coatings from ZrO_2 [1]. For ensuring efficient heat-barrier protection material of the sublayer should contain at least 80 vol.% of quasi-crystalline phase. Application of such material, which has low heat conductivity, instead of traditional Me–CrAlY (Me–Ni, Co, CoNi) should improve protection properties of the double-layer heat-barrier coating.

For the purpose of increasing hardness and wear resistance of coatings from AlCuFe alloys it is proposed to alloy them by refractory metals (chromium, molybdenum, tungsten, etc.), as well as boron and silicon in small amounts [2].

In patent [3] mixture of powders AlCuFe and FeAlCrB, containing brittle and ductile components, is proposed. Coating of such composition is characterized by increased resistance to abrasive wear.

For producing wear-resistant coatings it was proposed to introduce into AlCuFe-base alloy soft particles, such as polymers BN, clad BN, and Ni-graphite [4].

A number of multicomponent alloys with general formula $\text{Al}_a\text{Cu}_b\text{Co}_c(\text{B}, \text{C})_d\text{M}_e\text{Ni}_f$ (M — iron, chromium, manganese, nickel, ruthenium, osmium, molybdenum, vanadium, manganese, zinc, palladium; N — tungsten, titanium, zirconium, hafnium, rhodium, niobium, tantalum, yttrium, silicon, germanium, rare-earth metals; I_f — unavoidable impurities), in which one of the main components (iron) is replaced by cobalt, was patented [5]. Refractory, rare-earth and other metals, boron and carbon act as alloying elements.

The alloys contain 30 wt.% of one or several quasi-crystalline phases. They are divided into seven groups depending upon their designation: for operation in acid and alkaline atmospheres, resistant to oxidation, grain-growth-resistant alloys, alloys with increased hardness, toughness, etc. Despite high number of various versions of doping alloys AlCuFe, works are continued in this direction.

In this article for additional alloying scandium and chromium are selected on the basis of analysis of diagrams of state of aluminium alloys and literature data.

Information on influence of alloying by scandium on structure and properties of the Al–Cu–Fe system alloys is absent in the literature. At the same time it was established in the course of investigations of aluminium alloys, carried out within the last 20 years, that alloying by 0.25–0.50 wt.% Sc exerts positive influence on mechanical and corrosion properties of aluminium alloys [6]. Production of the alloy AlCuFe powders, alloyed by scandium for application of coatings using the method of thermal spraying, is proposed in [7].

Alloys AlCuFe, alloyed by chromium, are already used as heat protection coatings in production of household utensils (frying pans, irons, etc.) due to their low heat conductivity and high corrosion resistance [8]. However, data on study of powders from the alloy AlCuFe, alloyed by chromium, are absent. Alloyed powders, investigated in this work, were produced by developed in the Institute for Materials Science Problems of NASU new original method of the alloy spraying by high-pressure water on experimental technological line by Dr. O.D. Nejgov.

Chemical compositions of investigated alloys are as follows:



at. %	wt. %
$\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$	47.3Al–40.0Cu–17.7Fe
$\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$	42.71Al–40.08Cu–16.91Fe–0.3Sc
$\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$	42.54Al–40.05Cu–16.9Fe–0.5Sc
$\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$	47.02Al–30.2Cu–11.8Fe–10.98Cr

In the course of investigation complex methodology was used, which included metallography (optical microscope «Neophot-32» with attachment for digital photographing); scanning electron microscopy (scanning electron microscope JSM-840); X-ray spectral microanalysis (microanalyser «Camebax» SX-50).

X-ray diffraction phase analysis was carried out on diffractometer Dron-UM1 in monochromatized radiation CuK_α . Investigations were carried out both at room temperature and at heating within temperature range 20–900 °C in helium using high-temperature attachment UVD-2000. Amount of ψ -phase was determined using methodology described in [9]. For this purpose recording of radiograms was performed within angle interval, in which the most strong diffraction maximums of main phases were located: $40 < 2\theta < 50$.

In addition, resistance of powders to oxidation in air was studied using thermography. Experiments were carried out on derivatograph Q-1500 within temperature range 20–1000 °C at heating rate 10 K / min. Phase transformations during heating in helium up to the temperature 1500 °C were studied using method of differential thermal analysis (DTA).

Technological properties of powders (flow and bulk density) were determined according to GOST 20899–75 and GOST 19440–74. Before investigation powders were classified by fractions on vibratory sieves (GOST 18318–73), and each fraction was investigated separately.

It was established as a result of investigation of granulometric composition of atomized powders and construction of bar graphs of particle distribution by sizes that more than 70 wt.% of particles related to the fraction 25–100 μm , i.e. were fit for application of coatings by the method of thermal spraying (plasma, micro-plasma or detonation one). More coarse fraction of the powder (100–200 μm), content of which in the mixture is about 25 wt.%, may be used as a filler of flux-cored wires for application of coatings by the method of electric arc plating, and amount of fine powder (<25 μm), unfit for application of coatings because of high losses of aluminum during heating of the powder up to the melting state, does not exceed 2–5 wt.%.

Appearance of powders of doped alloys (Figure 1) is practically the same for all compositions. Particles of the powders have irregular, sometimes elongated shape with molten surface. Occasionally particles with sharpened edges and internal pores occur.

Metallographic analysis of the powder particles showed their fine and multi-phase structure (Figure 2), which mainly represents mixture of two

phases: crystalline (light, more soft) and quasi-crystalline (dark, more hard and brittle) ones.

Phase composition of the powders was investigated in more detail by radiographic method. So, on radiograms of powders of the alloys with scandium, especially with a highest content (Figure 3), near reflexes of ψ - and β -phases system of additional low-intensity lines was registered at diffraction angles 20.5; 29.05; 41.53 and 46.71. Analysis of angular position of these peaks showed their good coincidence with diffraction spectrum lines of equilibrium triple W -phase of the Al–Cu–Sc system with tetragonal lattice of the ThMn_{12} type [10]: experimental peaks of W -phase in our case correspond to values of the lattice parameters $a = 0.8688$ nm, $c = 0.5029$ nm and insignificantly differ from $a = 0.855$ nm, $c = 0.506$ nm for W -phase in the Al–Cu–Sc system with the composition $\text{Al}_{51.4}\text{Cu}_{39.7}\text{Sc}_{8.9}$ [11].

Disregarding small amount of W -phase, one may estimate content of ψ -phase in powders according to the methodology of [9]. The results obtained prove that doping of the alloy AlCuFe with 0.265 and 0.440 at.% Sc essentially increases content of quasi-crystalline icosahedron ψ -phase, whereby, like in case of non-alloyed powders, content of ψ -phase increases by means of size of the particles reduction (Figure 4).

For precision investigation of temperature influence on phase transformations of the alloy AlCuFe powder, alloyed by scandium, powder of the $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ composition and fraction 25–40 μm with content of ψ -phase about 78 wt.% was selected. It was established that introduction into alloy of 0.44 at.% Sc causes certain reduction of the period of lattice of ψ - and β -phases (Table 1) in comparison with non-alloyed powder AlCuFe, for which $a_\psi = 0.63466(7)$ nm, and $a_\beta = 0.29270(9)$ nm, which may be the evidence of scandium dissolution in lattices of ψ - and β -phases or of the change in them of the content of base elements.

As a result of seasoning the powder alloyed by 0.44 at.% Sc at temperature 600 °C for 1 h transforms practically completely into single-phase ψ -state (Figure 5), whereby lines of ψ -phase noticeably narrow down, i.e. the crystalline lattice improves. Cooling down to room temperature does not change single-phase state of the annealed powder, whereby period of crystalline lattice of ψ -phase is less than in initial powder (see Table 1).

At the temperature 700 °C lines of β -phase are registered again on the radiogram, whereby their intensity increases by means of temperature increase (see Table 1). At the temperature 900 °C in addition to lines of β -phase peaks of λ -phase are registered on the radiogram.

Formed at the temperature above 700 °C β -phase preserves during cooling down up to the room temperature, whereby parameter of its lattice does not remain constant (see Table 1).

Diffractogram of the powder, alloyed by chromium, contains in initial state ψ - and β -phases (Fi-

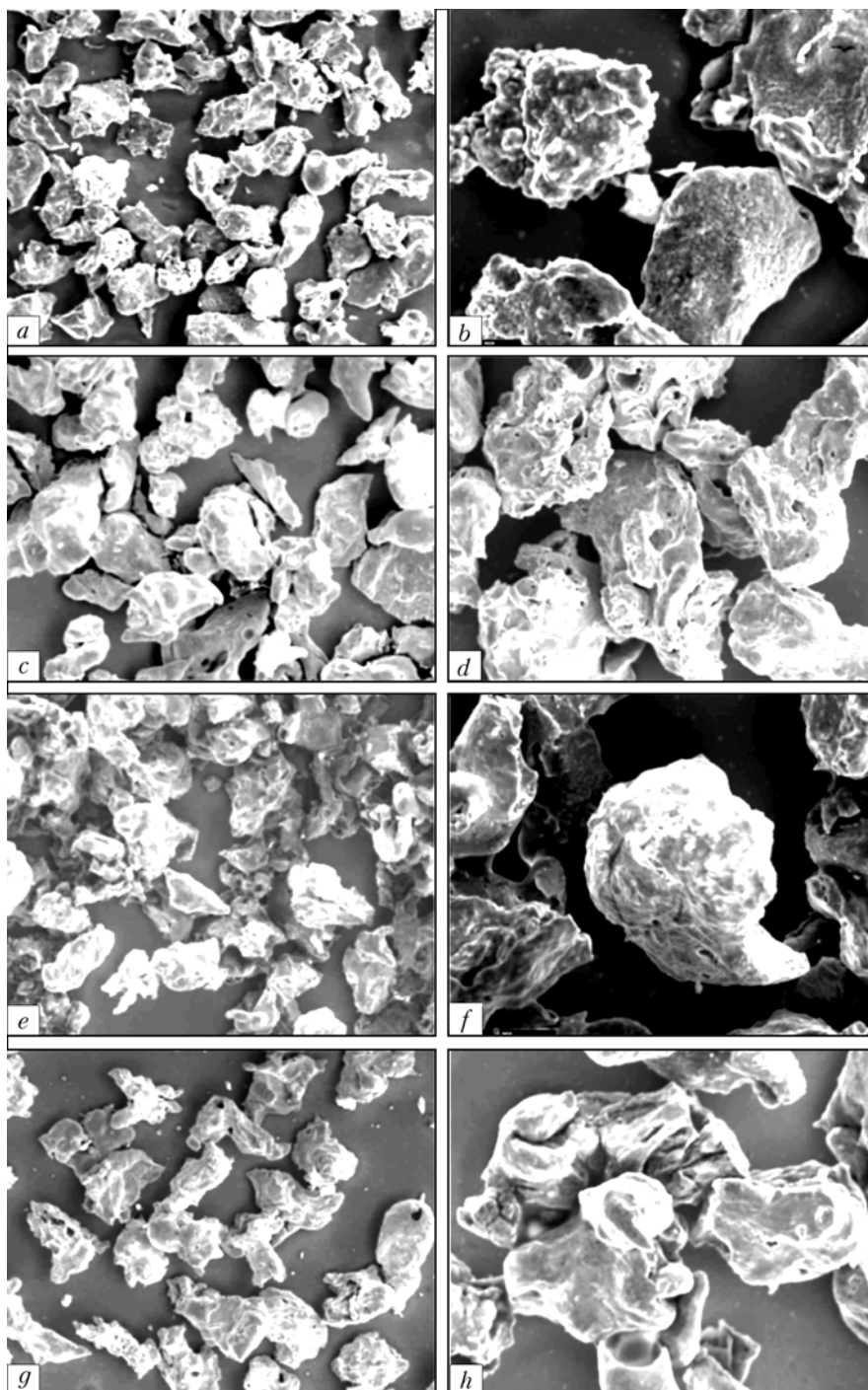


Figure 1. Appearance of powders: *a, b* — $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$; *c, d* — $\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$; *e, f* — $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$; *g, h* — $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$; *a, c, e, g* — $\times 200$; *b, d, f, h* — $\times 800$

figure 6, curve 1), whereby periods of the lattices of mentioned phases are as follows: $a_\psi = 0.64860(9)$ nm but $a_\beta = 0.29144(4)$ nm. This causes superimposition of the peak (110) β ($2\theta = 43.9^\circ$) on more intensive peak of ψ -phase with Kahn indices (20 / 32). Heating of the powder up to the temperature 600–800 °C enables increase of the β -phase period ($a_\beta = 0.29460(9)$ nm) and formation instead of ψ -phase of crystalline approximant of decagonal quasi-crystal — phase O_1 (Figure 6, curve 2). Phase O_1 of the Al–Cu–Fe–Cr system alloys is analyzed in detail in [12, 13].

In Figure 7 calculated diffractogram of orthorhombic phase O_1 (spatial group B, mm^2 , $a = 3.254$ nm,

$b = 1.237$ nm, $c = 2.357$ nm) is presented, which contains 660 atoms in the elementary cell. Very good coincidence of calculated and experimental diffractograms is registered.

Radiographic investigation of the alloy AlCuFe powders, annealed within 1 h in vacuum furnace and then cooled down to room temperature, showed that although after annealing at 500 °C new phase O_1 appears, significant amount of ψ -phase continues to exist, while after annealing at 550 °C practically the whole ψ -phase converts into O_1 .

Influence of alloying on resistance to oxidation was studied in relation to powders with size of particles

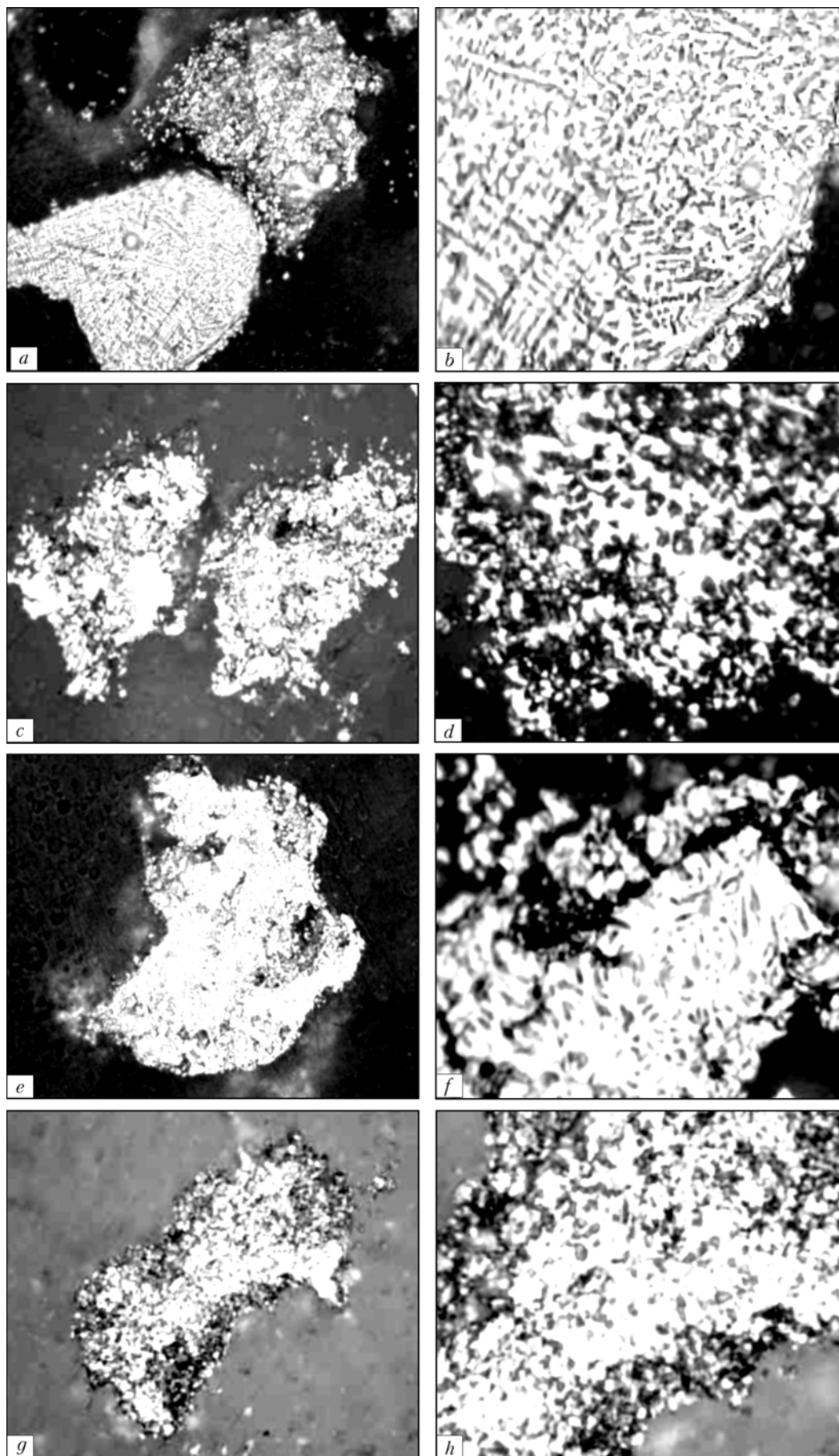


Figure 2. Microstructure of powder particles: *a, b* — $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$; *c, d* — $\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$; *e, f* — $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$; *g, h* — $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$; *a, c, e, g* — $\times 400$; *b, d, f, h* — $\times 1000$; etched

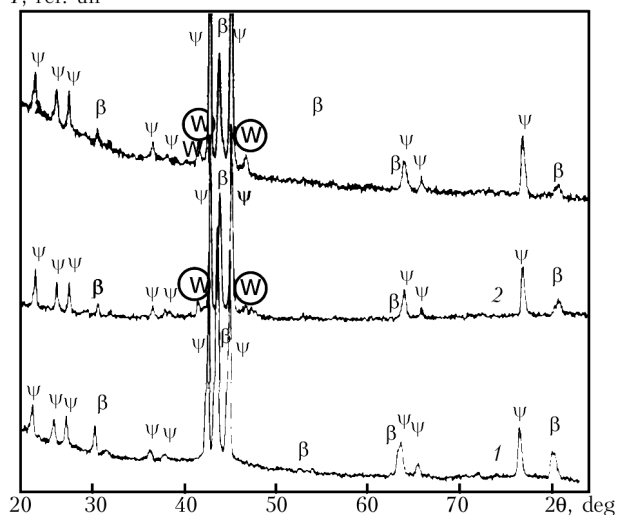
 I , rel. un

Figure 3. Fragments of alloy powder diffractograms: 1 — $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$; 2 — $\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$; 3 — $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$; I — intensity of radiation

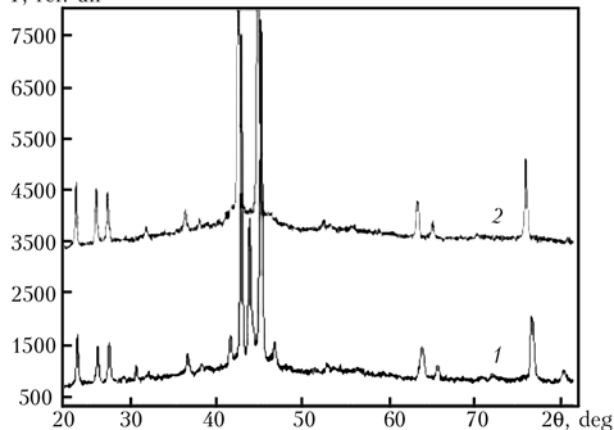
 I , rel. un

Figure 5. Fragments of alloy $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ powder diffractograms with size of particles 25–40 μm in initial state (1) and after seasoning for 1 h at 600 °C (2)

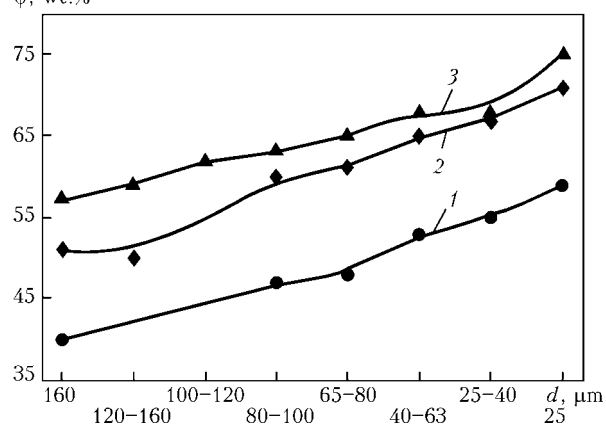
 ψ , wt. %

Figure 4. Influence of alloying by scandium on content of ψ -phase in powders of following alloys: 1 — $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$; 2 — $\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$; 3 — $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$; d — size of particles

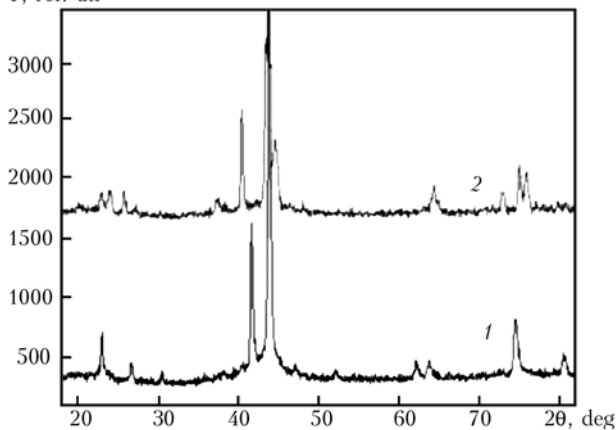
 I , rel. un

Figure 6. Fragments of alloy $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ powder diffractograms in initial state (1) and after heating up to 800 °C and cooling down to room temperature (2)

Table 1. Dependence of intensity I , half-width B , main parameters of X-ray peaks and lattice parameters of ψ - and β -phases of $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ alloy powder upon temperature

Filming temperature, °C	ψ -phase		β -phase		Period of lattice, nm	
	I , rel. un	Δ , deg	I , rel. un	Δ , deg	a_ψ	a_β
20, initial	38373	0.28	15500	0.28	0.63298(3)	0.29237(3)
600 after seasoning for 1 h	42528	0.22	—	—	0.63774(3)	—
20 after 600	45944	0.22	—	—	0.63149(4)	—
200	44375	0.22	—	—	0.63322(1)	—
400	42430	0.22	—	—	0.63522(2)	—
600	40865	0.21	—	—	0.63728(3)	—
700	38514	0.18	3486	0.17	0.63832(4)	0.29674(5)
800	35145	0.16	5264	0.17	0.63998(3)	0.29719(7)
600 after 800	37950	0.16	5493	0.18	0.63696(5)	0.29633(4)
600 after 850	28290	0.15	8354	0.14	0.64137(6)	0.29754(7)
600 after 900	29115	0.20	23228	0.24	0.63160(9)	0.29650(8)
20 after 900	31792	0.23	30905	0.26	0.62740(8)	0.29390(6)

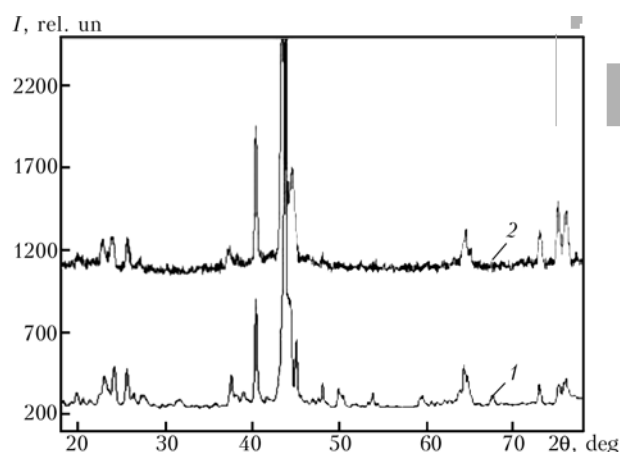


Figure 7. Calculated fragment of approximated phase O_1 diffractogram (1) and experimental alloy $Al_{66}Cu_{18}Fe_8Cr_8$ powder diffractogram after heating up to 800 °C and cooling down to room temperature (2)

80–100 μm . For comparison non-alloyed powders, produced by spraying with water and argon, were investigated under the same conditions. Analysis of the data (Figure 8) shows that temperature of initiation of non-alloyed powder oxidation (about 600 °C) does not depend upon the method of its production, while by means of temperature increase oxidation intensity of the powders, produced by spraying with water, increases in comparison with the powder, produced by spraying with argon. This is connected with higher specific surface of powder particles in the first case.

Oxidation initiation temperature of the powders, alloyed by scandium and chromium, somewhat increases (from 600 to 680 °C) in comparison with non-alloyed powders. As heating proceeds, intensity of oxidation of powder with chromium differs little from that of non-alloyed powder sprayed with water.

Powder, alloyed by scandium, is least resistant to oxidation. The same regularity is noted in [14]. Introduction of rare-earth metals in quasi-crystal $Al_{63}Cu_{25}Fe_{12}$ accelerates oxidation of iron and copper with formation of nano-dimensional structure of oxides.

Results of investigation of powders by DTA method are presented in Figure 9.

As far as preliminary investigations showed that size of the powder particles does not effect character of curves (DTA), we limited ourselves by investigation of the powder with size of particles 80–100 μm .

Comparison of curves (DTA) of the powders, alloyed by scandium, with curves of the unalloyed powder shows that scandium just insignificantly reduces temperature of initiation of phase transformation both during heating (curves 1, 2) and during cooling (curves 1', 2').

First endothermic effects (810–900 and 820–890 °C) for non-alloyed and alloyed alloys, respectively, may be referred to the melting point of ψ -phase, which, according to literature data, equals 870 °C (Figure 10).

Character of the curves within this range is, evidently, influenced by the effects connected with $\beta \rightarrow \psi$ transformation, which were established in in-

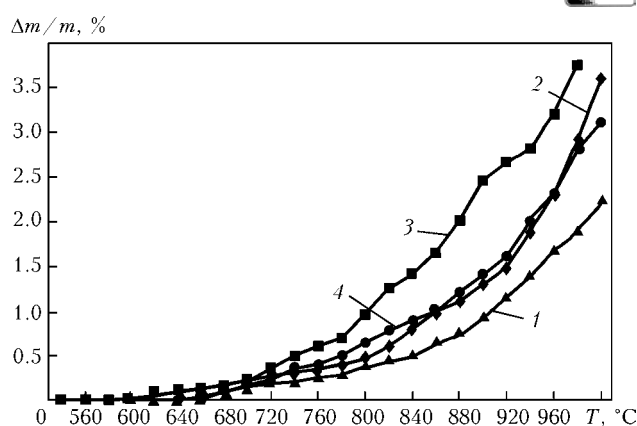


Figure 8. Relative change of mass $\Delta m / m$ of alloy $AlCuFe$ -base powders with size of particles 80–100 μm during heating in air: 1, 2 — $Al_{63}Cu_{25}Fe_{12}$; 3 — $Al_{62.56}Cu_{25}Fe_{12}Sc_{0.44}$; 4 — $Al_{66}Cu_{18}Fe_8Cr_8$; 1 — spraying with argon; 2–4 — spraying with water

vestigation of powders by the method of high-temperature radiography (see Table 1).

Second endothermic effect (930–1010 and 930–1000 °C) for the same compositions relates to the area $L + \lambda + \beta$ on the diagram of the $Al-Cu-Fe$ system phase equilibria (Figure 10). Lines of λ -phase together with β -phase are registered on radiograms at temperature 900 °C. The process terminates by formation of the melt at temperature above 1000 °C with subsequent two-stage solidification during cooling (Figure 9, curves 1', 2'). It is characteristic that ingots after DTA had spherical form, which proved absence of wetting by the crucible material melt (ZrO_2).

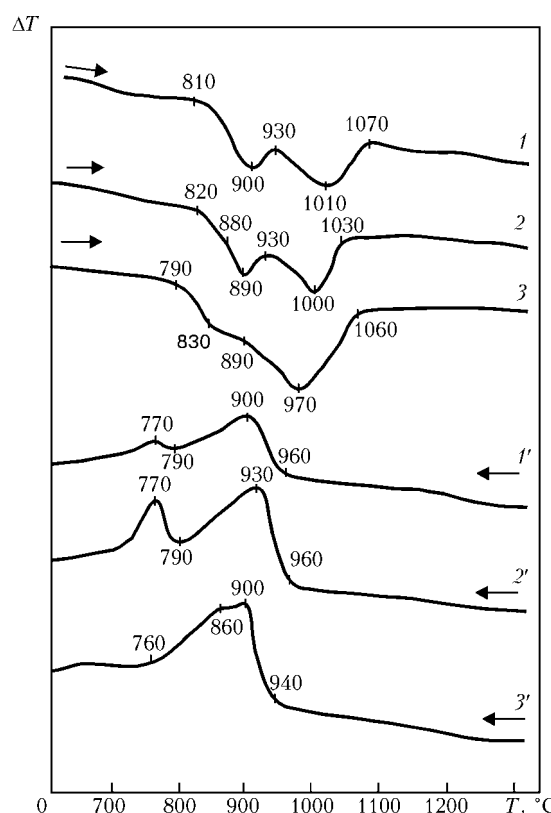


Figure 9. Differential thermal curves of heating (1–3) and cooling (1'–3') of powders $Al_{63}Cu_{25}Fe_{12}$ (1), $Al_{62.56}Cu_{25}Fe_{12}Sc_{0.44}$ (2), $Al_{66}Cu_{18}Fe_8Cr_8$ (3)

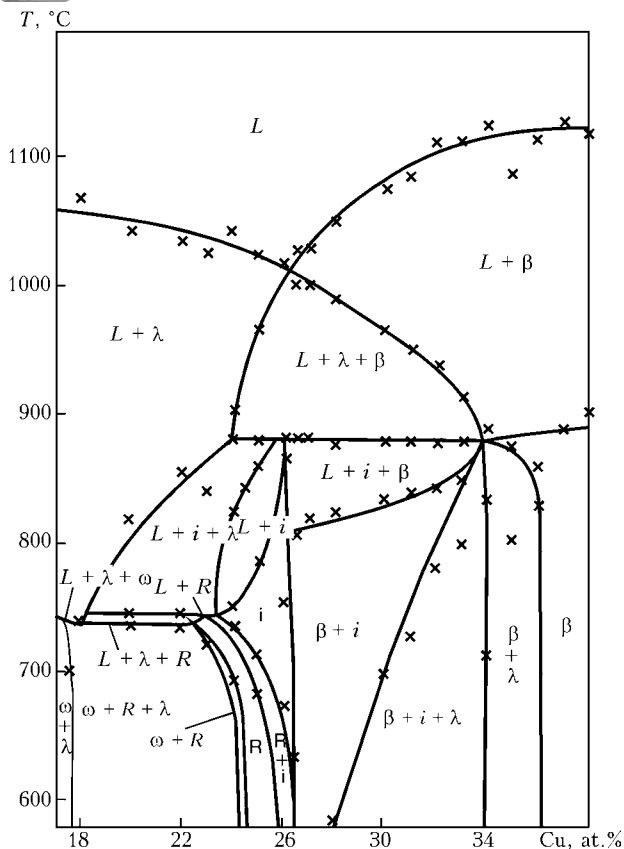


Figure 10. Polythermal section of phase equilibrium diagrams of system Al–Cu–Fe at 12 at.% Fe [15]: *L* — liquid; *i* — quasi-crystalline ψ -phase; *R* — approximant of ψ -phase; β , λ , ω — crystalline phases

Structure of ingots is rather coarse-grain (Figure 11, *a*, *b*) because of lower rate of solidification (80 K/s) in comparison with solidification rate of sprayed powders ($\approx 1 \cdot 10^5$ K/s), which allowed measuring microhardness of the main phase components. In the ingot from non-alloyed powder light β -phase had microhardness value of (7.5 ± 0.5) GPa, while in the ingot from alloyed powder it was somewhat lower — (7.32 ± 0.3) GPa. Detailed investigation inside β -phase grains allows differing rare dendrites of λ -phase of dark-grey color with microhardness (8.0 ± 1.5) GPa.

Microhardness of quasi-crystalline ψ -phase in the ingot from non-alloyed powder achieved 10 GPa, while in the powder alloyed by 0.44 at.% Sc it was (9.36 ± 0.5) GPa. Content of ψ -phase in the first case equaled, approximately, 22, in the second case was ≈ 29 wt.%.

Alloying by chromium is reflected on the character of curves in DTA more essentially: their view changes within the whole temperature range and area of thermal effects shifts into the area of lower temperatures.

On the heating curve 3 (Figure 9) flexes (790, 830, and 890 °C) are noted, which proves multistage character of phase transformations that precede liquid phase formation (970 °C). Solidification process covers wide temperature range, which may indicate overlapping of temperature ranges of phase transitions and high degree of the ingot chemical inhomogeneity.

Although in X-ray diffraction phase analysis two phases were detected (solid solution on the basis of

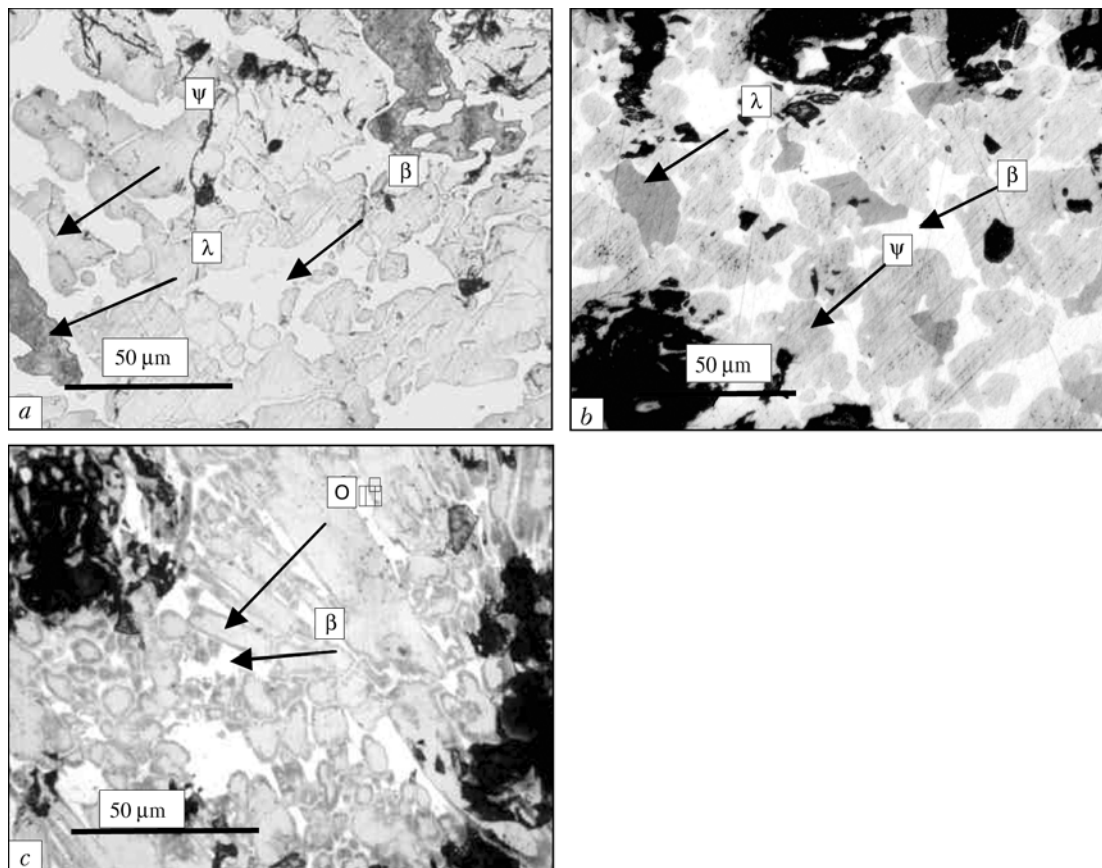


Figure 11. Microstructure of ingots (DTA) from powders $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ (*a*), $\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$ (*b*), $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ (*c*); etched

**Table 2.** Effect of alloying by scandium and chromium on technological properties of the alloy AlCuFe-base powders

Powder fraction, μm	Chemical composition of alloy							
	$\text{Al}_{62.735}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.265}$		$\text{Al}_{62.56}\text{Cu}_{25}\text{Fe}_{12}\text{Sc}_{0.44}$		$\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$		$\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$	
	Flow, s / 50 g	Bulk density, g / cm^3	Flow, s / 50 g	Bulk density, g / cm^3	Flow, s / 50 g	Bulk density, g / cm^3	Flow, s / 50 g	Bulk density, g / cm^3
> 200	Not flowing	1.15 ± 0.01	149	1.08 ± 0.01	Not flowing	1.10 ± 0.01	N / D	
160–200	80	1.11 ± 0.01	95	1.10 ± 0.01	105	1.11 ± 0.01	Same	
120–160	81	1.19 ± 0.01	70	1.25 ± 0.01	82	1.14 ± 0.01	»	
100–120	76	1.26 ± 0.01	85	1.30 ± 0.01	77	1.18 ± 0.01	»	
80–100	86	1.29 ± 0.01	68	1.34 ± 0.01	74	1.23 ± 0.01	63	1.38 ± 0.02
63–80	101	1.34 ± 0.01	74	1.42 ± 0.01	73	1.29 ± 0.01	Not flowing	1.33 ± 0.01
40–63	Not flowing	1.42 ± 0.02	Not flowing	1.52 ± 0.02	Not flowing	1.37 ± 0.01	Same	1.36 ± 0.01
25–40	Same	1.45 ± 0.02	Same	1.57 ± 0.02	Same	1.38 ± 0.01	»	1.30 ± 0.02

orthorhombic VCC-lattice O_1 and cubic VCC-lattice β), significant chemical inhomogeneity was registered in the process of the ingot etching, especially over edges of the phase O_1 grains (Figure 11, c). Microhardness of the main structural components varies within wider range than in previous cases. For β -phase it is (6.35 ± 7.0) GPa, for phase O_1 — (7.96 ± 1.25) GPa.

Investigation of technological properties of powders (Table 2) showed that doping of alloy AlCuFe by scandium and chromium increases flow of the powder fine fractions. While in non-alloyed powder flow was absent when size of particles was 63–80 μm and less, in alloyed powder it disappeared when size of particles was 40–63 μm . Inherent to the powders with higher content of scandium (0.44 at.%) is also higher flow in the fraction 63–80 μm and rather good flow in powders of more coarse fraction (more than 200 μm). However, technological properties of powders, produced by spraying with water, are inferior to those of powders, produced by spraying with argon, having spherical shape of particles and flow 35–60 s / 50 g for wide range of size of particles — from <25 to >160 μm .

CONCLUSIONS

1. It is established that doping of alloy $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ with 0.265 and 0.440 at.% Sc allows significant increasing content of icosahedron ψ -phase in powders from this alloy. In addition to crystalline β - and quasicrystalline ψ -phases forms crystalline W -phase, which is stable up to the temperature 600 °C. After annealing, powder with 0.440 at.% Sc completely transits at 600 °C within 1 h into single-phase ψ -state.

2. It is shown that in powders from alloy $\text{Al}_{66}\text{Cu}_{18}\text{Fe}_8\text{Cr}_8$ form ψ - and β -phases in, approximately, the same amount. After annealing at 550 °C within 1 h the whole quasi-crystalline phase transforms into phase O_1 , which represents crystalline approximate of decagonal quasi-crystalline phase.

3. It is determined that doping of alloy AlCuFe by scandium and chromium practically does not change qualitative phase composition of the powders, but significantly increases in them content of quasi-

crystalline phases without exerting significant influence on thermal stability thereof.

4. It is established that oxidation initiation temperature of alloyed powders increases, in comparison with non-alloyed powders, from 600 to 680 °C, while alloying with scandium significantly increases oxidation intensity at higher temperatures.

Authors express their gratitude to the National Technical Center in Ukraine for financial support of this work carried out within the framework of project 1630.

1. Dubois, J.-M., Archambault, P., Colletet, B. *Quasicrystalline aluminum heat protection element and thermal spray method to form elements*. Pat. 5888661 US. Publ. 30.04.99.
2. Shield, J.E., Goldman, I., Anderson, I.E. et al. *Method of making quasicrystal alloy powder, protective coatings and articles*. Pat. 5433978 US. Int. Cl. B22F9/08. Publ. 18.07.95.
3. Sordelet, D.J., Besser, M.F. *Abrasion resistant coating and method of making the same*. Pat. 6242108 B1 US. Publ. 05.07.2001.
4. Hermanek, F.J. *Abradable quasicrystalline coating*. Pat. 6254700 B1 US. Publ. 03.07.2001.
5. Dubois, J.M., Pianelli, A. *Aluminum alloys, substrates coated with these alloys and their applications*. Pat. 5432011 US. Publ. 11.07.95.
6. Milman, Yu.V., Lotsko, D.V., Sirko, O.I. (2000) Sc effect of improving mechanical properties in aluminum alloys. *Mater. Sci. Forum*, **331–337**, 1107–1112.
7. Milman, Yu.V., Lotsko, D.V., Efimov, N.A. et al. (2005) Sc alloying effect in cast Al–Cu–Fe quasicrystals. In: *Abstr. of Pap. of Int. Conf. on Current Materials Science: Achievements and Problems* (Kiev, Sept. 26–30, 2005).
8. Dubois, J.-M., Proner, A., Bucaille, B. et al. (1994) Quasicrystalline coatings with reduced adhesion for cookware. *Ann. Chem. Fr.*, **19**, 3–25.
9. Sordelet, D.J., Besser, M.F., Anderson, I.E. (1996) Particle size effects on chemistry and structure of Al–Cu–Fe quasicrystalline coatings. *J. Thermal Spray Technology*, **5**(2), 161–174.
10. Kharakterova, M.L., Dobatkina, T.V. (1988) Polymetric sections of Al–Cu–Sc system. *Izvestiya AN SSSR. Metall.*, **6**, 180–182.
11. Kharakterova, M.L. (1991) Phase composition of Al–Cu–Sc alloys at temperatures of 450 and 500 °C. *Metall.*, **4**, 191–194.
12. Dong, C., Dubois, J.-M., Kang, S.S. (1992) The orthorhombic approximant phases of the decagonal phase. *Phil. Mag. B.*, **65**(1), 107–126.
13. Dong, C., Dubois, J.-M. (1995) Structural study of crystalline approximants of the Al–Cu–Fe–Cr decagonal quasicrystal. *J. Appl. Cryst.*, **28**, 96–104.
14. Yamasaki, M., Tsai, P. (2002) Oxidation behavior of quasicrystalline $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloys with additional elements. *J. Alloys and Compounds*, **342**, 473–476.
15. Quiguandon, M., Calvayrac, Y., Quivy, A. et al. (1999) Phase diagrams and approximants. *Quasicrystals: MRS Symp. Proc.*, **553**, 95–106.



INVESTIGATION OF STRUCTURE AND MECHANICAL PROPERTIES OF Ti-7.2Al-2.9Mo-2.7W-3Nb-2.3Zr-0.4Si ALLOY

S.A. FIRSTOV¹, V.N. ZAMKOV², N.P. BRODNIKOVSKY¹, V.F. TOPOLSKY², A.V. KOTKO¹, A.V. SAMELYUK¹
and A.V. GOLOVASH¹

¹I.N. Frantsevich Institute of Materials Science Problems, NASU, Kiev, Ukraine

²E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Structure and mechanical properties of alloy Ti-7.2Al-2.9Mo-2.7W-3Nb-2.3Zr-0.4Si were studied after rolling and heat treatment. It is shown that complex alloying leads mainly to the solution hardening, though a small amount of silicides is precipitated. Oxidation in deforming in air affects ductile properties even at 550–600 °C. Increase of diffusion mobility enables reduction of strain hardening at above 600 °C and causes drastic reduction of yield strength above 650 °C. Reduction of fracture surface fragmentation by means of temperature increase from 550 to 650 °C up to achievement of 100 % relative reduction in area is explained by preservation of the amount of inhomogeneities of strain origin.

Key words: high-temperature titanium alloys, alloying, heat treatment, structure, mechanical properties, fracture

Hardening of titanium alloys by solid solution alloying allows having additional possibilities due to influence on stability of high-temperature β -phase and type and amount of products of its disintegration [1, 2].

Bi-phase ($\alpha + \beta$)-alloys are characterized by good combination of strength and ductility and are the most numerous group of titanium alloys. However, it is difficult to achieve high strength of ($\alpha + \beta$)-alloys at increased temperatures because of loss of strength stipulated by the phenomenon of structural super-ductility [3–6]. That's why working temperature of titanium ($\alpha + \beta$)-alloys usually does not exceed 400–500 °C and problem of increasing their high-temperature strength remains actual. In this work influence of complex alloying on high-temperature strength and structural stability of bi-phase titanium ($\alpha + \beta$)-alloy is considered.

Materials and methodology of investigations. Ingots of alloy for investigation were produced by double electron-beam cold hearth melting (EBCHM) and subjected to rolling in air according to standard technology for bi-phase alloys [7]. Content of alloying elements and impurities in the alloy was as follows, wt. %:

Ti	Al	Mo	W	Nb	Zr	Si	O	N	H
Base	7.2	2.9	2.7	3.0	2.3	0.4	0.18	0.026	0.0015

At the first stage rolling was started in β -area at temperature 1050 °C (temperature of polymorphous transformation is, approximately, 1020 °C). Five passes were made with general degree of deformation 55 %. At second stage produced billet of 32 mm thickness was heated in ($\alpha + \beta$)-area up to temperature

960 °C and subjected to rolling (11 passes) down to thickness 11 mm. Temperature of the end of rolling was 850 °C, and general degree of deformation in ($\alpha + \beta$)-area — more than 65 %.

Two modes of heat treatment were used for investigating structure of deformation after rolling: 850 °C, soaking for 2 h, cooling in air with subsequent ageing at 650 °C for 2 h; 950 °C, soaking for 2 h, cooling in air with subsequent ageing at 570 °C for 2 h. Hardness of the alloy in deformed state and after heat treatment was measured using hardness gage PMT-3 at the load 150 g, at which the imprint (approximately, 23 μ m diagonal) contained about 30 grains. Measurements were made using 10–12 imprints.

Temperature dependence of mechanical properties of the deformed alloy at static tension was defined within temperature range 20–750 °C. For this purpose flat specimens having 3.0×1.5 mm section and length of working part 15 mm were cut out from plates along the rolling. Tension was performed at rate of strain $1.2 \cdot 10^{-3} \text{ s}^{-1}$. For estimating influence of atmosphere on the properties, specimens were tested in air and in vacuum.

For the purpose of determining temperature values, at which change of the type of elementary restructuring of atoms, which control plastic deformation, takes place, diagram in coordinates $\ln \sigma_{0.2} - 1/T$ was plotted, inclination of which was interpreted using expression [8]:

$$\sigma_{0.2} = B \exp (\Delta U / 3kT), \quad (1)$$

where dependence B upon temperature may be neglected [8, 9]; k is the Boltzmann's constant; T is the temperature, K; ΔU is the change of internal energy connected with Gibbs activation energy; ΔG is the

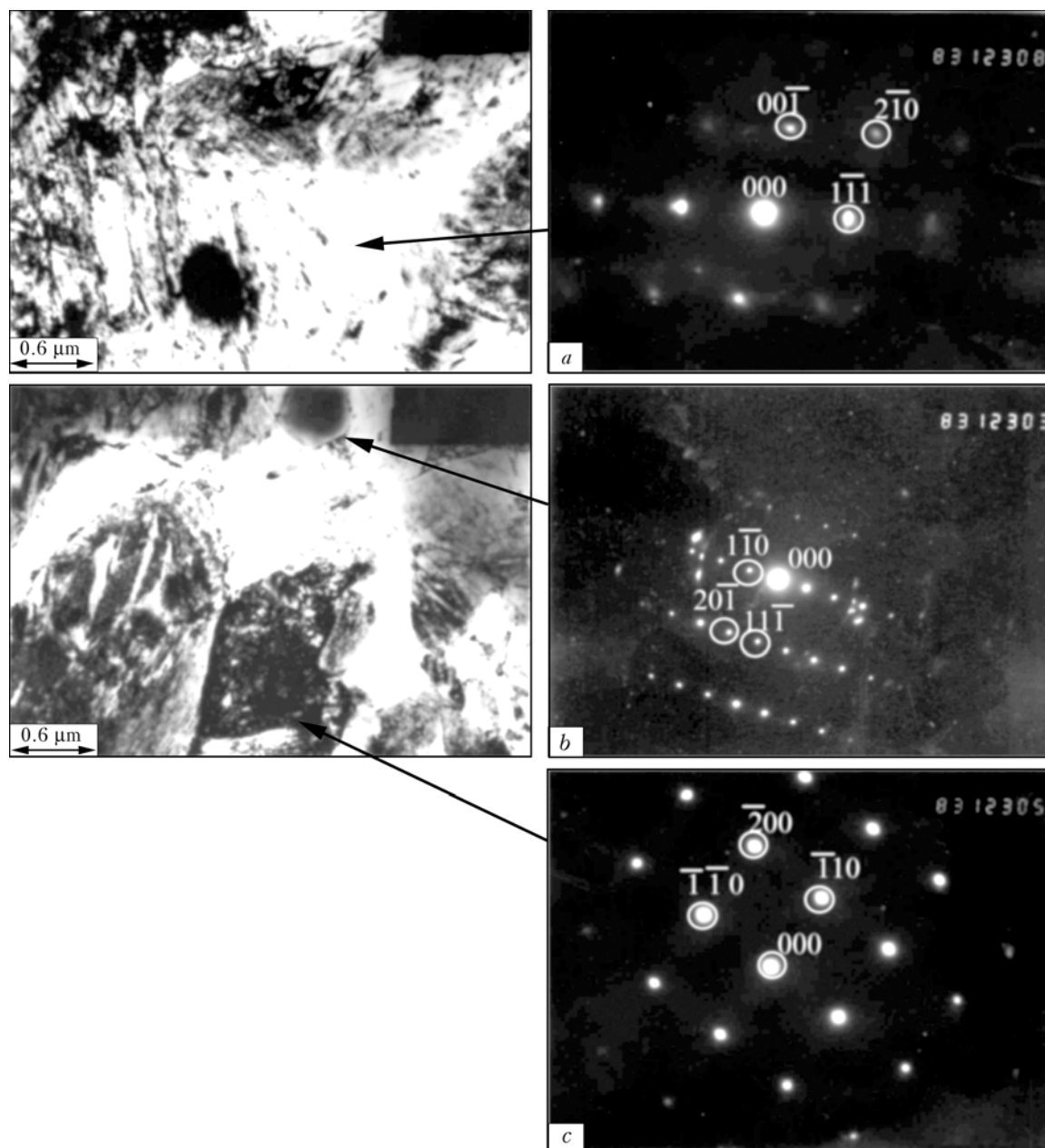


Figure 1. TEM-microstructure of alloys in post-rolling state: *a* — diffraction of electrons from α -Ti [121]; *b* — the same from particle Ti_5Si_3 [112]; *c* — the same from β -Ti [001]

characteristic of potential barrier, which is overcome when an elementary act of plastic deformation is performed according to the expression $\Delta G = \Delta U - T\Delta S$.

Investigation of the alloy structure was performed using transmission (TEM) and scanning (SEM) electron microscopes. SEM was also used for fractographic analysis of tested specimens.

Results of the experiment. Investigation of diffraction of electrons from the phases showed that the alloy mainly consisted of α - and β -phases (Figure 1). Identical in all investigated states of the alloy precipitations of particles of 0.3–0.4 μm size were detected (Figures 1, 2). It was established in study of the electron diffraction that these were particles of silicide Ti_5Si_3 , which, probably, formed in the process of the molten ingot cooling due to reduction of silicon solubility in titanium in $\beta \rightarrow \alpha$ transformation.

Heat treatment according to the first mode practically did not change size of the grains (1–5 μm) and quantitative ratio of α - and β -phases. Just a certain rounding of α -grains was registered (Figure 3, *a*, *b*). Heating up to 950 $^{\circ}\text{C}$ according to the second version of heat treatment caused growth of grains of α -phase and increase of its amount, probably, because of recrystallization and redistribution of alloying elements (Figure 3, *c*). Due to higher temperature of heating (950 $^{\circ}\text{C}$) activation of $\beta \rightarrow \alpha$ disintegration was noted. Inside β -grains acicular precipitates of α -phase with cross size of needles about 0.04 μm were more clearly seen (see Figure 2).

Microhardness of the alloy after rolling was (4.0 ± 0.3) GPa. Due to heat treatment according to the first mode its value increased up to (5.0 ± 0.28) GPa, but according to second one increased

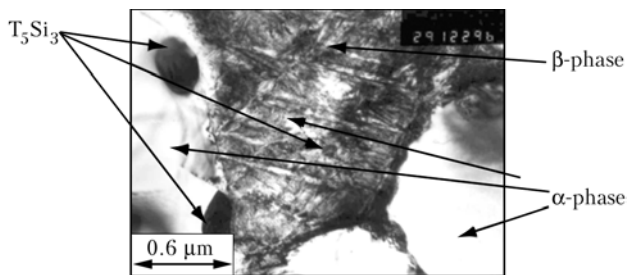


Figure 2. TEM-microstructure of alloy after heat treatment according to first mode

too but insignificantly — up to (4.4 ± 0.26) GPa. Evidently, after air hardening from 850 °C, heating up to 650 °C enabled disintegration of metastable β -phase, which caused additional hardening of the alloy. After heat treatment according to the second mode, loss of strength, which usually accompanies recrystallization (Figure 3, c), was compensated by disintegration of metastable β -phase during repeated heating up to 570 °C and soaking at this temperature.

Temperature dependence of the alloy properties after rolling at static tension is presented in Figure 4. As test temperature increases from 20 to 650 °C, values of strength characteristics change insignificantly, and at further increase of temperature drastically reduce. Relative elongation δ_0 and reduction in area ψ_0 start to increase drastically at temperature 550 °C. Above 650 °C starts growth of uniform elongation δ_u . It proves stabilization of strain and difficulty in forming the neck (Figure 5). As far as curves of temperature dependence of yield strength and ultimate tensile strength practically coincide above 650 °C, strain

hardening at these temperatures is absent (see Figure 4). Stability of plastic strain is ensured mainly due to appearance of rate dependence of flow stress [4, 5, 10]. In this case development of the neck is inhibited at the initial stage, because localization of strain in it is accompanied by increase of the strain rate and due to this increase of the flow stress is required. Appearance of rate dependence of flow stress is accompanied by beginning of its sharp temperature dependence.

In Figure 6 temperature dependence of yield strength is presented in semi-logarithmic coordinates. According to [8], sections of zigzag line determine temperature ranges of action of different strain mechanisms. In this very place near respective sections of zigzag line values of activation energies of thermally activated processes, obtained using equation (1), are presented.

In Figure 7 character of fracture of specimens at different temperatures is shown. In fracture of the specimens, which failed at 20 °C, mean value of facets equals 1.0–1.5 μm and corresponds to size of the grains, taking into account their, approximately, 50 % deformation in neck of the specimen (Figures 1–3). As test temperature increases up to 550 °C, fracture gets pit character, whereby size of pits achieves 5 μm . On their walls the relief was detected, which proves presence of internal structural elements, commensurable with size of separate grains. As temperature increases up to 600 °C, size of pits continues to grow.

One usually connects presence of pits on fracture surface with failure over boundaries of originated in

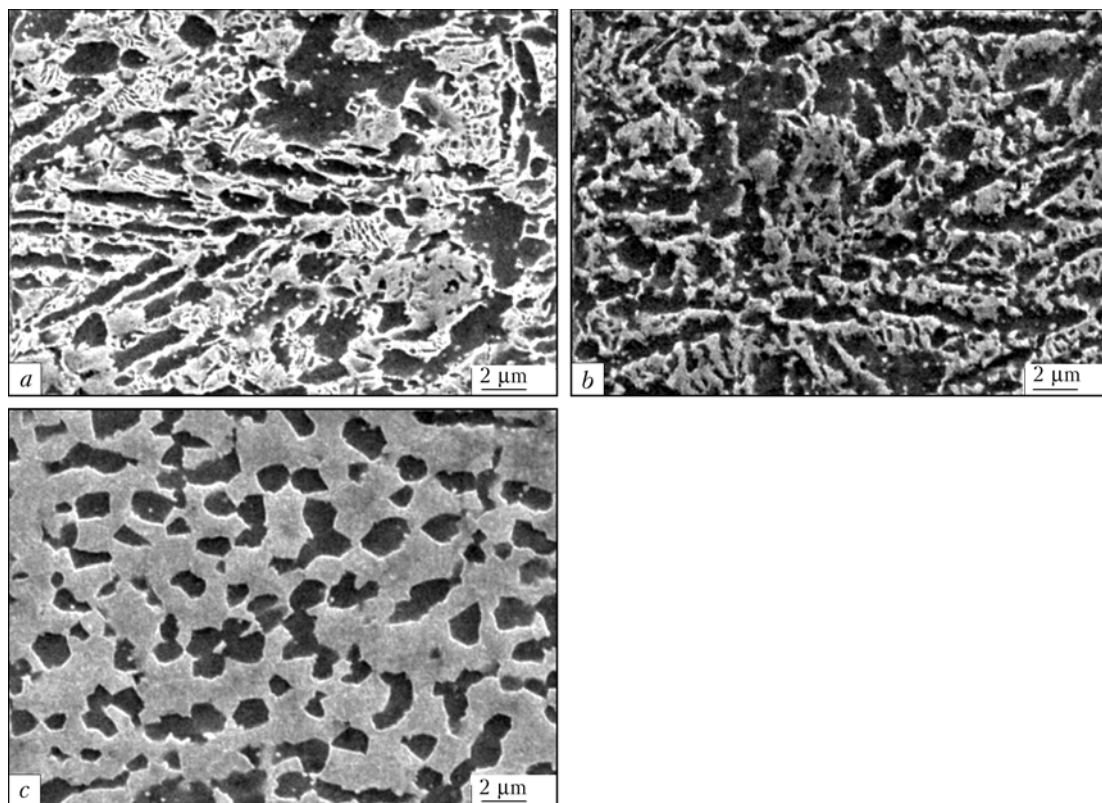


Figure 3. SEM-microstructure of alloy: a — after rolling; b — after heat treatment according to first mode; c — the same according to second mode

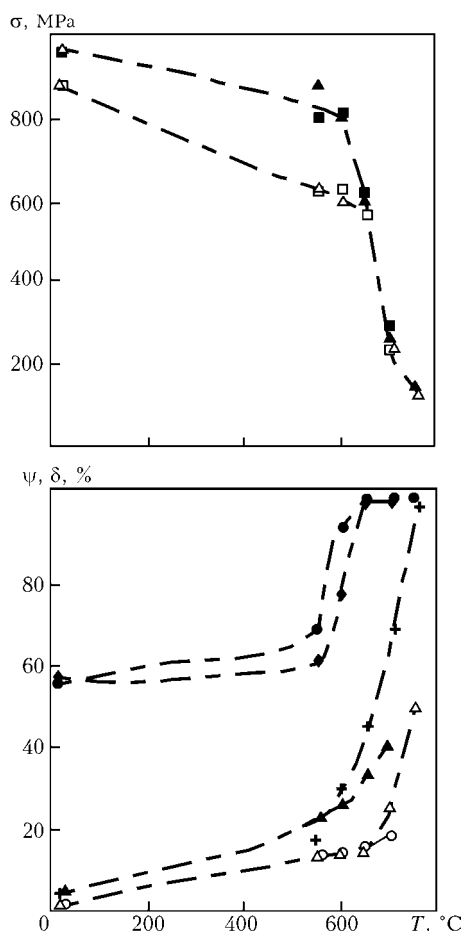


Figure 4. Temperature dependence of mechanical properties of alloy: ■ — σ_t , air; □ — $\sigma_{0.2}$, air; ▲ — σ_t , vacuum; △ — $\sigma_{0.2}$, vacuum; ◆ — ψ , air; ▼ — δ_0 , air; ○ — δ_u , air; ● — ψ , vacuum; + — δ_0 , vacuum; ▽ — σ_w , vacuum; δ_0 , δ_u — general and uniform elongation

the process of deformation cells in particles of the second phase [9, 11]. In this case particles in the bottom of pits were not detected. Size of pits exceeds size of grains, and taking into account stability of the structure at heating up to 850 °C can not be connected with elements of structure of strain origin.

Evidently, as test temperature increases within 500–600 °C range, strength of boundaries approaches strength of the grain body. At 650 °C this process finishes by the fact that fracture over structural elements ceases in general and a specimen is stretched and acquires shape of a needle (Figure 5). Noted above stabilization of deformation hinders its localization not just at macrolevel (shape of a specimen), but also at the level of the alloy microstructure. Stretching into the needle proves absence of strain localization over section of a specimen in separate elements of the material structure with formation of an internal neck.

Experiments showed that atmosphere, in which tests are carried out (air or vacuum), practically does not affect strength characteristics of the alloy. Lower values have ductile characteristics in tests in air than in vacuum (see Figure 4). Reduction in area in test in air is connected with premature fracture initiated by defects on the surface (Figure 8). Usually pit frac-

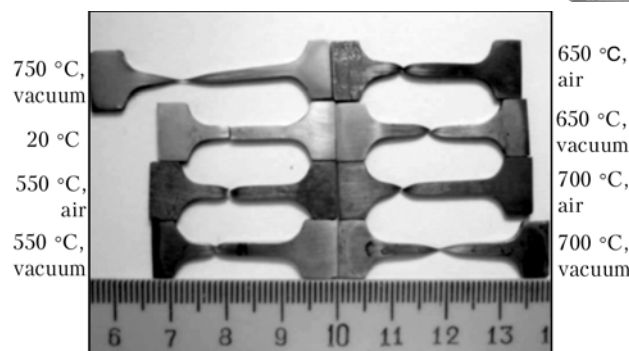


Figure 5. Appearance of specimens after tension at different temperatures in vacuum and in air

ture starts in center of a specimen, where character of loading is more rigid.

In test in air defects in the form of cuts are formed on surface as a result of oxidation. They are concentrators of stresses and reason of origination of pit fracture from the surface.

Reduction in area in consequence of oxidation in test in air starts to be registered at the temperature 550 °C (Figure 4). Influence of premature fracture on level of relative elongation gets notable only at 600 °C. It is explained by low contribution of last stages of deformation in the neck into elongation at a lower temperature (Figure 5). So, atmosphere of test does not affect temperature dependence of uniform elongation, because this characteristic is determined at early stages of strain, when action of surface defects does not exert its influence yet.

Discussion of the results. Possibility of using equation of type (1) for analysis of activation parameters of strain mechanisms within different temperature ranges is considered in [8, 9, 12–14]. For separation of the Gibbs free activation energy ΔG , which is characteristic of potential barrier for elementary deformation act and allows identifying these acts, it is necessary to introduce assumptions based on model approximations, upon which significantly depends the result to be obtained. That's why such data require for independent check, and only after this they may be used as substantiation of models used for performing calculations. And although it is impossible to determine specific strain mechanism on the basis of just tensile tests, calculation of internal energy of a crys-

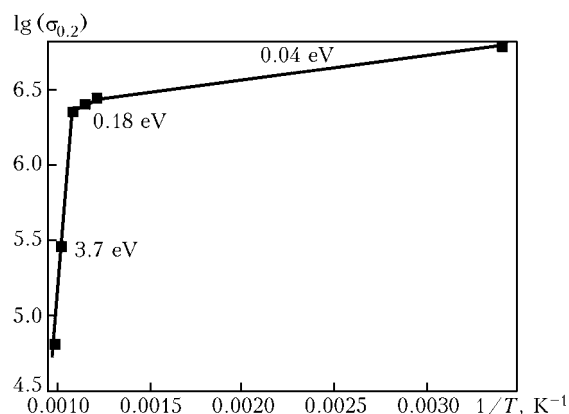


Figure 6. Temperature dependence of yield strength of alloy after rolling in tension

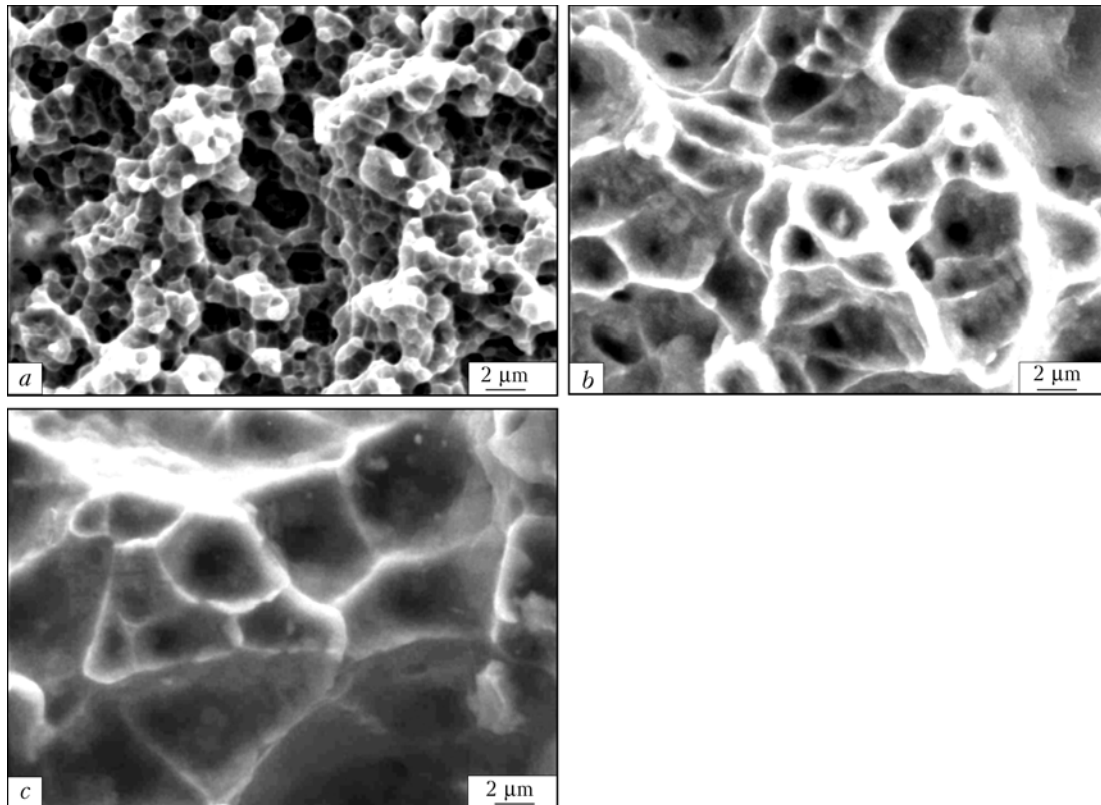


Figure 7. Character of fracture of specimen depending upon test temperature, °C: *a* — 20; *b* — 550; *c* — 600

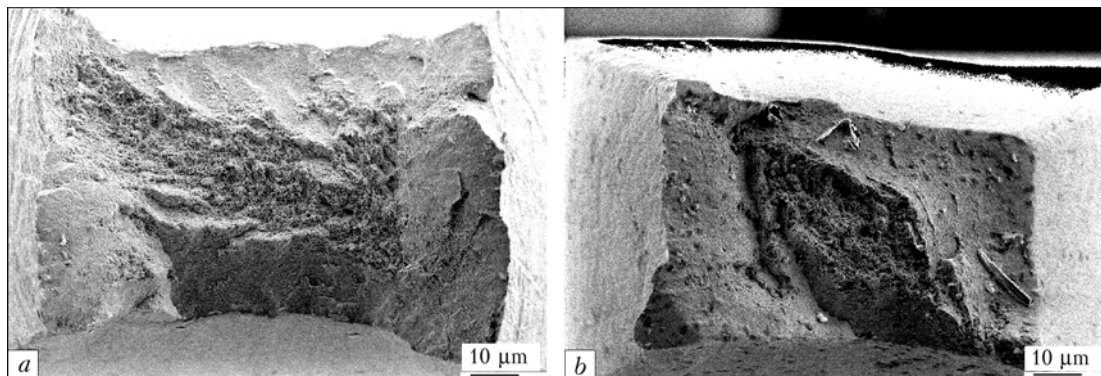


Figure 8. Character of fracture of specimen depending upon test atmosphere at 550 °C: *a* — air; *b* — vacuum

tal, which characterizes potential barrier and conditions of its overcoming and equals

$$\Delta U = \Delta G + T(\Delta S) \quad (2)$$

allows separating temperature ranges, within which act strain mechanisms of similar nature. Indefiniteness, connected with unknown value of entropic term $T(\Delta S)$, is superimposed by significant difference of potential barriers for different groups of strain mechanisms.

Value of activation energy, produced using equation (1) [5], may be divided into groups (Table), depending upon strain mechanisms and temperature ranges of their action. At temperature T strain mechanism with potential barrier not exceeding $50kT$ may be activated due to heat fluctuations [8, 14], whereby the strain will be controlled by the mechanism, which has maximum activation energy among all possible mechanisms for this material [15].

Of interest is investigation of chemical and phase composition and the alloy structure influence on set

Classification of strain mechanisms by activation energy levels

Temperature range	$\Delta\sigma$, eV	Characteristic of group
$(0.1-0.3)T_{\text{melt}}$	0.04–0.30	Overcoming of spot obstacles by separate dislocations
$(0.3-0.5)T_{\text{melt}}$	0.6–1.2	Break-off from Cottrell atmospheres from interstitial impurities
$0.5T_{\text{melt}}$	2.0–4.0	Mechanisms defined by diffusion of vacancies and substitutional atoms



of possible strain mechanisms and shift of the range of their action over temperature scale. Alloying, which shifts beginning of strain control by diffusion mechanisms into the area of higher temperatures, enables increase of high-temperature strength.

Carried out investigations showed that overcoming of spot obstacles by separate dislocations (activation energy is about 0.18 eV) in the studied titanium alloy in deformed state (grain size is 1–5 μm) controls strain up to relatively high temperatures ($0.4T_{\text{melt}}$). This, evidently, is result of solid solution hardening of titanium by refractory elements.

From mechanisms, connected with diffusion, starts to act at comparatively low temperatures ($0.4T_{\text{melt}}$) mechanism with activation energy 3.7 eV. So high value of activation energy, which is usually connected with grain-boundary glide, established rate of uniform elongation, drastic reduction of flow stress, and cessation of fracture over boundaries of grains are facts, which allow identifying mechanism of deformation that acts at the temperature from 650 °C and higher as inter-grain glide, on which structural super-ductility is based [2, 3].

In titanium ($\alpha + \beta$)-alloys glide over grain boundaries at increased temperature is facilitated due to additional possibility of removing nonconformities, which occur over boundaries, due to $\alpha \leftrightarrow \beta$ transformations. This, probably, also causes increased propensity of bi-phase titanium alloys to super-ductility. It is, evidently, possible to shift inter-grain glide into the areas of higher temperatures due to precipitation over α - and β -phases of disperse, non-deformed particles, for example, silicides.

Prediction of prospects concerning use of silicide is based on possibility of influence by application of heat treatment on precipitation of secondary silicides allowing for high solubility of silicon in β -phase and its drastic temperature dependence, and on precipitation of silicides during disintegration of β -phase.

CONCLUSIONS

1. It is established that solid-solution hardening of titanium-base alloys is especially efficient due to possibility of $\alpha \leftrightarrow \beta$ transformation control, which ensures production of disperse structure and precipitation of

different metastable phases that may be effected by application of heat treatments.

2. It is shown that solution hardening for production of high-temperature titanium-base alloys is limited by phenomenon of glide over grain boundaries, which causes drastic loss of strength of the alloys at temperature above 600–650 °C. For increasing high-temperature strength of titanium alloys it is necessary to use disperse hardening, in particular, in the studied alloy it is advisable to increase content of silicon.

3. It is determined that alloying of titanium alloys for the purpose of high-temperature strength increase should simultaneously increase their heat resistance, because in the process of test in air as early as at 550 °C on surface of the metal appear defects connected with oxidation, which effect its mechanical properties.

1. Kolachev, B.A. (1976) *Physical metals science of titanium*. Moscow: Metallurgiya.
2. Kollings, E.V. (1988) *Physical metals science of titanium alloys*. Moscow: Metallurgiya.
3. Solonina, O.P., Glazunov, S.G. (1976) *Heat-resistant titanium alloys*. Moscow: Metallurgiya.
4. Grabsky, M.V. (1975) *Structure superplasticity of metals*. Moscow: Metallurgiya.
5. Gulyaev, A.P. (1982) *Superplasticity of steel*. Moscow: Metallurgiya.
6. Kajbyshev, O.A. (1984) *Superplasticity of commercial alloys*. Moscow: Metallurgiya.
7. Aleksandrov, V.K., Anoshkin, N.F., Bochvar, G.A. et al. (1979) *Semi-finished products of titanium alloys*. Moscow: Metallurgiya.
8. Borisenko, V.A. (1984) *Hardness and strength of refractory materials at high temperatures*. Kiev: Naukova Dumka.
9. Trefilov, V.I., Milman, Yu.V., Firstov, S.A. (1975) *Physical principles of strength of refractory metals*. Kiev: Naukova Dumka.
10. Shtejberg, A.M., Gajduchenya, V.F. (1996) Influence of strain rate cycling on elongation of steel and copper specimens. *Metally*, **3**, 151–156.
11. Rybin, V.V., Vergazov, A.N., Solomko, Yu.M. (1978) Principles of intragrain fracture of metals with bcc-lattice. *Fizika Metallov i Metallovedenie*, **46**(3), 582–596.
12. Gibbs, G.B. (1969) On the interpretation of experimental activation parameters for dislocation glide. *Phil. Mag.*, **20**(166), 867–872.
13. Indenbom, V.L., Orlov, A.N. (1973) Introductory article. In: *Thermally-activated processes in crystals*. Moscow: Mir.
14. Dorn, D., Mout, D. (1966) Physical principles of creep. In: *New materials and methods of material and alloy examination*. Moscow: Metallurgiya.
15. Ivens, A., Roulings, R. (1973) Thermally-activated deformation of crystalline materials. In: *Thermally-activated processes in crystals*. Moscow: Mir.



INNOVATION TECHNOLOGICAL PROCESSES OF ELECTRIC FURNACE FERRONICKEL REFINING BY PROGRESSIVE INDUSTRIAL METHODS

Information 2. Thermodynamic investigations of processes and technology of ladle desulfuration of electric furnace ferronickel by sodium carbonate

N.V. NOVIKOV, I.I. KAPRAN, K.D. SOKOLOV, M.I. GASIK and A.N. OVCHARUK

«Pobuzhsky Ferronickel Integrated Works, Ltd.», NMetAU, Dnepropetrovsk, Ukraine

Three-stage scheme of crude ferronickel refining at «Pobuzhsky Ferronickel Integrated Works, Ltd.» (PFIW) is presented. Thermodynamic investigations of sodium compounds and processes of desulphurization of electric furnace ferronickel by soda are generalized. Results of mass-spectrometric examinations of Na_2CO_3 evaporation mechanism and composition of vapor phase are analyzed. Thermodynamic properties of products of Na_2CO_3 interaction with sulfur dissolved in ferronickel are given. Main principles of innovation-industrial technology of ladle desulfuration by soda of electric furnace ferronickel under conditions of PEIW are described.

Key words: electric furnace ferronickel, impurity elements, methods and process of out-of-furnace refining, sulphur in ferronickel, sodium carbonate, desulfuration in ladle, evaporations of sodium carbonate, mass-spectrometric data, thermodynamic properties of sodium sulfide, industrial technology of ladle desulfuration

Composition of commodity ferronickel produced at PEIW meets requirements of TU U27.3-31076956-009:2005.

For the purpose of improving quality and increasing competitiveness of ferronickel on international market, systemic developments directed at improvement of technology and electro-thermal equipment have been lately carried out at the integrated works, which will allow improving quality of ferronickel up to the level envisaged by the draft branch standard being developed (Table 1).

Ferronickel, produced by the method of ore-thermal reduction electric melting of import New Caledonian ore (2.2–2.5 % Ni), has the following chemical

composition, wt. %: 15–17 Ni; 0.3–0.4 Co; 0.5–5.0 Si; 0.5–2.0 Cr; 1.8–2.5 C; 0.013–0.020 Cu; 0.2–0.4 S; 0.01–0.02 P, the rest — iron. For reducing content of impurity elements, electric furnace (crude) ferronickel is subjected to three-stage refining: desulfuration by soda in ladle; oxidation refining in converter with acid (silica brick) lining for the purpose of reducing content of chromium and silicon; oxidation refining in converter with basic (periclase-carbon or periclase-chromite) lining for dephosphorization, decarburization, and final oxidation of silicon and chromium under basic slag.

In this work materials of analysis of thermodynamic premises and main principles of the technology of out-of-furnace (ladle) desulfuration of electric furnace ferronickel by sodium carbonate (soda ash) are presented.

Thermodynamic premises of electric furnace ferronickel desulfuration. Electric furnace ferronickel

Table 1. Requirements to chemical composition of ferronickel produced by method of ore-reduction melting in electric furnaces (draft branch standard for ferronickel)

Ferronickel grade	Share of elements, wt. %							
	Ni	Co	Ni	Si	Cr	C	S	P
	Not more than							
FN-5M	4.6–50.0	Ratio of Co to Ni is not more than 1:30	Not more than 0.3	2.0	1.5	1.5	0.08	0.04
FN-5K	14.0–20.0	1.5–8.0	1.0–3.0	0.05	0.08	0.03	0.3	0.05
FN-6	Not more than 5.0	0.1–0.4	Not less than 0.01	6.0	3.0	3.0	0.1	0.15

Note. The rest is iron.



represents an iron-carbon melt, containing 15–17 % Ni and increased content of impurity elements [1]. Impurities may be divided according to their influence on sulfur activity coefficient f_S into three groups (Figure 1): those increasing f_S (carbon, silicon, aluminum, phosphorus); those reducing f_S (copper, manganese, oxygen, sulfur); and those not effecting f_S .

Influence of base (nickel and iron) and impurity elements in ferronickel on activity coefficient and, as a result, on sulfur activity may be estimated by parameters of interaction of first order (the Wagner parameter), which represent ratio of partial derivative of logarithm of activity coefficient of an element (in this case sulfur) to weight share (%) of the impurity

element $e_i^j = \frac{\partial \lg f_S^i}{\partial [\% i]}$. Positive value of $\bar{a}_S^j$ means that

this element i increases activity of sulfur; negative value means that it reduces the activity, zero value means that it does not exert any effect. Below are given values $\bar{a}_S^j$, where j are the elements, which enter into composition of ferronickel ($\bar{a}_S^j \cdot 100$ in iron at 1600 °C):

C	Si	Al	P	N	Cu	Cr	Mn	S	O
11	6.3	3.5	29.0	0	-0.84	-1.1	-2.6	-2.8	-2.7
24	6.6	5.6	4.5	0	-1.2	-2.2	-2.5	-2.8	-18

It follows from presented data that carbon, silicon, aluminum and phosphorus increase activity coefficient of sulfur in ferronickel, while copper, chromium, manganese, sulfur and oxygen reduce it. Nickel, dissolved in iron, practically does not affect activity of sulfur in liquid iron. Activity and activity coefficient of sulfur reduce as temperature increases. Values $\bar{a}_S^j$ in different literature sources significantly vary.

Many impurity elements in ferronickel are characterized by ability to reduce activity coefficient of sulfur. But more important property of desulfurizer-elements is their ability to enter into reaction with formation of sulfides, which have high thermodynamic stability and low solubility in ferronickel.

Knowing parameters of interaction, let us determine activity coefficient of sulfur in crude ferronickel $\lg f_S^{\Sigma}$, %: (15 Ni; 3.0 Si; 2.0 C; 0.3 S; 0.15 P; 2.0 Cr):

$$\begin{aligned} \lg f_S^{\Sigma} &= e_S^{\text{Ni}} [\% \text{ Ni}] + e_S^{\text{Si}} [\% \text{ Si}] + e_S^{\text{C}} [\% \text{ C}] + \\ &+ e_S^{\text{S}} [\% \text{ S}] + e_S^{\text{P}} [\% \text{ P}] + e_S^{\text{Cr}} [\% \text{ Cr}] = \\ &= 0 + 0.198 + 0.48 - 0.0084 + \\ &+ 0.0068 - 0.044 = +0.6348. \end{aligned}$$

So, in crude ferronickel before its refining by soda $\lg f_S^{\Sigma} = +0.6348$. At the final stage of refining in basic converter content of oxygen may constitute up to 0.15 wt.%, if mass share of (each) impurity element in ferronickel is 0.01–0.02 %. At this chemical composition of ferronickel $\lg f_S = 0.0137$ and ratio $\lg f_S^{\Sigma} : \lg f_S^{(K)} = 0.6348 : 0.0137 = 46.34$, i.e. $\lg f_S^{(K)}$ is, ap-

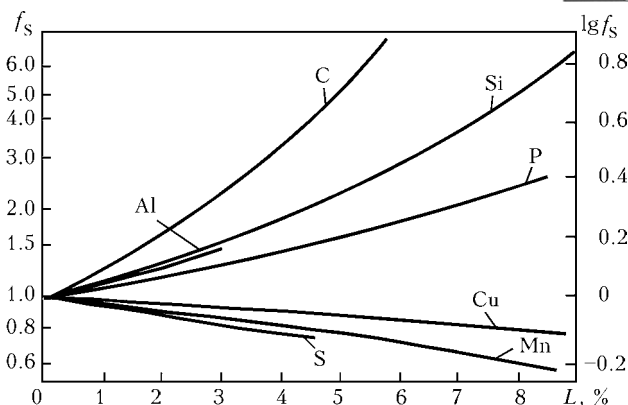


Figure 1. Influence of alloying elements L on activity coefficient of sulfur f_S in iron at 1600 °C. Standard state is infinitely dissolved solution of sulfur in pure liquid iron

proximately, 46 times lower than in $\lg f_S^{\Sigma}$ of crude ferronickel.

Characteristic of reagents for desulfuration of ferronickel. Different substances-reagents, including metal magnesium, calcium carbide CaC_2 , lime and sodium carbonate Na_2CO_3 are used for commercial out-of-furnace desulfuration of cast iron. For binding 1 kg of sulfur dissolved in ferronickel it is necessary to introduce into sulfides the following amount of reagent Q_r :

Desulfurizer-reagent	Mg	MgO	Ca	CaO	CaC_2	Na	Na_2O	Na_2CO_3
Sulfide	MgS	MgS	CaS	CaS	CaS	Na_2S	NaS	Na_2S
Q_r , kg / kg S	0.75	1.25	1.25	1.75	2.0	1.44	1.94	3.31

Temperature dependences of the equilibrium constant and change of the Gibbs reaction of formation of sulfides MgS, CaS and Na_2S with application of different reagents are given in Table 2. Thermodynamic data of the reaction of Na_2S formation with application of metal sodium were calculated by us, while the rest data were taken from works [4, 5]. Conditions $\Delta G_T^0 = 0$ at $P_{\text{Me}} = 101.3$ kPa for reaction with participation of magnesium, calcium and sodium are observed at the temperatures 2365, 7355, and 3937 K, respectively.

According to data presented in [4], Na_2O is by three-four orders stronger desulfurizer than CaO. However, this conclusion does not match data of enthalpies of formation of sulfides CaS and Na_2S . Thermodynamic preferability of Na_2S formation in comparison with MgS in case of using respective reagents is confirmed by enthalpy of formation of sulfides:

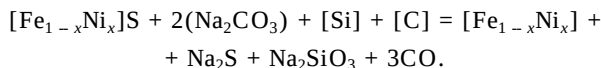
Sulfide	CaS	Na_2S	MgS	NiS
ΔG_T^0 , kJ / mol	475.68	374.1	351.1	94.05

Thermodynamic stability of compounds in the process of ferronickel desulfuration. Chemistry of the process of electric furnace ferronickel desulfuration by soda may be presented by the summary reaction:

**Table 2.** Temperature dependences of equilibrium constants and $\Delta G_T^0(\text{O})$ of desulfuration reactions of iron-carbon melts using different reagents

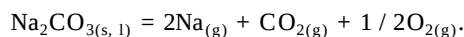
Desulfurizer-element	Reaction	$\frac{\lg K(1/T)}{\Delta G_T^0(T), \text{ J / mol}}$
Mg	$\text{Mg}_g + [\text{S}] = \text{MgS}_s$	$\lg K_{\text{Mg}} = \lg \left[\frac{a_{\text{MgS}}}{(P_{\text{Mg}} [\text{S}]_s^l)} \right] = \frac{22750}{T} - 9.63$ $\Delta G_T^0 = -435138 + 183.92T$
$\tilde{\text{Na}}$	$\tilde{\text{Na}}_g + [\text{S}] = \text{CaS}_s$	$\lg K_{\text{Ca}} = \lg \left[\frac{a_{\text{CaS}}}{(P_{\text{Ca}} [\text{S}]_s^l)} \right] = \frac{29806}{T} - 8.94$ $\Delta G_T^0 = -570200 + 171.0T$
Na	$2\text{Na}_g + [\text{S}] = \text{Na}_2\text{S}_l$	$\lg K_{\text{Na}} = \lg \left[\frac{a_{\text{Na}_2\text{S}}}{(P_{\text{Na}} [\text{S}]_s^l)} \right] = \frac{15190}{T} - 4.12$ $\Delta G_T^0 = -288673 + 78.31T$
CaO	$\text{CaO}_s + [\text{S}] + \text{C}_{\text{gr}} = \text{CaS}_s + \text{CO}$	$\lg K_{\text{CaO}} = \lg \left[\frac{(a_{\text{CaS}} P_{\text{CO}})}{(a_{\text{CaO}} a_{\text{C}} [\text{S}]_s^l)} \right] = -\frac{5540}{T} + 5.157$
Na_2O	$\text{Na}_2\text{O}_l + [\text{S}] + \text{C}_{\text{gr}} = \text{Na}_2\text{S}_l + \text{CO}$	$\lg K_{\text{Na}_2\text{O}} = \lg \left[\frac{(a_{\text{Na}_2\text{S}} P_{\text{CO}})}{(a_{\text{Na}_2\text{O}} a_{\text{C}} [\text{S}]_s^l)} \right] = \frac{4400}{T} - 5.74$ $\Delta G_T^0 = -83600 + 109.06T$
$\tilde{\text{Na}}\tilde{\text{N}}_2$	$\tilde{\text{Na}}\tilde{\text{N}}_{2s} + [\text{S}] = \text{CaS}_s + 2\text{C}_{\text{gr}}$	$\lg K_{\text{CaC}_2} = \lg \left[\frac{(a_{\text{CaS}} a_{\text{C}}^2)}{(a_{\text{CaC}_2} [\text{S}]_s^l)} \right] = \frac{19000}{T} - 6.28$ $\Delta G_T^0 = -363240 + 120.05T$

Note. In lower indices letters g, s, gr and l mean gaseous, solid, graphitized and liquid.



One of the most important discussion problems of processing iron-carbon melt by sodium carbonate at high temperatures (1300–1500 °C) is mechanism of the process with estimation of sequence of separate stages of Na_2CO_3 thermal dissociation of formation of intermediate substances and, in long run, of sulfide Na_2S . Below results of analysis of state-of-the-art thermodynamic data on thermal dissociation of Na_2CO_3 and probable scheme of interaction sequence of dissociation products with the sulfur of ferronickel are given.

Sodium carbonate has to be considered as product of interaction of components in the $\text{Na}_2\text{O}-\text{CO}_2$ system. Melt point of Na_2CO_3 equals 850 °C, boil point — 2597 °C. Several publications are devoted to investigation of the mechanism (chemistry) of thermal dissociation of Na_2CO_3 . In [6] composition of vapor phase above specimens and Na_2CO_3 was studied using effusive method and it was established that thermal dissociation occurs according to the following reaction:



Generalization and critical analysis of literature data of Na_2CO_3 thermal dissociation in case of evapo-

ration of double oxides are presented in the monography [7]. It is established by isotherms of Na_2CO_3 evaporation that at 959 °C partial pressure of sodium vapors equals $P(\text{Na}) = 5.26$, and at 969 °C $P(\text{Na}) = 5.74$ Pa.

In [8] mechanisms of Na_2CO_3 evaporation are studied using Knudsen method within temperature range 850–983 °C. It is established that vapor pressure of molecules $\text{Na}_2\text{CO}_{3(g)}$ above solid carbonate at temperature about 850 °C equals 11.83 Pa, and above the melt (925 °C) $D_{(\text{Na}_2\text{CO}_3)} \cdot 10^3 = 243.3$ Pa.

Temperature dependences of partial pressure values of molecules Na_2CO_3 in sodium carbonate sublimation (solid state) and evaporation (liquid state) have the following form, Pa:

$$\begin{aligned} \lg D_{(\text{Na}_2\text{CO}_3)_s} &= \frac{12660}{T} + 9.97; \\ \Delta H_{s, T(\text{Na}_2\text{CO}_3)}^0 &= 242.44 \text{ [J / mol]}; \\ \lg D_{(\text{Na}_2\text{CO}_3)_l} &= -\frac{11500}{T} + 8.96; \\ \Delta H_{l, T(\text{Na}_2\text{CO}_3)}^0 &= 219.45 \text{ [J / mol]}. \end{aligned}$$

According to data of [7], temperature dependence of pressure of thermal dissociation products has the following form, Pa:



$$\lg D = -\frac{10050}{T} + 10.55,$$

and heat of thermal dissociation reaction $\Delta H_T^0 = 192.28 \text{ kJ / mol}$.

The main product of Na_2CO_3 interaction with sulfur of ferronickel is sodium sulfide. In analysis of the cast iron and ferronickel desulfuration process this compound is assumed to be Na_2S . At the same time in the system Na–S exists a number of compounds, although diagram of equilibrium state of mentioned system, as it follows from reference data, is not yet, unfortunately, built. It is not mentioned in [9] about existence of any sodium sulfides. Review of 16 publications (1898–1953) is made in [10] and sulfide Na_2S_3 is noted, which melts at 230°C and disintegrates at heating above 550°C into $\text{Na}_2\text{S}_{1.9}$.

F. Schank [11] added data of R.P. Elliot, devoted to determination of structure of α - and β - Na_2S_2 , by analysis of [10]. Low-temperature modification of α - Na_2S_2 exists at temperatures below 100°C . Phase β - Na_2S_2 forms in heating of α - Na_2S_2 up to 250°C . Need in new investigations for checking literature data and further study of compounds in the system Na–S is noted [12].

In [13] data are presented on formation heat, standard entropies, and structure of a number of sulfides of the system Na–S according to data of the work of K.S. Mills (1974). Values of formation heat and entropy of sodium sulfides are as follows:

	Na_2S	NaS	Na_2S_2	NaS_2
$-\Delta f_{298}^0$ kJ / mol	374.11	201.06	432.21	205.66
S_{298}^0 , J / (K·mol)	79.42	44.78	101.57	83.60
T_{melt} , $^\circ\text{C}$	978	480	535	185

Sulfide Na_2S has crystal lattice of CaF_2 type. Temperature dependence of the Gibbs energy change of Na_2S formation from the elements has the form

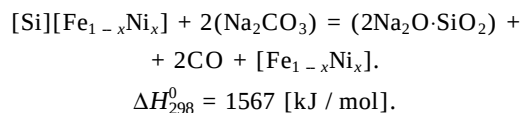
$$2\text{Na}_l + 1/2\text{S}_{2g} = \text{Na}_2\text{S}_s,$$

$$\Delta G_T^0 = -439945 + 131.46T \text{ [J / mol]} \text{ (371–1187 K)}.$$

Condition $\Delta G_{298}^0 = 0$ at pressure 101.3 kPa is fulfilled at 3346 K. These data confirm that sulfide Na_2S is thermodynamically rather stable compound, although sulfide Na_2S_2 is also characterized by increased stability ($\Delta H_{298}^0 = -432.2 \text{ kJ / mol}$).

Data on thermodynamic stability of Na_2CO_3 are of interest. According to [13], standard heat of Na_2CO_3 formation is $\Delta H_{298}^0 = 1129.85 \text{ kJ / mol}$, entropy $S_{298}^0 = 138.65 \text{ J / (K·mol)}$.

As far as thermal dissociation of Na_2CO_3 is accompanied by formation of Na_g , CO_2 and $1/2\text{O}_2$, one may assume that probability of oxidation of dissolved in ferronickel silicon by soda exists with formation of sodium silicate according to the reaction



So, oxidation of dissolved in ferronickel silicon by soda according to presented endothermic reaction is possible in respect to thermodynamics. Temperature increase should enable shifting of the reaction in direction of formation of the products ($2\text{Na}_2\text{O} \cdot \text{SiO}_2$) and 2CO .

In ladle desulfuration of ferronickel parameters of the process are optimized first of all for the purpose of achievement of as high as possible degree of desulfuration at lower specific consumption of soda.

Process of ladle desulfuration of ferronickel by soda is performed at temperature values 1450 – 1500°C with formation in addition to sulfide Na_2S of silicate Na_2SiO_3 . Result of analysis of thermodynamic data on processes of evaporation of melts of double oxides of the system $\text{Na}_2\text{O} \cdot \text{SiO}_2$ is of interest.

In system $\text{Na}_2\text{O} \cdot \text{SiO}_2$ form a number of silicates. Melt points of the most investigated compounds are as follows:

Sodium silicate	$2\text{Na}_2\text{O} \cdot \text{SiO}$	$\text{Na}_2\text{O} \cdot \text{SiO}_2$	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$
T_{melt} , K	1391	1362	1147

Evaporation of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system melts within temperature range 870 – 1100°C was studied by method of mass-spectrometry (Table 3). In mass-spectrum of steam-gaseous phase of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system, containing from 6 to 50 mol% Na_2O , within temperature range 870 – 1100°C only ions Na^+ and O_2^+ were detected.

In [14] thermodynamic properties of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system were studied using method of the Knudsen mass-spectrometry. In mass-spectra of saturated vapor above $\text{Na}_2\text{O} \cdot \text{SiO}_2$ ions Na^+ , Na_2O^+ , NaO^+ and O_2^+ were detected, which formed as a result of ionization of gaseous molecules Na , Na_2O , NaO , and NaO_2 , O_2 . On the basis of these experimental data activity of SiO_2 and Na_2O in the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system was determined.

Data of [15], in which qualitative analysis of vapor phase is performed and thermodynamic parameters of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system (excessive molar free Gibbs energy and heat of formation) are estimated, are of interest.

Table 3. Value of partial pressure of vapor Na_g above melts of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system [7]

Na_2O mole share x	$D(\text{Na}_g) \cdot 10^3$, Pa, at $\dot{O}$, K	
	1293	1423
0.06	3.99	39.9
0.22	10.64	230.1
0.36	106.4	518.7
0.40	199.5	970.9
0.50	212.8	2660.0

Under conditions of treatment by soda of carbonaceous ferronickel with high content of silicon and carbon, probability of sodium carbonate interaction with dissolved in metal chromium with formation of sodium chromates, in which chromium has different degrees of oxidation, is insignificant. Sodium chromates are characterized by relatively low melt points: Na_2CrO_4 — 790 °C and $\text{Na}_2\text{Cr}_2\text{O}_7$ — 350 °C.

It was established in investigation of volatility of sodium (potassium) chromates within temperature range 714–768 °C that evaporation of Na_2CrO_4 occurs congruently [16]. Temperature dependence of pressure within temperature range 714–768 °C is described by the equation

$$\lg P_{(\text{Na}_2\text{CrO}_4)} = -\frac{5072.161}{T} + 3.81.$$

Heat of solid chromate Na_2CrO_4 sublimation $\Delta H_{\text{s}, T_{(\text{Na}_2\text{CrO}_4\text{g})}}$ equals 96.98 kJ / mol.

Process of Na_2CrO_4 evaporation within temperature range 577–1177 °C was studied using method of mass-spectrometry, and results of the experiments are presented graphically [17]. In the course of processing of these data sublimation heat ΔH_{subl}^0 of chromate Na_2CrO_4 and its atomization energy ΔH_{at}^0 were calculated, [J / mol]:

$$\Delta H_{\text{subl}, 298}^0 (\text{Na}_2\text{CrO}_4) = 342;$$

$$\Delta H_{\text{at}, 298}^0 (\text{Na}_2\text{CrO}_4) = 2613.$$

So, chromate Na_2CrO_4 is characterized by high thermodynamic stability and in case of ferronickel desulfuration by soda (1.5–2.0 % Cr) may, evidently, form and dissolve in soda slag. Its existence in this slag depends upon content of silicon in ferronickel, whereby as content of silicon increases probability of chromate formation reduces. Presence in soda slag of small amounts of silica should enable formation of silicates of bivalent chromium $2\text{CrO} \cdot \text{SiO}_2$.

Technological operations in case of ladle desulfuration of ferronickel by soda. Through technology of ferronickel refining consists of the stage of desulfuration by soda in ladle with subsequent oxidation-reduction refining processes in vertical converters with acid and basic fire-brick lining. Sodium carbonate in the form of powder (soda) or fusion cake (secondary material) is used as a desulfurizer. Ferronickel

is discharged from electric furnace into a ladle with a certain amount of soda. In the process of ferronickel discharge its mixing with soda takes place, which at 850 °C transits into liquid state. For achieving efficient mixing it is necessary to determine critical height of liquid ferronickel fall.

Let us designate constant of reaction rate between ferronickel and soda melt by symbol K_r , and in case of their mixing — by symbol K_m . We accept ratio K_r / K_m as a convenient criterion for quantitative change of the action of mixing components of the model.

It was established in experiments connected with modeling of influence of mixing in the system amalgam (mercury with 0.2 % Na)– H_2SO_4 that pouring of amalgam into the acid ensures higher degree of mixing in comparison with blowing of the acid by gas or use of a mixer [18]. It should be noted that after exceeding critical value of the jet fall height efficiency of mixing increases insignificantly.

Products of desulfuration are thermodynamically strong sulfide Na_2S and sodium silicate, which dissolve in liquid sodium carbonate and form «soda» slag. For the purpose of increasing desulfuration degree double pouring of ferronickel from a ladle into a ladle is used, whereby into the ladle designed for receiving ferronickel from notch of the furnace 70 % of the required amount of soda (fusion cake) is placed. Then ferronickel with soda slag is poured into another ladle, into which the rest amount of soda (30 %) is placed.

In case of ferronickel treatment by soda ash, degree of desulfuration constitutes 70–85 %. Activity of sulfur in electric furnace ferronickel is effected by dissolved in the latter silicon and carbon; together with increase of content of these elements activity of sulfur increases, and thermodynamic premises of more efficient desulfuration of ferronickel enhance. For establishing analytical connection of dependence of sulfur content in ferronickel and desulfuration degree upon concentration of silicon in the latter, graphic dependences (Figure 2) were obtained by means of mathematical processing of a big array of experimental data on commercial melting designed for ferronickel desulfuration by sodium carbonate, which are described by the following equations:

$$[\% \text{ S}]_{\text{final}} = -0.8961 \lg [\% \text{ Si}] + 0.1211;$$

$$\eta_{\text{S}} = 21.9274 \lg [\% \text{ Si}] + 65.826.$$

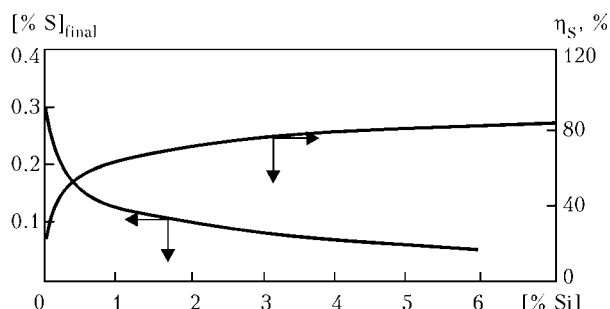


Figure 2. Dependence of final content of sulfur and desulfuration degree upon content of silicon in crude ferronickel (15–17 % Ni)

Technological operations of ferronickel ladle desulfuration finish by pumping off «soda» slag. At the next stage of refining ferronickel (intermediate product) is poured into converter with acid (silica brick) lining and subjected to oxygen blowing for the purpose of oxidizing silicon, chromium, and partially carbon. At the final stage ferronickel is discharged from acid converter into a ladle with its subsequent pouring into the basic converter with periclase-carbon (periclase-chromite) lining, in which carbon and phosphorus are oxidized and content of sulfur is reduced. In



melting ferronickel using rich nickel ore (from New Caledonia) content of phosphorus in electric furnace ferronickel exceeds 0.015–0.017 %, that's why refining process in the basic converter is performed for the purpose of oxidizing carbon and further reduction of sulfur amount.

So, on the basis of data of thermodynamic investigations under conditions of PFIW Ltd. innovation-industrial technology was developed for out-of-furnace desulfuration of electric-furnace high-percent ferronickel by sodium carbonate.

1. Reznik, I.D., Ermakov, G.P., Shneerson, Ya.M. (2003) *Nickel*. Vol. 2. Moscow: Nauka i Tekhnologiya.
2. Grigoryan, V.A., Stomakhin, A.Ya., Ponomarenko, A.G. et al. (1989) *Physico-chemical calculations of electric melting processes*: Manual for institutes of higher education. Moscow: Metallurgiya.
3. (1965) *Steel production in electric furnaces*: Collect. Ed. by V.A. Grigoryan. Moscow.
4. Vegman, E.F., Zherebin, B.N., Pokhvisnev, A.N. et al. (1978) *Cast iron metallurgy*. Moscow: Metallurgiya.
5. Efimenko, G.G., Gimmelfarb, A.A., Levchenko, V.E. (1981) *Cast iron metallurgy*. Kiev: Vyshcha Shkola.
6. Semyonov, G.A., Volkov, A.D., Frantseva, K.E. (1973) Mass spectrometric examinations of carbonate sodium evaporation. *Trudy Leningrad. Tekh. In-ta Tselul.-Bumazhn. Promyshl.*, **30**, 153–160.
7. Kazenas, E.K. (2004) *Thermodynamics of double oxide evaporation*. Moscow: Nauka.
8. Kroger, C., Stratman, J. (1961) Vaporization and Silicatglaser and decomposition pressures of alkali compounds of glass melt. *Glas Tech. Ber.*, **34**(6), 311–314.
9. Hansen, M., Anderko, K. (1962) *Structures of binary alloys*. Moscow: Metallurgizdat.
10. Elliot, R.P. (1970) *Structures of binary alloys*. Vol. 2. Moscow: Metallurgiya.
11. Schank, F. (1973) *Structures of binary alloys*. Moscow: Metallurgiya.
12. (1997) *Constitution diagrams of binary metallic systems*: Refer. Book. Ed. by N.P. Lyakishev. Vol. 3. Moscow: Mashinostroenie.
13. Kubashevsky, O.I., Olkock, S.B. (1982) *Metallurgical thermochemistry*. Moscow: Metallurgiya.
14. Zajtsev, A.I., Shchelkova, N.V., Mogutnov, B.M. (2000) Thermodynamical properties of alloys of system $\text{Na}_2\text{O}-\text{SiO}_2$. *Izvestiya RAN. Neorgan. Materialy*, **36**(6), 647–662.
15. Begman, C., Bennour, F., Chastel R. et al. (1998) Etude thermodynamique des systemes d'oxydes par effusion de Knudsen couplee a la spectrometrie de masse. *Rev. Met.*, **95**(9), 1101–1108.
16. Afonsky, I.S. (1962) Study of volatility of sodium and potassium chromate. *Zhurnal Neorgan. Khimii*, **7**(11), 2640–2641.
17. Kuligina, L.A., Semyonov, G.A. (1979) Mass spectrometry analysis of dissociation energy of gaseous chromates of alkali metals and thallium. In: *Abstr. of 8th All-Union Conf. on Calorimetry and Chemical Thermodynamics* (Ivanovo, Sept. 1979).
18. Shanakhhan, K.E. (1963) Study of effectiveness of slag and metal stir on models. In: *Physical chemistry of steelmaking*. Moscow: Metallurgizdat.

METHODS AND TECHNOLOGIES OF REPAIR AND RESTORATION OF CRITICAL BUILDING METAL STRUCTURES AFTER THEIR LONG-TERM SERVICE BASED ON THE RESULTS OF THEIR EXAMINATION

Methods and technologies have been developed for repair and restoration of critical building structures after long-term service. Technology of their reinforcement and repair is developed, taking into account the statement of technical condition of the operated structures made by the results of their examination and checking calculations. The causes for defects and damage are considered and methods for their prevention during further service are sought.

The developed technology of repair, restoration and reinforcement takes into account and specifies application of the base and auxiliary materials, welding process, preheating, structure unloading before repair, application of thermal jacks, bead sequence, using the required monitoring and diagnostic equipment and other elements of technology.

Purpose and applications. Extension of the operating life of critical building structures, namely bridges, cranes and crane beams, latticed towers, pipes, etc.

Status and level of development. Procedure of investigation and technology of reinforcement and repair of metal structures have been successfully tested in repair of a pedestrian bridge across the Dnieper river to Trukhanov island and the E.O. Paton motor-road bridge in Kiev.

Form of co-operation. To be determined during negotiations. Examination procedure, technology of repair and reinforcement of metal structures is offered for sale on contract basis.

Dr. Kovtunenko V.A.
E-mail: paton48@paton.kiev.ua



THE DANIELI METALLURGICAL EQUIPMENT*

V.M. SOJFER

Company «STC Standarteletkro-C», Moscow, RF

Metallurgical equipment of the «Danieli» company manufacture is certified.

Key words: arc steel melting furnace, ladle-furnace, vacuum degassing installation, machine for continuous casting of billets, heating furnace, rolling mill, hot galvanizing unit

Body for certification of machine-building products «STC Standarteletkro-C» has been certifying beginning from 2003 metallurgical equipment produced by the Danieli company for electric steel melting and rolling production.

Here under metallurgical equipment are meant arc steel melting furnaces; ladle-furnaces; vacuum degassing installations; machines for continuous casting of billets; heating furnaces; rolling mills; hot galvanizing units.

The Danieli products meet most state-of-the-art requirements and are in demand on the world market, including Russia. This is confirmed by estimation of technical solutions performed in the process of certification. The following technical peculiarities of certified equipment should be noted.

In arc steel melting furnaces produced by the Danieli steels of wide range of grades are molten, including steels for cold upset and die forging, special spring steels, bearing, high-carbon, free-cutting steels for production of motor vehicles, air-space and agricultural equipment, construction, production of seamless pipes (including pipes designed for operation under high pressure), stainless steels, nickel alloys, and tool steel [1]. The Danieli produces furnaces with fully bearing structure, split casing, a system for loading ferroalloys, and oriel outlet [1, 2].

One of peculiarities of arc steel melting furnaces of the Danieli are regulators of electrodes and foamy slag of the Hired Plus type, application of which enables increasing efficiency of operation of the furnaces and reduction of electric power consumption [3]. In a number of cases continuous feeding of scrap [3] and automatic sampling and temperature control [1, 4] are ensured. The Danieli supplies furnaces with modular system Danarc [2, 3], which replaces conventional lances for injection of oxygen, carbon, and lime. Modular system Danarc fulfills functions of the pool carbon depletion, supply of heat energy, and formation of a foamy slag. For injection of oxygen and carbon the Danieli also uses the Jet BOxTM (here-

inafter Jet BOx) system, which represents combined oxygen-carbon injection. This system ensures supply of oxygen nearer to the melt surface in comparison with traditional lances, due to which increases efficiency of oxygen use. For example, application of the Jet BOx system at the Dongkuk Steel Plant in South Korea ensured reduction of electric power consumption by 10 % and increase of the furnace productivity by 2–3 melts a day. Due to advancing fuel-oxygen burner (injector) into the furnace permeability of oxygen increases, whereby regulation of the process of carbon injection and slag foaming improves, consumption of electrodes reduces, and quick decarburization is ensured. Oxygen nozzles are installed on water-cooled copper casing located in the distance from side wall of the furnace. Injection of carbon by the Jet BOx system enables intensive foaming of slag, while neighborhood with burners protects injection nozzles against their clogging by slag. Each injector of the Jet BOx system ensures flow of oxygen injection 42 m³ / min, and its lances allow injecting solid particles as well [5].

The Danieli furnaces may operate on solid charging (including up to 100 % of pellets) or using in a charging up to 40 % of liquid cast iron. In the Danieli furnaces up to 28–35 melts per day are produced [4].

At Moldavian Metallurgical Plant operate arc furnaces of the Danieli with four bottom lances for supply of oxygen, which ensure oxidizing of carbon and melting of scrap in difficult for access zones and good mixing of liquid steel. Application of bottom lances in melting of steel in arc furnaces enables reduction of electric power consumption by 28–36 (kW·h) / t [6].

Gas treatment installations include primary tract for exhaust gases, a hood, a chamber filter, a sequentially installed cyclone and system of noise killers on chimney stack [4]. System for reburning technological gases is envisaged [6].

A ladle-furnace makes it possible to bring liquid steel refining operations outside melting furnace, which significantly reduces duration of melting from tapping to tapping and electric power consumption. In addition, practice of operation of ladles-furnaces, manufactured by Danieli, showed that they represent «buffer accumulation» of metal before continuous casting and enable precise organization of continuous casting works.

In the Danieli ladles-furnaces bottom blowing of metal by inert gas, most frequently by argon and in

*The article is published in abridged version.



some cases by nitrogen, is used. Blowing of metal by inert gas in the ladle-furnace ensures uniform distribution of temperature and homogenization of chemical composition all over mass of the melt, improvement of steel and slag mixing, diffusion and uniform distribution of additives (ferroalloys) in liquid melt, whereby required chemical composition of steel, accurate temperature of the metal necessary for continuous casting, and reduction of consumption of ferroalloys are ensured. In the Danieli ladles-furnaces various grades of steel are processed — low- and medium carbon, low- and medium-alloyed, steel for shipbuilding, pipe steel, steel for production of galvanized strips, for deep drawing, for motor vehicle components, pressure vessels, corrosion-resistant, bridge, and many other kinds.

Two-position ladles with arches with inert atmosphere, a system for turning electrodes, operation of immersed into slag arc, and automatic control system may be supplied. Ladle-furnace installations of the Danieli company ensure high rate of heating, efficient removal of sulfur and nitrogen from liquid steel, and low consumption of electrodes. Two-position installation may simultaneously process steel in two ladles (in one of them steel is heated, in the other alloying elements are introduced and mixing is performed), whereby high productivity of the installation is achieved [1–3]. Specific power of arc is 1.8–2.2 MW per 1 m² of metal surface area depending upon ratio of diameter to height of the ladle [7].

The Danieli installations for vacuum-oxygen decarburization are designed for wide range of steel grades (carbon, stainless, austenite, ferrite corrosion-resistant, silicomanganese, chromium, chromium-silicon, chromium-vanadium, chromium-molybdenum, siliceous, free-cutting, chromium-nickel, bearing steels and steels with low content of carbon).

Synchronization of operation of installations for vacuum-oxygen decarburization with arc steel melting furnaces is envisaged. After vacuum-oxygen decarburization content of hydrogen in steel reduces 2–6 times depending upon its initial content and duration of blowing by oxygen.

The Danieli company produces installations for double vacuum-oxygen decarburization with two vacuum chambers. In the course of blowing by oxygen content of carbon and rate of decarburization are controlled by special instruments, due to which an additional economic effect is achieved. After vacuum-oxygen decarburization steel has good mechanical properties, in particular high ductility and low content of hydrogen. Rate of pressure reduction exerts great influence on final content of carbon in metal [2]. In addition to installation for vacuum decarburization gas analyzer of spectrometer type and auxiliary equipment are supplied [3, 2].

On MCCB produced by the Danieli, slabs of 70–270 mm thickness and 900–3250 mm width, thin slabs for a strip of 90 mm thickness, various blooms (for example, a square 650) of 250×300, 390×510 size, ect.,

billets: square 100–200 mm, section billets 160–200 mm, beam billets 280×400 mm etc.; strips of 0.7–0.8 mm thickness, super-thin, rolled and other strips are cast. According to chemical composition, on the Danieli machines low-, medium- and high-carbon steels, steels with super-low content of carbon; low-, medium- and high-alloy; high-strength low-alloy; stainless, including austenite with low content of carbon, austenite with titanium, martensite and ferrite, boron containing, siliceous, and other steels are cast. Among mentioned steels there are those designed for automotive industry, production of air-space and agricultural equipment, shipbuilding and construction industries, production of pipes, atmosphere-resistant structures, springs, shafts, solid wire, special structure, valve, bearing, free-cutting steel and steel designed for electric household appliances.

From the viewpoint of further technological process, on the Danieli MCCB steels designed for cold upset, cold die forging, manufacturing of steel structures, cold and hot rolled stock, drawing, and malleating are cast. Machines for continuous casting of the Danieli company have radius of curvature from 4 to 16 m and system of multipoint bending within wide range. Productivity of these machines is 0.35–2.90 mln t per year, casting speed is 1.0–7.5 m / min, number of strands is up to 7 [1–5].

The Danieli MCC of steel are equipped with a device for electromagnetic mixing of metal in the mould. In the process of mixing, movement of steel causes origination of two circulation loops in liquid metal (upper and lower ones) when steel hits opposite narrow facet of a slab and divides into two flows. Such phenomenon is called «butterfly-like» mixing. As a result of movement of the steel, number of crystallization centers increases that enables solidification with formation of equiaxial crystals and favorably affects quality of the metal. In addition, axial liquation and porosity reduce, and during rolling waviness of the surface reduces [3].

Multimode electromagnetic mixer consists of four electromagnetic agitators, installed along wide facets of the mould. Depending upon parameters of casting and the product itself these agitators may automatically either decelerate or accelerate movement of the flow, or mix steel at the level of meniscus by rotational movement. Application of this technology allows increasing MCCB productivity, increasing output of suitable product and reducing need in finishing cast items. Application of electromagnetic mixer eliminates fluctuation of meniscus, reduces by 40 % quantity of defects near surface of the billet, and reduces by 40–75 % number of surface defects at the beginning of the process (slag inclusions and spot defects) [1].

An important technical peculiarity of the Danieli MCCB is design of a zone for secondary cooling of the metal. Four-zone system of secondary cooling is used with application of the technology of cooling by water vapor, control of which is performed through three independent circuits with automatic regulation



[4], whereby system of dynamic cooling control is available, which ensures correct solidification of the metal within the whole process.

In secondary cooling zone releasable rollers of small diameter are used. Such design limits bulging of the metal over axis, reduces deformation of crust, and increases stability of liquid metal level in the mould. Cooling chamber is equipped with exhaust blower. In the Danieli systems of delayed cooling, water-air drip cooling with adaptive regulation, and secondary sputtering cooling are used.

One of significant technical peculiarities of MCCB produced by the Danieli is mechanism for swinging the mould and control system of this mechanism, which is dynamically readjusted depending upon grade of steel and speed of casting, whereby dynamic check of the billet width and parameters of the mould swinging is performed.

The Danieli MCCB are supplied with a system of dynamic soft reduction of an ingot with liquid core. This system together with a hardening chamber ensures hot fit of the billets.

The whole process in MCCB is completely automated; mathematical models of solidification and control of the position of liquid metal meniscus are used for the purpose of optimizing soft reduction and cooling of the ingot.

In MCCB a measuring device, which combines radioisotope and electromagnetic sensors for precise control and regulation of actual level of the metal in the mould and thickness of the mould lubrication, is used. System for preventing break of the crust and sticking of the ingot to the mould walls, which operates using chart of temperatures in the mould, is also used. The mould has variable conicity.

Application of the Danieli technology allows drastic reducing number of the mould components, which have to be replaced when passing over from one thickness of a slab to another. This enables significant reduction of capital investments and subsequent operation expenditures. This peculiarity is typical for all slab MCCD supplied by the Danieli, into composition of which enter systems for metal level control in the mould (of electromagnetic type), automatic regulation of the mould width, and braking of metal in the mould.

A number of technical peculiarities of the Danieli MCCB are connected with ladles (quick replacement of a ladle and change of a nozzle, double bogie for transportation and hoisting of an intermediate ladle, system for weighing intermediate ladle on the bogie, system of stopper control for regulation of steel flow from intermediate ladle). Both, open jet and closed methods of casting through immersed nozzles with a system of stoppers are used.

Other peculiarities are connected with a system of multipoint dressing, tilt stand of «butterfly» type, straightening-stretching machines, improved systems of power supply, distribution boards, control units, and lay-out systems of wiring of the boards.

For heating furnaces with walking beam systems for reducing formation of scale, reduction of specific electric power consumption, software for calculation of mathematical models, heating curve control, and organization of the furnace operation are developed. A water conditioning installation, a pusher mechanism, loading-unloading roller conveyers, a kickoff on the side of unloading, an engine control center, and an automatic control system are supplied together with the furnace.

On small-section-wire mills of the Danieli company steels of wide assortment of grades are rolled, including low- and high-carbon, structural steel for drawing and cold upset, spring, bearing and many other grades of steel. Productivity of these mills achieves 150 t / h, speed of rolled wire rolling is 110–120 m / s; mass of bundles most frequently constitutes 1.8–3.4 t. Some technological peculiarities of wire mills are rolling with welding, rolling without braiding of strings, feeding of hot-rolled breakdown from intermediate group of stands into finishing group over two separate lines (in this case rolling is performed in two independent finishing groups) [1, 2, 4].

The Danieli company developed for the first time in the world for wire mills a bearing-less coil-forming device, in which rotor of the working head is installed not in the bearings, as it used to be, but is held in rear position by the magnetic field. A new bearing-less coil-forming device ensures absence of vibrations even at the highest speeds of rolled wire reeling into bundles, low wear of the guiding tube, and increase of its service life. It does not require for maintenance due to absence of subject to wear mechanical parts, which enables significant reduction of operation expenditures [4].

The Danieli supplies small-section-wire mills with multi-blade scissors, fast-acting data analyzer, ergonomic control panel, chambers for hardening and tempering (located on the output side of finishing blocks), a line for controlled cooling of rolled wire, equipment for cold finishing of the products, fast-acting scissors for automatic cutting of front and rear ends of rolled wire before the coil stacking tripper, an electric equipment, automatics, and metal structure control system [1, 2, 4].

Reeling and unreeling of rolled wire is worth special mentioning. Developed by the Danieli technology ensures reeling without braiding hot-rolled metal into high-quality super-dense and super-heavy bundles and envisages unreeling of bundles without distortion of the products. That's why hot-rolled stock may be fed to the cold finishing line directly from bundles that makes unnecessary traditional operations of unreeling of cold bundles, dressing and stretching of rolled stock, its repeated reeling into bundles and significantly reduces expenditures for rolling processes [1].

On small-section-wire mills of the Danieli absence of skew during winding and residual axial stress, high density of bundles and ductility of the metal, and high yield of suitable metal are ensured.



Here are several examples of some technical decisions of the Danieli company, which concern medium- and heavy-section rolling mills. So, in 2003 the company supplied a unit for dressing high-speed rails with a manipulator for operative dressing of hardened rails. This system ensures the strictest allowances necessary for application of rails on high-speed railways. A bar-rolling mill with a cooler, devices for feeding and withdrawal of products, a unit for current multi-line dressing and cold cutting into measured length, a magnetic piler, and an automatic device for batching and binding is supplied [3].

Rail rolling mills are supplied with electric equipment, automatics, a technological process control system, a robotized system for accelerated automatic replacement of rolls and guides, engineering networks, and auxiliary structures.

Medium-section mills for rolling beams and channel sections are completed with a device for accelerated readjustment of programs, a cooler, a machine for dressing in the mill flow, edging saws, automatic pilers and banders, a laser caliber HIPROFILE (which ensures continuous measurement and control in the flow of the rolled item parameters), and equipment for heat treatment in the mill flow [4].

Mills for rolling flange beams are supplied with fast-acting mechanisms for change of rolls, a cooler, dressing equipment built into the mill line, automated equipment for finishing and batching of products, electric equipment, and automation system.

Rolling mills for round rolled sections are completed with the HIGAUGE devices for measuring diameter of billets, an automatic system for technological process of low-temperature rolling control, coolers, equipment for cold finishing of products, and equipment for heat treatment [1].

Technical peculiarities of hot galvanizing lines are a system for leveling coating thickness by compressed air, the basis of which are nozzles, angular position of which as well as their position relative the strip may be regulated over vertical and horizontal, a direct-fired furnace, a high-pressure air blower for feeding compressed air into the system, vertical section of electrolytic degreasing, a unit for finishing surface, a straightening-stretching machine, and a chromate treatment section. Application of zinc coating is performed using three-roll blocks [4, 2].

Heating furnaces for dip galvanizing lines are developed in the following versions: a section with open flame followed by a radiation tube complete with close circuit jet cooler; only with radiation tubes and jet coolers; a section with open flame followed by the chamber for soaking equipped with electric heaters and jet coolers.

All of them have vertical or horizontal arrangement and operate at speed from 17 to 200 m/min. Heating flame systems are designed and tested for operation with all kinds of fuel (from natural to coke and mixed gas, when burners are equipped with auxiliary burners for ignition of the main one, or only with ignition and detection system both for free flame burners and burners with a radiation tube). Furnaces in the Danieli hot galvanizing lines may operate with a strip from 0.25 to 4 mm thickness and width from 650 to 1650 mm [3].

The Danieli company developed scissors of drum type for strip mills, which are characterized by high quality of cutting and strict allowances as to the length of cutting. The scissors are equipped with two straight knives attached to their drum at a special angle of inclination [3]. The Danieli company has also developed super-scissors with PNC for longitudinal cutting. Using these scissors, to which the cutting tool (to be automatically replaced) is reliably attached, it is possible to cut superplastic strip into high number of bands. For example, cutting of steel for injection needles, ultimate strength of which is about 500 N/mm² at relative elongation 50 %, is tested: a strip of 0.12 mm thickness was cut into bands of 9 mm width (later 6 mm) in continuous mode. In these scissors brakes with vacuum booster of the drive are used, which reduce friction and external action on the strip [1].

At present certification of sheet mills, vacuum pans, and mini-plants of the Danieli company manufacture is carried out.

CONCLUSIONS

1. The Danieli metallurgical equipment is certified: arc steel melting furnaces, gas treatment installations, ladles-furnaces, installations for vacuum-oxygen decarburization of steel, MCCB, heating furnaces, small-section-wire mills, medium- and heavy-section mills, water hardening lines, hot galvanizing units, tribo-apparatuses, and scissors. All this equipment received Russian certificates of correspondence.

2. Metallurgical equipment of the Danieli company manufacture corresponds to high technical level and state-of-the-art requirements, contains many original technical solutions, and is in high demand on the world market.

1. *DaNews*. Selection of Danieli Group publications for 2004.
2. (2005) *DaNews*. Danieli Droup, 141.
3. (2003) *DaNews*. Danieli Droup, 135.
4. (2003) *DaNews*. Danieli Droup, 136.
5. (2003) *Steel Times International*, 11.
6. Lopukhov, G.A. (2005) Application of oxygen in arc steel-making furnaces. *Elektrometallurgiya*, **3**, 2–27.
7. Dyudkin, D.A., Grinberg, S.E. (2005) Some aspects of technology and structure of ladle-furnace unit. *Ibid.*, **8**, 25–28.

TO ISSUE ON SPECIFIC ELECTRIC RESISTANCE OF THERMOANTHRACITE

B.F. PETROV² and V.I. LAKOMSKY²

¹«Ukrainian graphite» Ltd., Zaporozhie, Ukraine

²E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Three concepts of specific electric resistance are analyzed used by process engineers when calcinating «raw» anthracite in electric calcinators.

Key words: *thermoanthracite in the state of pillar, powder, fraction, specific electric resistance, different degrees of dispersion*

Specific electric resistance (SER) of electrode thermoanthracite is the main parameter of quality of the widely distributed carbon material characterized, in comparison with initial feedstock (fossil anthracite), by rather high electric conductivity, which makes it fit for manufacturing electrodes used in certain electric arc furnaces and aluminium electrolytic furnaces.

Electrode thermoanthracite is produced mainly in heated by gas drum furnaces and in shaft furnaces. Both in the first and in the second cases anthracite is crushed down to a certain fraction composition prior to its heat treatment in the furnace. Quality of the produced coal calcination product is determined by the value of its SER. However, instrumental determination of SER is performed on the material crushed according to requirements of respective methodologies, which are standardized in many countries of the world, down to the powder state.

In the CIS territory GOST 4668 is valid, according to which for measurement of the anthracite SER a specimen of a lumpy material is sampled according to a respective standard from the calcinated material lot. After repeated quartering the anthracite specimen is dried and crushed, and then its SER is determined. For this purpose the powder is poured into a round hollow die with internal section $s = 200 \text{ mm}^2$ manufactured from electrical insulating wear-resistant material and compressed under pressure $(5.88 \pm 0.03) \text{ MPa}$. Through the produced column of compressed powder of height $l = (18 \pm 0.1) \text{ mm}$ direct current (0.5 A) is passed and voltage drop U is measured using potentiometer probes installed into the die at the distance 8 mm from each other over the vertical. Having determined in this way primary data (U) , value of the anthracite SER is calculated like in the case of conventional linear conductor $\rho = \frac{U s}{I l}$.

Produced value ρ represents an especially individual parameter of a specific thermoanthracite lot, which characterizes anthracite in the crushed state $(0.315\text{--}0.400 \text{ mm})$. It can not be used for describing

properties of thermoanthracite, because electric resistance of any crushed material is always higher (and rather significantly) than of non-crushed compact material.

By introducing standard determination SER its developers wished to obtain qualitative characteristic of thermoanthracite, which could be used by both a producer and a consumer for independent determining under the same conditions mentioned physical property of thermoanthracite and controlling quality of both supplied and consumed products.

Conditionality of this value is proved by the fact that for determining SER value the standard ISO 10143 is used in West-European countries, according to which thermoanthracite is crushed down to the fraction $0.5\text{--}1.0 \text{ mm}$ using a die with internal section 706.5 mm^2 ; the powder is pressed under pressure $3 \text{ MPa} \pm 1\%$; value of the current passed through the pressed coal is $(1 \pm 0.002) \text{ A}$. A specimen from the coal lot is sampled in somewhat different way. Other important differences also exist.

Certainly, experimental data obtained according to these two standards don't coincide because of significant difference in parameters of both the instrument itself and methodologies of the measurement. Comparison of the results of SER measurements of different thermoanthracite lots showed that results of determining SER according to GOST 4668 exceed data obtained according to the European standard ISO 10143 approximately 2.5 times. This has to be taken into account when analyzing quality of electric thermoanthracite produced at the enterprises of CIS countries and abroad.

Such known Norwegian company as ELKEM ASA CARBON (world leader in the field of electrode thermoanthracite) uses for determining SER of its product methodology, which differs from two mentioned standards. For example, they crush thermoanthracite down to the fraction $0.25\text{--}1.00 \text{ mm}$.

So, obtained according to the presented standards values of SER are quite unfit for estimation of either thermoanthracite itself as an electro-conductive material or electric resistance of the thermoanthracite charge in the process of coal calcination in the shaft electric furnaces.



In [1] experimental determination at room temperature of thermoanthracite SER in the state of pillar is presented. As showed analysis of scientific-technical literature, such experiment was performed for the first time. The following results were obtained:

Specimen No.	ρ , $\mu\text{Ohm}\cdot\text{m}$	Specimen No.	ρ , $\mu\text{Ohm}\cdot\text{m}$
1	134.1 ± 0.4	5	108.0 ± 1.1
2	128.4 ± 1.2	6	101.7 ± 0.9
3	117.2 ± 0.6	7	84.7 ± 2.1
4	113.3 ± 0.7	8	74.8 ± 2.1

Presented data on measurements were obtained on specimens of $7 \times 7 \times 40$ mm size cut from pieces of coal calcinated in the rotating drum furnace. Selection of the furnace was determined by known inhomogeneity on macro-scale of properties of the produced in it thermoanthracite. Taking into account structural inhomogeneity of fossil anthracite, properties of which depend not only on the coal deposit or a coal mine, but also on the production face. Anthracite for calcination was supplied by the «Obukhovskaya» Donetsk concentrating mill of the «Gukovantratsit» association.

The specimens were cut out from pieces of thermoanthracite irrelatively of their schistose structure, which stipulated difference in the results of measurements because of anisotropy of properties of the schistose structure materials in general and thermoanthracite in particular [2]. This explains 1.79 fold difference in measured SER values between specimens 1 and 8 (134.1 and 74.8) despite the fact that they were produced from the same thermoanthracite lot. Thermoanthracite of other deposits had higher and lower values of SER. Sharp difference between SER values is observed only in case of insufficient calcination. As far as the measurement methodology is concerned, which was used in [1], it is sufficiently accomplished, because parallel measurements on the specimens vary within rather narrow limits ($\pm 0.3 - \pm 2.8$ %).

Mean arithmetic SER value of thermoanthracite obtained as a result of the measurements makes up (107.7 ± 15.6) $\mu\text{Ohm}\cdot\text{m}$. In comparison with graphitized carbon material used for production of electrodes of arc steel-melting furnaces (8–10 $\mu\text{Ohm}\cdot\text{m}$), SER value of thermoanthracite is one order higher, but it is quite acceptable for producing from it electrodes for arc furnaces used for melting calcium carbide and ore-smelting electric furnaces.

Comparison of SER of thermoanthracite and the graphite single crystal [3] looks as follows. Because of high anisotropy of electric and other properties of graphite, SER in the direction parallel to hexagons of the graphite lattice is extremely low (0.385 $\mu\text{Ohm}\cdot\text{m}$), which is close to SER of certain metals, because in this case transfer of electric charges is performed in the same way as it is done in metals — by the flow of electrons. In the direction perpendicular to flat elementary lattice of graphite SER is 2 orders higher (52.0 $\mu\text{Ohm}\cdot\text{m}$), which is just 2 times lower than in thermoanthracite.

A process engineer engaged in heat treatment of anthracite in shaft furnaces is interested in the coal SER in the furnace shaft column. Determined according to the standard methodology SER of crushed thermoanthracite and thermoanthracite in the state of pillar can not be used in this case. The point is that the former ones depend upon fractional composition, temperature, and pressure exerted on loose mixture of the coal [2, 4, 5].

SER values of thermoanthracite in shaft of an electric calcinator can be obtained in two ways: experimentally using special probes and by the calculation method.

In [4, 5] as a result of mathematical modeling of electric conductivity of the disperse system analytical dependences of thermoanthracite (loose material) SER $\rho_{l.m}$ upon radius of the coal grain r of medium fractions [4] and fine powder [5] are established. For this purpose reduced radius of the electric contact spot a according to Holm was used. In case of the coal calcination in the electric calcinator analytical dependence looks as follows:

$$\rho_{l.m} = \rho_0 \frac{r}{a},$$

where ρ_0 is SER of thermoanthracite in compact state (in the form of a pillar).

New for this article value a was proposed for the first time by the known German specialist in the field of theory of electric contacts R. Holm [6], who used open by Maxwell phenomenon of contraction of electric lines of current during passage of the latter through a narrowing of a conductor and peculiar to it additional electric resistance.

Two solid bodies, irrespective of the carefulness of processing of their abutting surfaces, contact just in separate points. Such is the nature of the solid body surfaces. Irrespective of the fact if the surface was subjected to machining or not it always has microprotrusions and micro-troughs. The difference consists just in level of the roughness. That's why when two solid bodies touch each other, real contact is established only between protrusions of opposite surfaces. These points of real contacts were called by Holm a -spots. Investigations showed [6] that a -spots are located on the contact surfaces not uniformly, but in the form of separate accumulations (colonies). Surfaces of copper sheets of powerful pressure contacts of copper with electrodes from carbon materials on Acheson furnaces, which are destroyed not uniformly over the whole visible abutting surface, but in separated places — colonies of a -spots, are confirmation of Holm conclusions.

Value a , included into the formula, represents a reduced radius of imaginary sum of separate real contact spots. Despite conditional character of this parameter, its value is easily determined in experimental way. Experiments on electric heater of the coal charge at Dneprovsky Electrode Plant [7] made it possible to establish that value of this parameter for thermoanthracite of fraction composition 4–6 mm is 7.9 μm . For the same material, having fraction composition

Parameters, $\mu\text{Ohm}\cdot\text{m}$	SER of crushed thermoanthracite at T , °C					
	500	800	1100	1400	1700	2000
ρ_T	65150	58250	51360	44460	37560	30660
ρ_P	53420	47770	N / D			

6–8 mm, value a will be different — 8.2 μm . As a whole one may state that by means of thermoanthracite grain size increase value a increases very insignificantly.

Direct experiment, carried out under production plant conditions, showed for the fraction 6–10 mm $\rho_{l,m} = 43916 \mu\text{Ohm}\cdot\text{m}$ [7].

By using mentioned formula one can calculate SER value not just for separate fractions of thermoanthracite, but also for calcinated in the furnace coal charge as a whole. For calcination of anthracite at Dneprovsky Electrode Plant coal of fraction composition 6–25 mm is used. If we divide all this coal into the groups 6–10 mm (40 %), 10–15 mm (30 %), 15–20 mm (20 %), and 20–25 mm (10 %), it will be possible to calculate SER values of thermoanthracite for the groups and the coal charge as a whole. Results of the calculation show that thermoanthracite SER of 6–10 mm fraction is 53850, 10–15 mm — 84140, 15–20 mm — 94240, and 20–25 mm — 110150 $\mu\text{Ohm}\cdot\text{m}$. Weighted average SER value of mentioned mixture under these conditions equals 76650 $\mu\text{Ohm}\cdot\text{m}$.

It should be noted that calculated SER value is obtained without taking into account influence of temperature. In [1] in addition to SER value of thermoanthracite, temperature coefficient value of electric resistance β is established (0.0003 K^{-1} with negative sign). The latter means that electric resistance of thermoanthracite reduces by means of temperature increase. Taking into account linear dependence of resistance upon temperature $\rho_T = \rho_0(1 - \beta T)$, obtained SER values may be easily corrected in regard to the thermoanthracite temperature in each zone of the furnace.

The Table shows influence of temperature on SER of the coal charge of mentioned fraction composition heated in the process of the coal calcination in the shaft furnace from 500 (the temperature, up to which thermoanthracite is heated on the furnace mouth) up to 2000 °C (possible temperature of the coal in the heating locus under lower end of the upper electrode).

It is necessary to correct obtained calculated values ρ_T taking into account influence of external pressure on elementary electric contacts. Resistance ρ_P , shown in the Table, is possible only in upper layers of the thermoanthracite charge column at the temperatures up to 800 °C. In lower layers of the charge column SER of thermoanthracite will reduce, because pressure on the points of real contact between coal grains causes, taking into account brittleness of thermoanthracite, increase of the area and, as a result, increase of radius of a -spots.

It is shown in [8, 9] that as pressure on a single electric contact increases, its resistance always re-

duces. It should be noted that when pressure increases n times, contact resistance reduces $\sqrt{n}$ times.

The lowest horizon of the coal charge column experiences, according to our estimation, pressure of the higher coal levels not more than 40 kPa. Therefore SER of thermoanthracite at the lowest horizon will be 18 % lower than that of thermoanthracite located at the level of the furnace mouth. In order to calculate SER of thermoanthracite over the charge column height, it is necessary to divide mentally the column into several horizons, and calculate external pressure on contacts of thermoanthracite grains in each horizon taking into account bulk specific density of the anthracite charge.

In the last line of the Table values of thermoanthracite SER from lower layers of the column in the electric calcinator shaft are given calculated only for the coal at the temperatures registered before its discharge from the furnace.

So, owing to joint efforts of employees of the E.O. Paton Electric Welding Institute and Dneprovsky Electrode Plant parameters of thermoanthracite were established, which allow analyzing elementary processes of thermoanthracite production in shaft calcination electric furnaces.

In this article we wish to draw attention of process engineers, engaged in production of electrical thermoanthracite, to specificity of the term SER for thermoanthracite and its distinctive features:

- SER of thermoanthracite determined according to standard methodology (GOST 4668) at room temperature;
- SER of thermoanthracite as the material itself (in state of pillar) and its temperature coefficient of resistance, which allows calculating SER at any assigned temperature that does not exceed temperature of the coal annealing;
- SER of thermoanthracite in the process of its calcination in the shaft furnace, which depends upon fraction composition of the coal, temperature, and external pressure on elementary contact spots between grains of the coal.

1. Bykovets, V.V., Lakomsky, V.I. (2003) Specific electric resistance of thermal anthracite. *Advances in Electrometallurgy*, **4**, 46–48.
2. Fialkov, A.S. (1997) *Carbon, interlayer bonds and composites on its base*. Moscow: Aspekt Press.
3. Ostrovsky, V.S., Virgiliev, Yu.S., Kostikov, V.I. et al. (1986) *Artificial graphite*. Moscow: Metallurgiya.
4. Lakomsky, V.I. (2003) Mathematical model of calculation of specific electrical resistance of grained thermoanthracite depending on its fractional composition. *Advances in Electrometallurgy*, **3**, 44–47.
5. Lakomsky, V.I., Tsybulkin, G.A. (2004) Analytic model of dispersion system of current-conducting material. *Dopovidi Nats. Acad. Nauk Ukrainy*, **10**, 109–113.
6. Holm, R. (1961) *Electric contacts*. Moscow: Inostr. Literatura.
7. Bykovets, V.V., Lakomsky, V.I., Kirilenko, V.P. (2004) Specific electric resistance of lumpy thermoanthracite in thin layer. *Advances in Electrometallurgy*, **1**, 44–45.
8. Lakomsky, V.I. (2004) Volt-ampere characteristic of thermoanthracite contacts. *Ibid.*, **4**, 44–46.
9. Lakomsky, V.I., Lebedev, V.A. (2004) Dependence of contact electric resistance of thermoanthracite on temperature and pressure. *Ibid.*, **4**, 42–43.

ECONOMIC EFFICIENCY OF RAILWAY WHEEL PROFILE RENOVATION BY SURFACING OF WORN TREADS

V.V. MATVEEV

Viltrans, Ltd., Kiev, Ukraine

Quantitative estimation of influence of different factors on efficiency of wheel profile renovation by surfacing is made, in particular after annealing of a hardened in the process of operation tread. For increasing efficiency of the tread surface renovation it is proposed to use annealing of the tread, multi-electrode surfacing, and heat treatment of surfaced and turned wheels.

Keywords: efficiency, renovation, railway car wheels, tread defects, HFC annealing, multi-electrode surfacing

According to the data of All-Union SRI «Commercial Institute» (Moscow, RF), 3.0–3.5 mln of railway car wheels are annually produced in the world, 40–50 % of which are produced and used in CIS countries. It proves their low actual service life (calculated service life of railway car wheels produced in CIS is 12 years). Service life of the wheels is mainly determined by turnings, during which significantly greater amount of metal is removed than in the course of their operation. Railway car wheels with worn after operation treads (Figure 1) are turned for renovation of the initial profile (Figure 2, curve 4) on wheel turning machines using a template [1] with reduction of the rim thickness (Figure 2) measured at the distance 70 mm from external edge of the rim. Early in 1990s service life of the railway car wheel pairs reduced to 4–5 years because of high intensity of wear of flanges and the need to reduce rim thickness when renovating profile of the wheels [2]. Average term of operation between turnings of railway car wheel pairs, dismantled for current repair because of flange wear, was 10.6 months in 1996, including 4.6 % with operation term up to 3 months, 16.5 % — from 3 to 6 months,

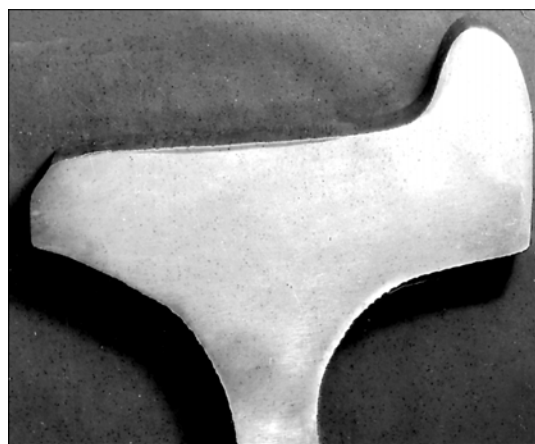


Figure 1. Macrosection of wheel with defects on its tread (DVRZ)

and 17.8 % — from 6 to 9 months [3]. As a result of measures directed at reduction of wear of flanges and rails (toughening of norms of railway track maintenance and rolling stock operation, improvement of the railway car repair and maintenance technology, lubrication of rails and curves, introduction of profiles optimally fitting profile of rails [2]) wear of wheel flanges and rail heads reduced 2 times. Surfacing of railway car flanges before their turning (Figure 2, curve 3) allowed reducing thickness of the layer removed from the rim [4, 5]. However, adequate increase of the term of operation (service life) of railway car wheels (up to 6–8 years) did not take place. The main reason of the wheel rim reduction became exclusion of the need to turn defects of thermal origin [2].

Efficiency of the flange surfacing is influenced not just by change of the price on new wheels and expenses connected with their renovation, but also by wear of the flange and depth of defects on the rim, which effect reduction of the rim thickness as a result of turnings. At present surfacing of flanges is performed

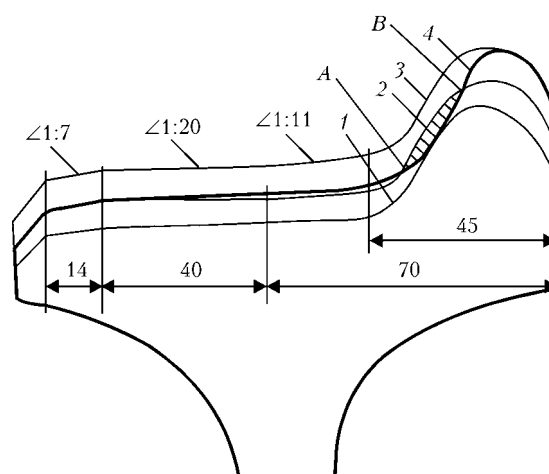


Figure 2. Scheme of wheel profile renovation: 1 — worn surface of wheel; 2 — turning line after renovation of wheels by surfacing of flange and rim; 3 — turning line after flange surfacing (A, B — places of flange surfacing beginning and finishing, respectively); 4 — line of turning without surfacing

without preliminary turning of defects on the tread, which sharply reduces its efficiency. Despite reduction of the number of defects on the tread, thickness of the layer removed in turning of the wheels having defects on the tread did not reduce and new problems occurred in turning of wheels with increased hardness.

At present in Russia, Kazakhstan and Ukraine in addition to production of increased hardness wheels [6, 7] idea of manufacturing cast wheels is actively lobbied [8], for example, according to technology of the American company Griffin Wheel [9], the main advantage of which consists in its cheapness. In case of increase of the run on American railways up to 1 mln km it is cheaper to exclude wheels from operation than to carry out their turning. However, this technology envisages multi-stage expensive system of control in the process of production and operation and need in frequent change of expensive moulds (one mould per 1000 wheels). The Griffin Wheel cast wheels are more brittle, because they are manufactured from steel with high content of carbon (0.67–0.77 %), which does not exclude possibility of occurrence of surface defects of brake origin and their propagation inside the wheel in case of their operation on railways of CIS countries.

Technical solution of the Valdunes company (France), which is the world leader in development of technologies for production of railway wheels, consists in application of medium- and low-carbon wheel steels alloyed by chromium, manganese and silicon, and containing 0.22 % C [10]. Such chemical composition allows limiting formation of martensite. At the same time it was noted at XXIII International Congress on Wheel Pairs (Rome, 2001) that from economic viewpoint it is more profitable to operate wheels with applied coating from low-carbon bainite steel [11], in which despite formation of creep nuclei development of pockholes and cracks does not take place, which allows reducing thickness of the layer that is removed in wheel turning and increasing term of the wheel operation.

So, in Russia and Ukraine economic efficiency of the flange surfacing as well as planned tasks and volumes of actual surfacing reduced. Number of installations also reduced. At the same time technologies for renovation of the railway car wheel profile by the method of surfacing of worn tread surfaces (Figure 2, curve 2) using low-carbon wire [5, 12, 13] are not introduced in repair of rolling stock in CIS countries.

In this work possibility of increasing service life of wheels as a result of surfacing of worn treads is studied. Factors are estimated, which effect increase of wheel profile renovation efficiency by surfacing, in particular after annealing of the tread [14, 15]. Technologies of wheel renovation using multi-electrode surfacing of the rim after annealing and heat treatment of the wheel rim by high-frequency currents after their surfacing and turning are described [16], whereby it is necessary to take into account following circumstances.

Firstly, renovation of railway car wheels by surfacing is connected with loss of the level of compres-

sion stresses created by hardening of wheels at the manufacturer-plant and the need in removing defects of metallurgical origin. As showed investigation of 18835 wheels, which were turned at Darnitsa Railway Car Repair Plant (DVRZ), Kiev, they had worn parts and defects, which caused reduction of the rim thickness at the depth from 2 to 23 mm [15]. Metallographic investigations of the wheels, which were delivered for repair with rim thickness about 30 mm, carried out in the E.O. Paton Electric Welding Institute of the NAS of Ukraine confirmed that microstructure of the wheel rim metal consisted of sorbite-like pearlite and thin interlayers of ferrite with microhardness HV 1-2540–2560 and HV 1-1850 MPa, respectively, hardness of the rim metal was about HRC 20 and flange — HRC 21–23. Manganese sulfides having size not less than 0.49 mm and complex silicates with high hardness HV 1-7420–7220 MPa were detected in the wheel rim metal. Severity of the wheel steel contamination with sulfides and silicates corresponds according to GOST 1778–70 to 3–4 points [17] (according to GOST 10791–89 «Whole-rolled wheels» severity of sulfide inclusions and silicates in the wheel steel should not exceed 3.5 points). Because of irregular shape these inclusions may be concentrators of stresses, which may enable formation of cracks and their increase as a result of cyclic loads during operation.

According to GOST 10791–89 and ISO 1005 / 6, convergence of the rim after radial cutting of the wheel (in the state of delivery) should be not less than 1 mm; divergence of the wheel is not allowed. In the process of operation convergence of the rim ends after cutting achieves due to action of mechanical loads on the tread –(1–2) mm. In a number of cases after brake tests stresses transformed into the tensile ones (1–2 mm) [18]. According to our data, wheels with thickness of the rim less than 45 and more than 30 mm without visible defects on the tread, which are delivered for repair to the railway car repair plants after their operation, have divergence of the rim ends after cutting 1 mm.

So, one of the main requirements in development of technology for renovation of whole-rolled wheels is, in our opinion, preservation in them of the compression stress level confirmed by operation of wheels within long period.

Secondly, as far as the wheels are manufactured from high-carbon steel (0.55–0.65 % C) their tread is subjected as a result of operation to local surface hardening and deep work hardening under influence of thermal and mechanical actions. Frequently 2–3 creep flaws are detected in them of 1–2 mm depth, hardness of the creep flaw metal of about 25 % of wheels is more than HRC 50 at the depth 3 mm, there are pits in metal of 5 mm and higher depth, and defects on the tread (squeezing of metal to the tread periphery, lamination of metal, cracks, and damages of fatigue character in the area of the wheel contact with a rail).

Before surfacing of the wheel rim (Figure 2, curve 3) it is necessary to turn defects to the depth of their

occurrence, otherwise they may act as concentrators of stress in deposited layers and cause their destruction. When turning hardened tread having defects on the rim it is necessary to undercut defects to the depth up to 5–6 mm under metal «crust» and increase thickness of chips by 2–3 mm. To prevent increase of impact load on cutters and machines revolutions are reduced. In this case electric energy consumed by the machine, use of the cutting tools, and duration of the turning increase.

Thirdly, wheel steel relates to the category of hardly welded ones. To avoid formation of hot cracks in deposited metal, surfacing of wheels is usually performed by low-carbon wire. Due to application of special measures (increased speed of surfacing, reduction of the base metal penetration and share of the base metal participation in the deposited metal) carbon content in the surfaced metal does not exceed 0.2 % [4]. For removal of cold cracks, which may occur in the deposit heat-affected zone (HAZ) as a result of formation of hardening structures and action of welding stresses and diffusion hydrogen, preheating of the wheel rim is performed before surfacing with retarded cooling after it and calcination of flux for the purpose of reducing amount of hydrogen [4, 5].

In any kind of surfacing structural changes take place in HAZ metal, which enable increase of the grain and worsening of the base metal strength characteristics. Increase of the wear thickness causes increase of heating and heat input per unit of length (area of the wheel surface) and, as a result, increase of HAZ width and probability of formation of cracks both in the deposited and base metal of the wheel. So, increase of the renovated layer thickness reduces productivity of the process (duration of the rim wear surfacing up to 4 mm is 3.5–4.0 s) [12].

Annealing of the tread surface allows reducing metal hardness at least 2.5 times, which significantly reduces chip thickness during turning [19]. For the purpose of preserving base metal of the wheel and reducing thickness of deposited metal it is recommended to anneal tread prior to fulfillment of surfacing works [14]. During 5 months at DVRZ, Popasnyansky (PVRZ) and Stry (SVRZ) railway car repair plants about 65 % of wheels were turned with normative thickness of chips less than 4 mm after annealing of tread prior to surfacing of flanges, the rest — till rim thickness reduced to 23 mm (average reduction of the rim thickness equaled 5.1 mm). In Ukrainian State Center (USC) «Ukrspetsvagon» annealing of the tread surface was not performed, 25 % of wheels were turned with thickness of chips 3–4 mm, the rest — several times with reduction of the rim thickness down to 23 mm (average reduction of the rim thickness made up 6.5 mm). So, reduction of the distribution maximum 2.6 times and shifting of histogram to the right, in comparison with the results of turnings at railway car repair works at 1.4 mm, is connected with absence of the tread annealing prior to the flange surfacing (Figure 3).

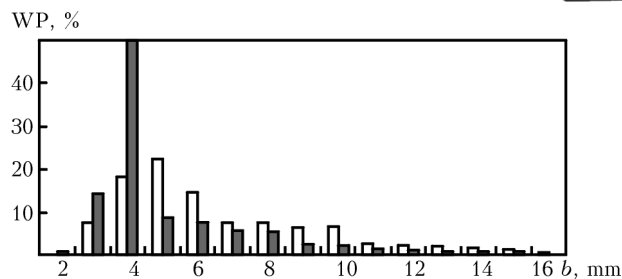


Figure 3. Number of wheel pairs (WP) depending upon reduction of rim thickness b : ■ — mean index; □ — «Ukrspetsvagon»

Repair of wheels with application of high-frequency heating is more economical and causes lower strain, because a heated layer constitutes a small share of the wheel mass [20]. Peculiar feature of such heating is generation of heat energy directly in the item being heated, which ensures high rate of heating up to the temperature values, at which structural transformations take place in the metal.

HF heating of the wheel tread was performed using the TI2-100 / 10M installation (Figure 4). At frequency 10 kHz and power 100 kW structural transformations start to take place at the depth 2 mm. Comparison of the wheel tread metal microstructure before (Figure 5) and after (Figure 6) HFC annealing of the tread allowed establishing the following:

- microstructures of metal in zone with acicular martensite structure and in the area with granular bainite structure after HFC annealing undergo transformation with formation of fine-grain bainite (at the depth 2.4 mm from the tread) and as a whole get more homogeneous;

- HFC annealing influences metal structure at a limited depth (microstructure and microhardness at the depth above 2.4 mm practically do not change).

So, surface annealing before surfacing enables transformation of martensite structure in this zone into the bainite one and refining of the grain, which allows surfacing of the rim without turning of defects [14, 16] and reducing probability of cold crack formation in surfacing. Grinding of the tread in the place of location of deep defects instead of turning over the

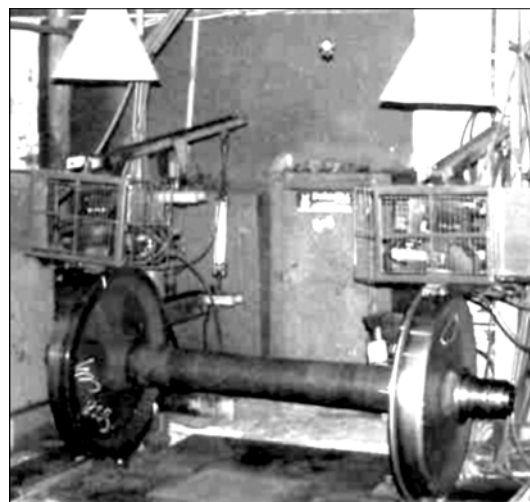


Figure 4. TI2-100 / 10M installation for annealing wheel treads

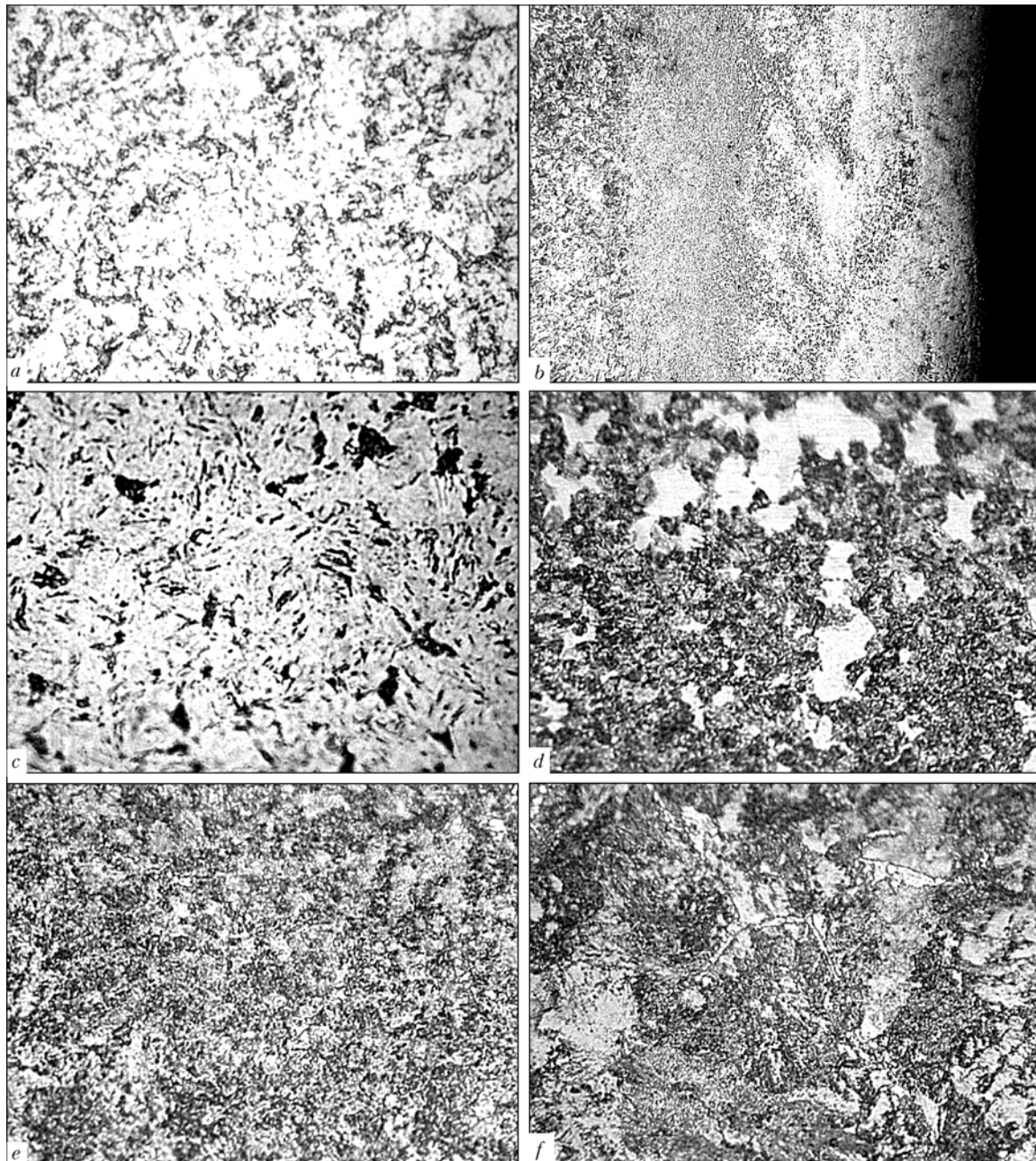


Figure 5. Metal microstructure in different surface areas of wheels: *a* — flange HAZ ($\times 1000$); *b* — wheel rim ($\times 40$); *c*, *d* — near-surface light and grey rim surfaces, respectively ($\times 1000$); *e* — near-surface grey layer ($\times 1000$); *f* — wheel base metal ($\times 1000$)

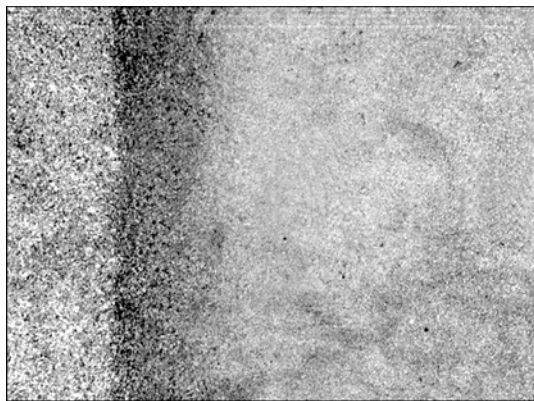


Figure 6. Metal microstructure of wheel rim surface areas after HFC annealing ($\times 40$)

tread circumference also makes it possible to preserve the rim.

Annealing increases level of tensile stresses in the wheel metal, which occur during their manufacturing. It is established that divergence of wheels after annealing on the HFC installation equals 1 mm, after annealing and surfacing of flanges by one electrode — 2.5 mm, after annealing, turning of defects and additional heating on the HFC installation prior to surfacing of the flanges — 3.5 mm, which enables detection of defects (microcracks) on the wheel surface up to the sizes that are detectable visually, up to occurrence of cracks in the wheel rim [15]. Tensile stresses, which occur after HFC annealing, enable detection of wheels with defects. Since 1997 due to tread annealing, turning down to the depth of defects,



Figure 7. Microstructure of wheel renovated by method of multi-electrode surfacing

and surfacing of worn flanges on railway car repair enterprises of Ukraine cracks in the rim were detected in 0.2 % of delivered for repair wheels, which allowed ensuring accident-free operation of 270,000 repaired wheels with surfaced flanges. Experience of continuous operation of renovated wheels allows assuming maximum divergence of the wheel rims after cutting 3.5 mm that may be accepted as a criterion.

For the purpose of achieving high quality of deposit after annealing of the wheel tread and maximum productivity of its renovation it is possible to use multi-electrode rim surfacing [21]. Due to successive pulse character of the arc burning, its movement across the rim, and de-concentration of heat input, penetration depth, share of the base metal in deposited metal, and deformation of wheels after surfacing reduce [22]. It is possible to increase yield point, impact toughness, corrosion resistance of the wheel rim deposited layer metal, resistance to mechanical wear at significant impact loads, deformability of items, and reduce probability of formation and propagation of cracks by alloying of the deposited layer.

However, liquid metal pool does not have significant volume and is slowly cooled during solidification in case of multi-electrode surfacing. This causes coarse-columnar structure of the deposited metal, base metal overheating near zone of its fusion with the weld metal (Figure 7), and grain increase in the coarse grain areas (CGA) of deposit HAZ metal. As a result mechanical properties of carbon steels worsen, especially impact toughness. In addition, increase of heat input causes increases of wheel divergence up to 6.5 mm.

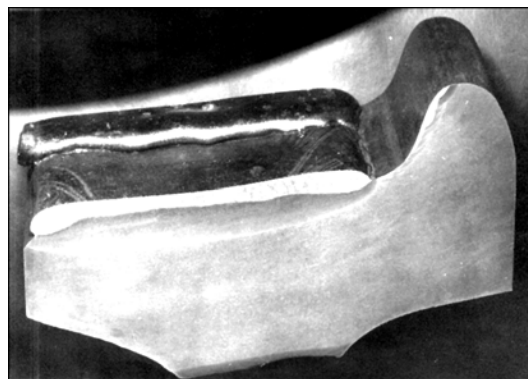


Figure 9. Macrostructure of wheel surfaced by method of multi-electrode (10 electrodes) surfacing in one and two layers

By means of the UON-2 experimental installation (Figure 8) single-pool multi-electrode surfacing of one and two layers was carried out on the wheel rim using welding wire Sv-08KhM of 3 mm diameter and flux AN-60 (Figure 9). Single-pool surfacing of flanges was performed on the UNG-2M installation (Figure 10) by one or two electrodes using welding wire Sv-08KhM of 3 mm diameter and flux AN-348AM by means of successive application of beads. Wire was used for surfacing, which at present serves for surfacing of railway car wheels at enterprises of railway transport of Ukraine.

It is established that surfacing of a rim of 100 mm width of a railway car wheel, having diameter not less than 850 mm, may be performed by 10 electrodes. Number of electrodes is stipulated by width of the rim, which has to be surfaced, and ability to ensure conditions for multi-electrode process of surfacing (distance between electrodes should make up 3–4 of electrode diameters [22]). To prevent spread of the weld pool and save welding consumables in surfacing, the wheel pair was inclined at the angle not less than 5° to horizon in such way that the wheel profile to be parallel to horizon [23]. Speed of surfacing and total welding current are interdependent. For example, at 500–600 A current maximum speed of surfacing is 6–7 m / h, minimum — 4 m / h; at 1200 A current maximum speed is 15 m / h (duration of the rim surfacing is 10 min), minimum speed is 10 m / h (duration of the rim surfacing is 16 min). At higher speed of rotation liquid metal from the pool spreads over

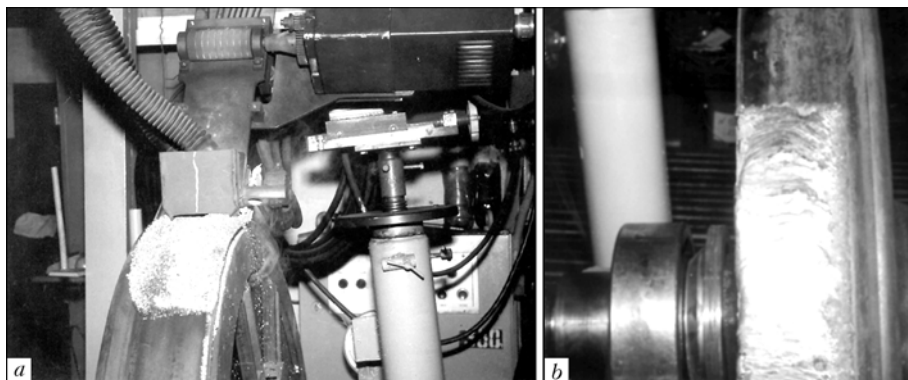


Figure 8. Welding head of UNO-2 installation for multi-electrode surfacing (a) and wheel rim (b) surfaced by single-pool method on UNO-2 installation with 10 electrodes using wire Sv-08KhM of 3 mm diameter and flux AN-60

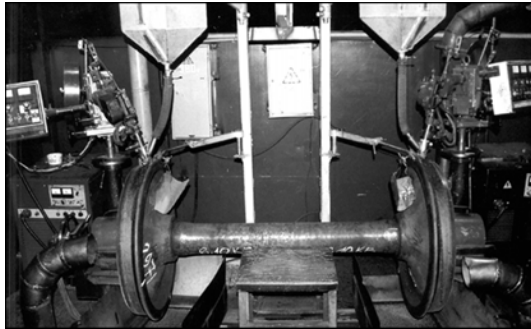


Figure 10. UNG-2M installation for surfacing flanges of railway car wheels

the wheel, at lower speeds interruption of multi-electrode surfacing process was detected.

Microstructure of the deposit metal represents bainite with microhardness HV 1-2850–3220 MPa, hardness HRC 23–27. Microstructure of CGA metal in deposit HAZ is represented by bainite with microhardness HV 1-2540–3660 MPa, hardness HRC 20–31. The first value of hardness was measured near surface of the metal produced by multi-electrode surfacing, while the latter near the fusion line. Carbon content in deposited metal is 0.29 %, cracks in the deposited metal and in the deposit HAZ metal were not detected.

Due to the welding current reduction, manipulations with electrodes, surfacing speed increase, and surfacing of two layers at maximum possible speed it is possible to reduce base metal penetration and transition of carbon from base metal into the deposited layer, and size of grains in CGA of deposit HAZ metal.

Essential increase of multi-electrode surfacing productivity on rim of the railway car wheel of 850 mm diameter (minimum duration is not more than 11.5 min, thickness is 9 mm) was achieved after increase of surfacing speed of first and second layers: $v_{s1} = v_{s2} = 14$ m / h, $I_1 = I_2 = 1100$ –1200 A (Figure 11), whereby grain in CGA of deposit HAZ metal was refined (Figure 12) and made up mainly 8 points, while the rest grains had 5–7 points. Reduction of carbon in deposit down to 0.1 % enabled increase of the ferrite component size in the deposit microstructure and reduction of hardness down to values HRC 20 and microhardness (in the first layer microhardness in center of rim is HV 1-3090, in second — HV 1-2740–2970 MPa). One may also expect significant increase of the deposited metal wear resistance



Figure 11. Microstructure of metal produced by method of two-layer multi-electrode (10 electrodes) surfacing of wheel rim using welding wire Sv-08KhM of 3 mm diameter and flux AN-60 ($\times 40$)

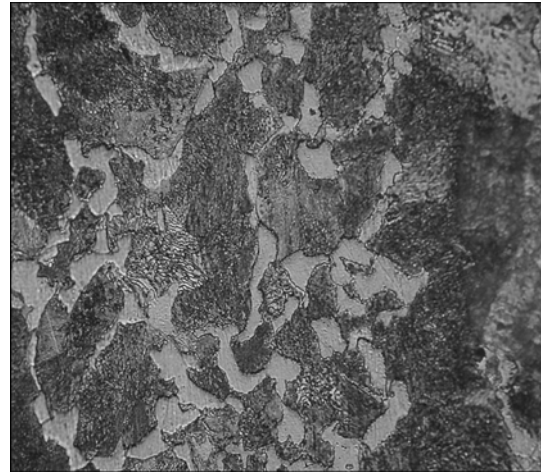


Figure 12. Microstructure of CGA of HAZ metal produced by method of two-layer multi-electrode (10 electrodes) surfacing of wheel rim using welding wire Sv-08KhM of 3 mm diameter and flux AN-60 ($\times 1000$)

due to rather high content of chromium (0.79 %) and molybdenum (0.54 %).

It is established that reduction of divergence of wheel ends after cutting may be achieved by high-frequency heating of the renovated and turned wheel tread. Renovation efficiency increases in case of using the TI2-100 / 10M installation, which was earlier used for tread annealing. Heating is performed at a rate 150–160 °C / s up to the temperature above A_{c1} , cooling down to the temperature below the point A_{r1} within 5–6 s, and repeated heating for 5–6 s up to the temperature below A_{c1} . Accelerated cooling at the rate not less than 50–60 °C / s is performed using water sprayer established directly into the inductor (Figure 13). Due to such heat treatment of a wheel its divergence after cutting reduced to 3.5 mm.

Suggested technology of renovation of worn railway wheels should include the following:

- annealing of wheel tread on the HFC installation at frequency 10 kHz at the depth about 2.5 mm, which ensures possibility of increasing divergence stresses, detecting defects and processing wheels after surfacing, and reducing thickness of a necessary for renovation layer being deposited;
- grinding of the places of deep crack occurrence at the depth more than 3 mm instead of turning over the tread circumference;



Figure 13. Process of wheel heat treatment on TI2-100 / 10M installation after surfacing and turning



- multi-electrode surfacing on the wheel rim or single-pool 10 electrode 2 layer surfacing using alloyed wire, which ensure high productivity and quality of the deposited metal (grain number in CGA of HAZ metal is not less than 6–8);

- surfacing of worn flanges;

- heat treatment on the HFC installation of surfaced and turned wheels, which ensures level of the divergence after cutting not less than 3.5 mm.

So, surfacing of low-carbon metal with increased wear resistance characteristics allows reducing development of defects on the tread in operation, reducing thickness of the removed layer in the course of turning of the wheels, and increasing their service life. Renovation of thin-rim wheels with rim thickness less than 30–35 mm, which were earlier rejected, will make it possible to increase service life at least 2 times.

- (1977) *TsV/3429: Manual on inspection, examination, repair and formation of car wheelsets*. Moscow: Transport.
- Bogdanov, V.M., Zakharov, S.M. (2004) Current problems of rail-wheel system. *ZhD Transport*, **1**, 57–62.
- Bogdanov, V.M., Kozubenko, I.D., Romen, Yu.S. (1999) Technical state of car and wear of wheel flanges. *Ibid.*, **3**, 23–25.
- Asnis, A.E., Gutman, L.M. (1948) Building-up of worn rim flanges by surfacing. In: *Transact. on Automatic Submerged-Arc Welding*. Kiev: PWI.
- Pavlov, N.V., Kozubenko, I.D., Byzova, I.E. et al. (1993) Cladding of wheelset flanges. *ZhD Transport*, **7**, 37–40.
- Pasholok, I.L., Tsyurenko, V.N., Samokhin, E.S. (1999) Increase of wheel hardness. *Ibid.*, **7**, 41–43.
- Tsyurenko, V.N. (2002) Service reliability of freight car wheelsets. *Ibid.*, **3**, 24–28.
- Zhyabirov, Kh.F. (2004) Wheel–rail system: optimal interaction. *Evrasiya Vestn*, **6**, 3–4.
- Kulagin, A. (2003) Strength testing. *Ekspert*, **26**, 7–8.
- Stevenot, G., Damilly, F. (2002) L'innovation dans les roues ferroviaires et l'évolution des marches. *Rev. Gen. des Fer.*, **5**, 33–39.
- Cassidy, Ph. (2001) Wrought materials may prolong wheel life-wheel set technology. *Int. Railway J.*, **12**, 40–41.
- Asnis, A.E., Gutman, L.M., Stepenko, V.P. et al. (1958) *Submerged-arc welding in repair of locomotives*. Moscow: Transzheldorizdat.
- (2001) ESAB delivers engineered automatic welding station to Ghana in Africa for build-up welding of worn railway wheels. *Svetsaren*, **1**, 20–21.
- Matveev, V.V. *Method of building-up of railway wheel roll surface*. Pat. 44373 Ukraine. Int. Cl. C21D9 / 34. Publ. 15.02.2002.
- Matveev, V.V. (2005) Surfacing of train wheel flanges after annealing of the tread surface in car-repair plants of Ukraine. *The Paton Welding J.*, **6**, 36–41.
- Matveev, V.V. (2005) Repair of railway wagon wheels by cladding with preliminary annealing of roll surfaces. *Ibid.*, **11**, 29–33.
- Matveev, V.V. (2005) Diagnostics of railway wheels during their repair by surfacing. *Tekhn. Diagnostika i Nerazrush. Kontrol*, **4**, 1–4.
- Uzlov, I.G. (1985) *Wheel steel*. Kiev: Tekhnika.
- Ivanov, I.A., Urushev, S.V. (1998) About increase of life of solid-rolled wheels. *ZhD Transport*, **7**, 25–26.
- Vologdin, V.P. (1974) *Surface induction hardening*. Moscow: Oborongiz.
- Emelianov, N.P. (1962) Multi-electrode submerged-arc and electroslag cladding. In: *Transact. of All-Union Res. Inst. of Rail Transport*. Moscow: Transzheldorizdat.
- Melikov, V.V. (1988) *Multi-electrode surfacing*. Moscow: Mashinostroenie.
- Matveev, V.V., Olshevsky, V.I. *Method of building-up of surface profile of railway wheel*. Pat. 61794 Ukraine. Int. Cl. C27B60B3 / 02, B 23PC / 00. Publ. 15.07.2005.

APPLICATION OF STEAM-PLASMA PROCESS FOR PYROLYSIS OF ORGANIC WASTES INCLUDING MEDICAL AND OTHER HAZARDOUS ONES

S.V. PETROV, G.S. MARINSKY, A.V. CHERNETS, V.N. KORZHIK and V.M. MAZUNIN

E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Analysis of state-of-the-art state of hazardous waste processing and existing technologies is presented. It is shown that plasma processing is an alternative to traditional processes of combustion and disposal of processed wastes, especially organic ones. Main advantages and shortcomings of the latter ones are presented. Method of steam-plasma (water steam is used as a plasma gas) gasification is proposed, which received the name PLAZER. Data on the main technological peculiarities of the process are presented. It is shown that proposed process of steam-plasma conversion of wastes will make it possible to guarantee higher efficiency and environmental safety of waste processing, and application of obtained as a result of the waste processing synthesis-gas for organization of electrical energy and liquid fuel production will enable development of alternative processes of energy production.

Key words: steam-plasma processing; hazardous wastes, plasma gasification, PLAZER, pyrolysis, thermodynamic parameters, synthesis-gas

Plasma technologies and equipment, which are widely used in metallurgy, welding, and application of structural and functional coatings, find nowadays new and new areas of use. So, they seem to be very promising for solution of two important tasks:

- environment protection and processing of hazardous wastes, including organic ones;
- development of new alternative methods for production of various fuels.

A significant share of constantly forming wastes is presented by organic substances (plastic utensils and items, medical waste, automobile tires, etc.). Volumes of these wastes are huge; many of them, especially plastics, practically don't decompose under

usual conditions. Frequently they are hazardous for people and environment. So, according to the Basel Convention of 1989 on control over transborder transportation of hazardous wastes and removal thereof, one of the most hazardous categories, which is in the first position in the list of 45 kinds of wastes, are wastes of health institutions [1–2], which contain toxic and infectious substances. According to the presented data [3–5], every year in the USA form about 3 mln t medical wastes, in Russia and China — up to 1 mln t, and in France — up to 600 ths t. Approximate (calculated) amount of medical wastes formed in Ukraine makes up about 350 ths t per year. Not less hazardous are such wastes as prohibited or unfit for application pesticides (according to official data, about 20 ths t of them have been accumulated in Ukraine) and a number of other wastes. The issue of their destruction (disposal) is not solved till now and gets more and more acute.

Many specialists consider that separation into the groups with application of each component as a feed stock should precede disposal of medical wastes. However, because of extreme complexity and high cost of organizing such separation it is, evidently, more advisable to process mentioned wastes under conditions of high temperature action, which ensures destruction of all components that enter into composition of the wastes.

At the same time such action under open atmosphere conditions can not but cause formation of harmful substances, in particular halogenated dioxins and dioxin-like substances. Mentioned substances are super-toxicants, especially harmful and toxic products of synthetic chemistry, by-products of a number of chemical production processes and associated micro-emissions of industry and economic activity of people, which practically were not mentioned till 1990s in educational and scientific literature.

In contrast to the simplest ones, halogen-containing dioxins represent chlorinated or brominated benzene rings connected by oxygen bridges, so called polychlorodibenzodioxins and polychlorodibenzofurans and, respectively, polybrominated dibenzodioxins and polybrominated dibenzofurans. They represent a special hazard because of the fact that despite their insolubility in pure water and pure air, they dissolve in the water, which contains humic acids or fulvic acids from the soil humus. It is connected with their high propensity to complex formation with components of humus. Dioxins form complex compounds with air aerosols, and due to their high adherence capacity are carried over well not just by land, but also by air. Dioxins decompose in sole within 20–30 and more years, in water — within two and more years [6].

Extreme hazard of dioxins for men should be noted. If dioxins are present in human habitat, they are accumulated in human organism due to their significant affinity to protein. The main source of dioxin supply into human habitat is production of chlorine- and bromine-containing preparations. Action of pre-

sent in the natural environment dioxins even at the level of traces is hazardous also due to the fact that practically they can not be detected by conventional methods of analysis. At the same time accumulation of dioxins in a living organism causes occurrence of many oncological diseases, hypercholesterinemia, etc.

For analysis of natural objects for the purpose of detecting presence of dioxins special and often difficult for carrying out methods are required (concentration and separation from the background substances, application of gas chromatography and mass-spectrometry with high resolution).

In recent years typical source of contamination of natural environment by halogenated dioxins is, in addition to mentioned production processes, low-temperature combustion of various wastes. Tests showed that dioxins are high temperature resistant. Moreover, at 800 °C formation, but not disintegration, of bromine-containing dioxins takes place. And only at the temperature 1200–1400 °C within 4–7 h, which is technically complex and expensive, takes place irreversible destruction of halogenated dioxins.

That's why when disposing of organic wastes one has to try using technologies, which prevent formation of mentioned substances in the course of their processing. In this connection the most known and widely used during many years technologies of combustion and disposal get more and more frequently into conflict with valid requirements of environmental safety and are rejected in majority of countries of the world, where new waste processing enterprises are built. At the same time new organic wastes may be an additional source for producing synthetic fuel in the form of synthesis-gas or diesel fuel (up to 700 kg from 1 t of wastes).

As shows presented in [7, 8] analysis, one of the most promising directions in processing and disposal of hazardous wastes is application of technological processes based on use of plasma arc energy. Despite the fact that technologies of plasma processing of different kinds of hazardous wastes started to be used comparatively recently, many companies, including those from advanced industrial countries, demonstrate their activity exactly in this direction. So, works connected with plasma disposal of wastes are actively carried out in the USA, Russia, India and a number of other countries [7, 8].

Plasma technology as an alternative to any method of combustion consists in transformation (decomposition) of complex molecules of all substances into very simple ones under conditions of extremely high temperatures and absence of free oxygen.

This technology is characterized by a number of the following evident advantages:

- plasma jet temperature is able to completely destroy any organic and biological materials, destroy with guarantee the most toxic poisons, remelt and evaporate the most refractory non-organic compounds, and significantly reduce volume of wastes as



a whole. Even stable at high temperature components can not withstand the process of plasma processing;

- plasma gasification process (pyrolysis) ensures environmentally clean processing of feedstock (wastes) without formation of resins, dioxins, aerosols, etc. and complete extraction of the whole carbon from the waste material, while in all combustion processes solid residue contains up to 30 % C. Plasma gasification process ensures the highest degree of cleaning of processed materials (up to 99.99 % and more);

- plasma gasification products are high-calorific gas (mixture of $H_2 + CO$) and neutral solid residue in the form of a vitrified slag;

- gas and slag, produced in carbon-base plasma gasification of wastes, have commercial value. Gas may be used immediately as a stock for future use and transported to a distant consumer. Gas may be an efficient source of fuel for producing electric energy or a feedstock for producing synthetic motor fuel, etc.;

- ash removed from a reactor in liquid state is safe for disposal. Slag melt after its discharge may be granulated and directed for construction, while metal melt may be used for producing alloys, master alloy, refining treatment, etc. However, this metal residue is, as a rule, rather small. Application of plasma technologies makes unnecessary burial of wastes;

- plasma gasification enables significant reduction of a solid substance mass. Ratio of the waste material mass to solid residue ash achieves 400:1, i.e. degree of processing makes up more than 99.7 %. Other technologies usually ensure ratio not more than 5:1, i.e. 60 %;

- plasma gasification installations are modular ones, rather small space is needed for their location, they are convenient in servicing, repairable, adaptable to certain requirements, quick increase of their productivity is possible, they may be located inside existing infrastructures and under ground;

- plasma torch is an independent source of heating, which allows flexible controlling process of gasification, i.e. immediate responding to the change of processed material composition;

- cost of construction and maintaining of plasma gasification process is much cheaper than any conventional modern combustion system;

- results of tests, carried out by many companies, prove that in case of using plasma gasification technology, concentration of toxic emissions into atmosphere and amount of solid residues are lower than valid standards.

At the same time, despite mentioned advantages of plasma processes, they have certain shortcomings, which prevent successful introduction of mentioned technologies and equipment into the market.

In practice electric arc generators, which work on both inert and oxygen-containing gases, are used as plasma sources of heating. In the working space zones with extremely high temperatures (from thousands

to dozens thousand degrees) and high gradients of parameters are present. This circumstance causes difficult-to-solve issues connected with choice of the design and the material for the reactor walls (high-temperature and chemically inert in relation to the waste materials are needed) and technological accuracy and reproducibility. Rates of reactions depend exponentially upon temperature, that's why location of the materials being processed in different temperature zones stipulates significant scatter of the material processing rate and, as a result, results of the process.

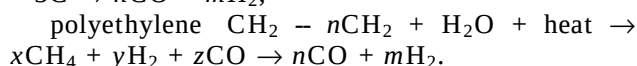
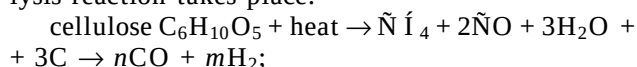
Another principle problem in industrial implementation of large-capacity plasma installations with long cycle of continuous operation consists in the need to use rather powerful (above 100 kW) plasmatron of indirect actions having rather limited real continuous operation life, which is connected with unavoidable erosion of the most widely used copper electrodes. So, electric arc plasmatrons with relatively short cycle of continuous operation (several hours) and, in single cases, with long cycle (more than 100 h) are widely used in industry, whereby real ways of significant increasing mentioned service life of the most popular copper electrodes are not seen.

Other designs that would be able to really ensure significantly longer service life, in particular self-recovering from gas phase cathodes and tungsten consumable graphite anodes, which are complex and exotic structures, are not considered in this case by us in regard to these technological processes.

The rate of erosion of copper electrodes (cathode and anode), which determines service life of a plasmatron, is connected with many factors, especially with the arc current, whereby erosion characteristics of anode and cathode, depending upon dynamics of near-electrode processes, may both completely coincide and demonstrate significant discrepancy. One of the main issues is ensuring of invariability of the specific erosion level of electrodes during long operation within the range of pre-critical currents.

For solution of mentioned issues a new technological process, which excludes burning, is proposed (Figure 1) based on application for waste pyrolysis (high-temperature gasification) of water steam with high thermodynamic parameters (temperature about 1100 °C).

Analysis of the process showed that for processing (plasma gasification) of 1 kg medical waste (approximately 60 % of cellulose + 30 % of plastics + 10 % of liquid) about 1 kW·h of electric energy will be needed for dissociation of these substances with production of synthesis-gas ($CO + H_2$) in the amount 1.1–1.4 nm³ from 1 kg of the waste, whereby the following pyrolysis reaction takes place:



During combustion of synthesis-gas heat is released:

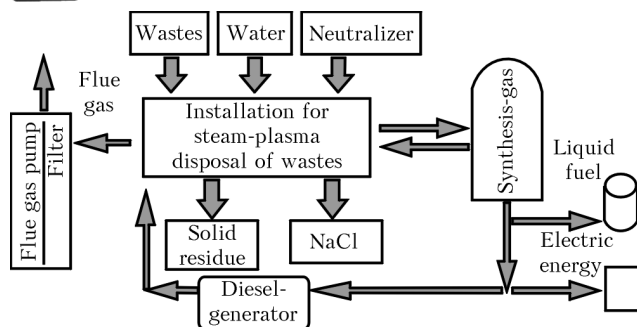
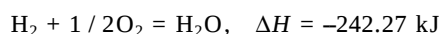
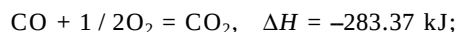


Figure 1. Scheme of process of steam-plasma processing of wastes



with total energy $\Delta H = -525.64 \text{ kJ/nm}^3$. It corresponds to 11732 kJ/nm^3 , which is equivalent to $3.26 \text{ kW}\cdot\text{h}$ of electric energy, i.e. as a result of pyrolysis of 1 kg of medical wastes of considered composition fuel is formed, power of which, recalculated into electric energy, equals $3.59\text{--}4.56 \text{ kW}\cdot\text{h}$. In case of using formed in the course of processing synthesis-gas for feeding the installation for plasma pyrolysis and allowing for efficiency of the diesel-generator at the level of 30 %, practically zero energetic balance is ensured, when necessary for performance of the process energy is formed completely due to combustion of generated synthesis-gas.

At steam pressure in the reaction volume 0.1 MPa and temperature 1100°C , which is close, according to our preliminary estimation, to optimum conditions of the process, volume of water increases 6330 times, and enthalpy equals 4877 J/g , whereby required full heat power for conversion of 1 kg/h water into steam equals 1354.7 W .

For ensuring productivity of the installation at the level, approximately, 200 t of wastes per year, which corresponds to needs of a medium clinic or a mobile installation, plasmatron of about 40 kW capacity and water flow 30 kg/h will be needed. Taking into account efficiency, converter power coefficient, and own needs of the plasma installation, power consumed from the mains will make up $40.642 / (0.7\text{--}0.8) \approx 51\text{--}58 \text{ kW}\cdot\text{A}$.

Amount of steam at temperature 1100°C , pressure 0.1 MPa and water flow 30 kg/h will achieve, approximately, $190,000 \text{ m}^3/\text{h}$. Depending upon diameter of the nozzle within the range of 20–100 mm, under conditions of mentioned productivity steam velocity may be achieved within 6.7–168 m/s.

It should be noted that at present any other technical means, except plasmatron, are not available for producing water steam with necessary thermodynamic indices, and in this case we speak about using so called steam-plasma (i.e. plasma, in which water steam is used as a plasma gas).

Proposed process, which was called PLAZER, allows solving many issues of traditional plasma gasification technologies.

So, all known installations of plasma processing of wastes are characterized by high gradients of parameters in the reaction zone, which is stipulated by properties of plasma jets. Due to this different volumes of wastes are gasified at different rates, and in high-temperature zone new undesirable compounds may form, for example, nitrogen oxides, etc.

In high-temperature steam pyrolysis all over reaction volume the same temperature and concentration conditions are established due to high indices of water steam transportation properties, and the process becomes completely controllable. It is very important for processing wastes of variable chemical composition, when it is necessary to regulate parameters of fed into the reactor steam for the purpose of minimizing duration of processing and maintaining optimum composition of synthesis-gas, i.e. constant assigned ratio CO / H_2 .

PLAZER ensures high-efficient (up to 100 %) processing of organic wastes (including medical and other hazardous ones) without emission into environment of such harmful substances as dioxins, resins, phenols, aerosols, etc., whereby synthesis-gas is formed as a target object, which is a valuable fuel, and safe solid processing products fit for further use, for example, in construction.

In the course of processing such hazardous elements as chlorine, fluorine and other, which enter into composition of many plastic materials, are bound and easily removed. In gasification of coal-containing substances by water steam at high thermodynamic parameters compounds of sulfur are absent in gaseous phase, because it completely remains in solid residue (slag).

Absence of ballast nitrogen and free oxygen in the reaction chamber prevent formation of nitrogen oxides, which, in addition to absence of argon and other gases, enables ensuring of high quality of produced synthesis-gas and does not require for using additional operations connected with its separation and cleaning.

Process of steam-plasma gasification is not sensitive to humidity of processed wastes, that's why it does not lose its destruction efficiency with change of humidity and composition of the solid substance.

Application of steam-plasma conversion allows achieving significantly higher degree of the waste material conversion (irrespective of its composition) into the target product — synthesis-gas. This ensures new technical means for setting more rigid environmental norms in regard to emission of toxic substances, including dioxins.

At steam conversion temperature above 900°C (Figure 2) [9] equilibrium carbon is absent in the system. That's why the issue of complete carbon gasification from all compounds is determined only by kinetics of the process, i.e. duration of the solid phase contact with chemically active heat carrier (in this case water steam with high thermodynamic parameters). It is evident that by means of temperature increase reaction rate (and, respectively, productivity)

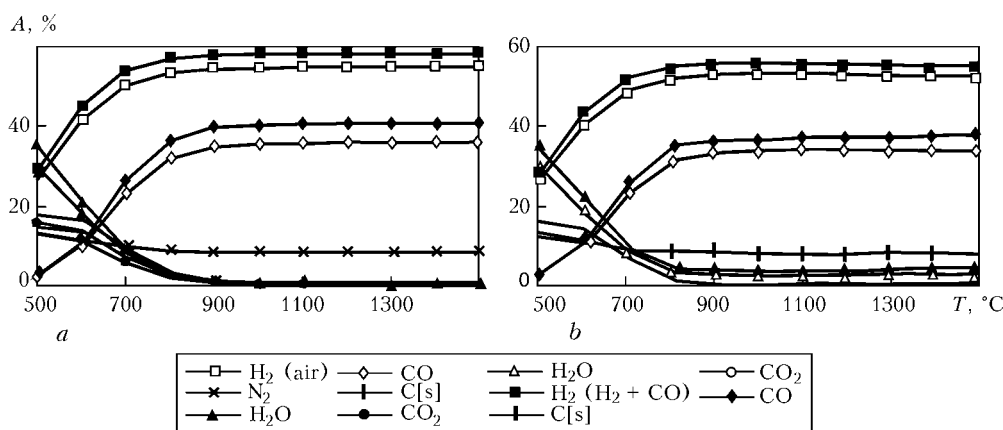


Figure 2. Change of composition A of converted by plasma gas in processing of medical wastes under conditions of stoichiometric (a) and 1.5 stoichiometric humidity (b)

will increase according to exponential curve with proportional reduction of overall dimension of the installation. Upper temperature level will be mainly determined by resistance of the reactor material.

Application of synthesis-gas, produced in the course of processing, for independent feeding of the installation itself allows significant reducing energetic expenses on disposal of wastes, thus making the process practically energy independent and, in addition, simultaneous organizing production of electric energy and liquid fuel.

Service life of this plasmatron (steam plasma generator) is much longer than of the traditional one. In opinion of the authors, development of a steam plasmatron having capacity up to 300 kW and continuous operation life up to 300 h is quite realistic.

Used for implementation of this method equipment is characterized by reduced mass and overall dimension (3–5 times in comparison with the best analogues). It may be made in stationary and mobile versions (on automobile or railway platforms, sea or river ships, etc.), which stipulates creation of technical basis for disposal of wastes in the place of their formation and accumulation.

Different organic wastes, including high-toxic and hazardous ones, may be proposed as an object for their processing by the PLAZER process:

- medical — syringes, gloves, bandage materials, organic residues, etc.;
- pesticides and toxic chemicals;
- used plastic utensils and vessels;
- automobile tires;
- timber chips;

- other organic substances.

Mentioned advantages of the PLAZER method allow overcoming shortcomings of other processes and are a reliable base for its entry into the market. The equipment may be used both in Ukraine and for export, because it is needed all over the world. According to preliminary estimation, need of just Ukrainian market in industrial medium productivity (1000 t per year) installations for steam-plasma disposal of organic, including medical and other hazardous (high-toxic) wastes is, approximately, 300–350 units. Needs of European and world markets (taking into account known data on amount of accumulated wastes of health establishments) are practically unlimited.

1. (2003) *Waste of public health institutions: state-of-the-art, problems and ways of their solution*. Ed. by L.P. Zueva. St.-Petersburg.
2. (1989) Basel Convention on control of transfrontier shipment of hazardous waste and their disposal. Final act. In: *Program of UNO on environmental protection*. Geneva.
3. <http://www.ru/rushina.net/ecol>
4. <http://www.asozd.duma.gov.ru/intranet/kom13nsf/1/1B3583664B3140BC3-25BF40041657F?OpenDocument>
5. <http://www.tulane.edu/~greenclb/audit/medwaste.html>
6. Fyodorov, L.A. (1993) *Dioxines as an ecological risk: retrospective review and prospects*. Moscow: Nauka.
7. Paton, B.E., Chernets, A.V., Marinsky, G.S. et al. (2005) Prospects of using plasma technologies for disposal and recycling of medical and other hazardous waste. Part 1. *Advances in Electrometallurgy*, **3**, 49–57.
8. Paton, B.E., Chernets, A.V., Marinsky, G.S. et al. (2005) Prospects of using plasma technologies for disposal and recycling of medical and other hazardous waste. Part 2. *Ibid.*, **4**, 46–53.
9. Hale, K., Liang, W., Liu, P. et al. (2003) Thermal conversion of wastes to hydrogen for fuel cell applications. In: *Startech Environmental Corp. Presentation*, March 31.



NEW FUNCTIONAL MATERIAL — OXIDE CATHODE OF WELDING ELECTRIC ARC Information 2

V.I. LAKOMSKY

E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Typical structures of welding electric arc oxide cathode and forms of existence of oxide cathode chemical components in different zones of solid active insert, liquid emission film, and electric arc atmosphere are presented.

Key words: electric arc, oxide cathode, destoichiometrical oxides, liquid emission film, emission-active additives

Welding arc oxide cathodes are manufactured from powder materials. At the very first ignition of the arc active insert is subjected to the process of sintering under action of heat flow, which enters into the active insert from the cathode spot.

Well compressed in dead hole of water-cooled copper holder powder insert is characterized by high density of physical contacts between separate powder components of the mixture, that's why heat flow heats compressed mass quickly and efficiently. Caused by this heating sintering process is to significant degree similar to the process, which proceeds in self-sintering Soderberg electrodes used in powerful ferroalloy furnaces for more than a century. Hence the name of oxide cathodes, which they received early 1990s — self-sintering thermo-chemical cathodes [1].

Like in Soderberg electrodes, in steady-state oxide cathode sintering process several structural zones are distinctive on semi-microscale. In Figure 1 typical picture of active insert diametric section is given. Three zones of oxide cathode are well seen under binocular microscope at natural illumination and 5–16 fold magnification.

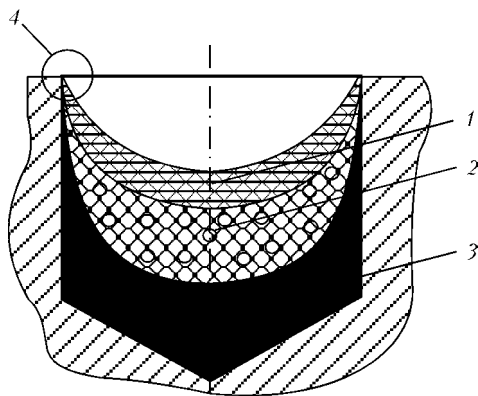


Figure 1. Scheme of arrangement of three zones of oxide cathode active insert: 1 — first; 2 — second; 3 — third zone; 4 — area of simultaneous contact of liquid phase (first zone) with solid phase (third zone) and gas phase (arc atmosphere)

By moving from open surface of the active insert into the depth we may single out the *first zone 1*, which is identified by color, structure, and shape. In general case longitudinal section of the zone has crescent form, because it copies form of the active insert crater.

Usually this zone has grey or dark-grey color and its structure is presented by a homogeneous molten material. It is possible to distinguish in it at high magnification (1000 times and more) two areas with different grain structures. Near very interface of the first zone with gas phase area of fine equiaxial crystals (5–15 μm), having thickness from $1/4$ to $1/3$ of the considered zone thickness, is located. Greater part of the zone is presented by area of columnar comparatively coarse crystals (Figure 2), each of which achieves in diameter 50–60 μm . Boundaries between columnar crystals are thin, their thickness is up to 1 μm , they have brightly saturated light-yellow color against grey background of crystallites. Micro-X-ray diffraction analysis showed that boundaries of crystallites are enriched with barium. Columnar crystals are oriented along the normal to open surface of the emission film.

In liquid state in the process of arc burning the film is homogeneous, it emits into the arc column flow of electrons, which ensures its stable burning.

Such structure of solidified emission film is, in all probability, explained by different rates of solidification of mentioned areas of the first zone after extinguishing of the arc. First thin layer of liquid film, directed at the gas phase, is solidified. Here the highest rate of solidification is registered, that's why grains are the finest in this area. Second area of liquid emission film is solidified at lower rate and columnar crystallites oriented along the normal to the crater profile grow comparatively slowly deep into the insert.

General thickness of the emission film (first zone) on the insert axis is 400–600 μm and does not depend upon the arc current within 300–650 A. Near copper wall of the dead hole width of the first zone gets wedge-like thinner down to 25–50 μm . In Figure 1 position 4 designates the place, in which the first zone

gets in direct contact with the third zone. Here in one point converge solid, liquid, and gas phases of oxide cathode and arc discharge.

Material structure of the first zone is dense, it does not have at mentioned magnification pores, micro-hardness of the zone is rather high and usually achieves 14000–16000 MPa.

Second zone differs from the first one by light-grey color with characteristic light yellowness. Its thickness varies from 1000 to 1200 μm . The zone is arranged in the form of a bent strip of practically the same thickness from one to another wall of the hole. Structure of this zone is also molten and has metal gloss. Rather big number of pores (Figure 3) was detected in this zone, the biggest of which achieves 200 μm in diameter. Shape of the pores is mainly spherical, their edges are smooth, which proves their gas or vapor origin. Exactly in this zone copper component of the active cathode insert transits into gas phase. Structure of the zone etching is multiphase one. Microhardness of the zone is inhomogeneous: from 16000–18000 MPa near first zone to 200–500 MPa near interface with third zone.

Third zone is much darker than the second one, boundary between them is clear (see Figure 3). Third zone has dark red tincture because of copper, which enters into composition of the active insert. At low magnification of microscope the zone is homogeneous, but at magnification above 50 separate components of powder mixture get well distinguishable.

Thickness of the third zone is not stable and by means of the cathode operation it changes from 3000 μm (at first striking of the arc) to zero in case of the cathode resource exhaustion.

Pressure applied for powder compression into the dead hole of copper holder is so high that it causes cold welding of copper particles of the powder mixture with copper walls of the hole. It is very important peculiarity of oxide cathodes, due to which good heat withdrawal from the active insert to copper water-cooled holder is ensured. In oxide cathodes with a compact zirconium insert heat transfer from the insert to the holder is a difficult issue, which explains their comparatively low resource.

Third zone, as well as the second one, is porous. Its general porosity is 4–7 vol.%, size of the pores varies from 5 to 50 μm ; the pores have quite different shapes. Boundaries of pores represent edges of separate particles of powder mixture components. Near contact with the second zone partial sintering of the mixture powder components is detected in case of using alumobarium cathode in the charge.

Temperature distribution over active insert section. Temperature of cathode spot on emission oxide film, consisting of pure de-stoichiometrized zirconium oxide, achieves, approximately, 4000 K [2]. Evidently, in our case because of positive action of barium oxide, which reduces electron work function from emission film, it will be 500 degrees lower. At the bottom of the active insert, in the place of its contact

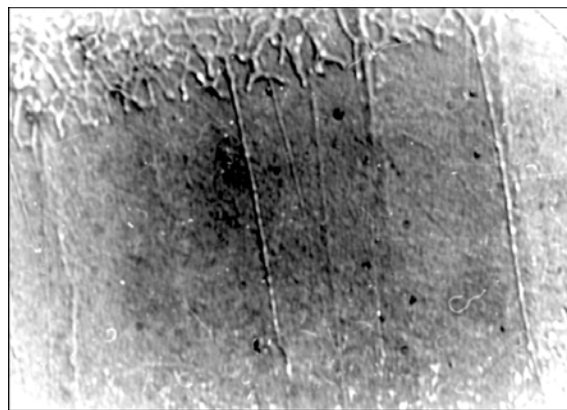


Figure 2. Microstructure of first zone site at boundary between fine- and coarse-grain areas

with copper holder temperature is 413–421 K. So, the lowest temperature gradient, at which heat flow at the beginning of the cathode work is withdrawn from the active insert into copper holder, makes up $\frac{3500 - 421}{5} = 616$ degrees per 1 mm, where 5 is the dead hole depth, mm. Corresponding to this gradient specific heat flow into the dead hole bottom is 213 W/cm. This is minimum value of the flow; into side walls of the hole heat flows are directed, which are several times higher because of lower length of the flow way over the insert body from the place of the cathode spot tie to the wall.

Heat conductivity of the compressed powder mixture in the third zone is rather high due to the copper addition and makes up 0.3 W / (cm·K), which is even higher than a respective index for zirconium in compact state (0.27 W / (cm·K) at 400–500 K).

In the first zone the highest temperature gradient is registered, which makes up $1 \cdot 10^4$ deg / mm [2]. So,



Figure 3. Area of the second zone (light, porous) abutting on third one (dark) ($\times 50$)

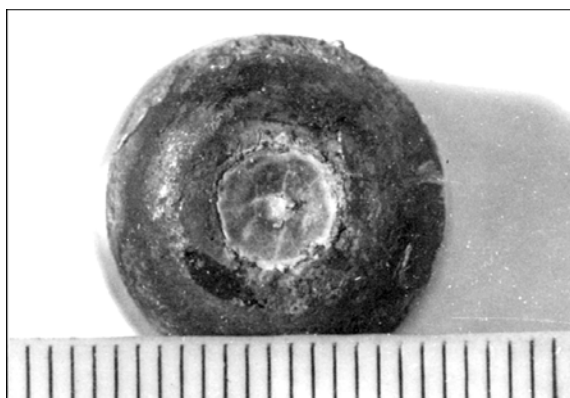


Figure 4. Front view of oxide cathode after arc work ($\times 4.5$)

over the insert axis within liquid emission film temperature varies from 3500 to 2300–2500 K.

In the second zone one order lower temperature gradient is detected (890–900 deg / mm). Temperature over the insert axis is distributed as follows: near the boundary 2300–2500 K, and at the boundary with the first zone — 1400–1430 K.

As far as the third zone is concerned, temperature here reduces from 1400–1430 to 413–421 K. Temperature gradient increases by means of the cathode erosion in the process of burning.

In the method of measuring local temperatures in the oxide cathode third zone we used rigid connection between parameters of elementary lattice βSiC and temperature [3].

For local temperature measuring silicon carbide chips, which were preliminary radiated by a flow of neutrons for their lattice to «swell», are placed into certain places of the active insert third zone. After termination of the cathode operation chips are withdrawn and judgment is made about temperature in the place of their location on the basis of the lattice

parameters. This method is fit for measuring temperature within the range 300–1500 K with error ± 6 deg.

Surface of the emission film on the side of electric arc looks in the same way as in case of purely zirconium cathode — both light and dark areas of the film are present (Figure 4). Place of the arc tie in the crater bottom is usually light, while crater slopes are dark. When inspecting non-etched film at high magnification of the cathode spot, one can see on screen of a scanning microscope granular structure with streaks of eutectics (Figure 5, a). At the same time such structure was not detected on the crater slopes (Figure 5, b).

Oxygen is distributed irregularly in the emission film material and composition of the film significantly differs from stoichiometric one; in addition, in center of the crater in place of the arc column tie oxygen content is somewhat higher than that on the crater slopes (Table).

X-ray diffraction and electron-graphic studies of the emission film showed that in addition to ordered solid solution of barium oxide in compound of zirconium with oxygen in the emission film barium metazirconate was unambiguously detected [4]. This phase, as could be expected, is located over grains of solid solution, where it is displaced as a result of impurity segregation in process of the oxide film solidification and due to manifestation of surface-active properties of barium oxide in the zirconium oxide melt. Coefficient of barium oxide distribution in titanium dioxide (close analogue of zirconium) may achieve 150 [5].

Form of existence of active insert components in three phases. In order to track, in which form are in each of three phases (in solid phase — third zone of active cathode insert; in liquid phase — second and first zones of the insert, and in gas phase — arc discharge atmosphere) oxide cathode components, analysis of behavior of these components in the process of transition from one phase into the other was carried out [4], whereby not just action of temperature, but also of gas-vapor phase was taken into account. Results of this analysis are presented in Figure 6.

Temperature in the third zone is so low, that majority of the third phase components are in solid phase. Exceptions are copper and barium, if the latter is introduced into the oxide cathode charge in the form of rather low-melting alumobarium. As far as during

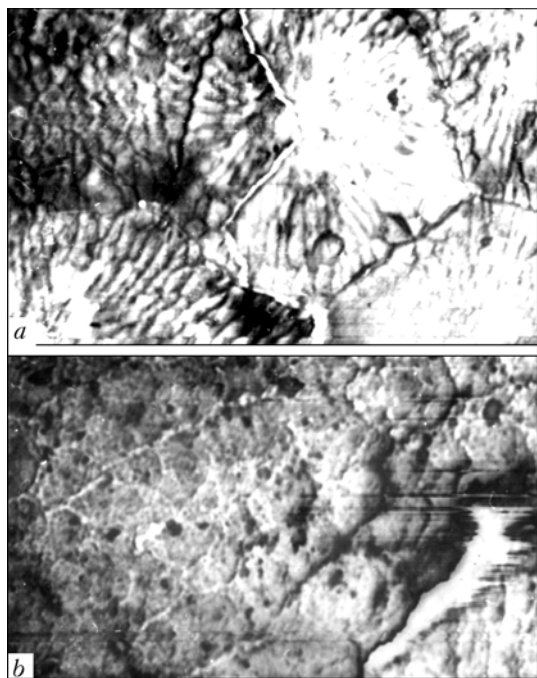


Figure 5. Microstructure of emission film surface in area of arc column tie (a) and on crater slopes (b) ($\times 2300$)

Site of sampling	Weight share of oxygen, %	Stoichiometric coefficient of oxygen $2-x\text{ZrC}_{2-x}$
Crater center (light areas)	23.2	1.72
	19.4	1.37
	15.6	1.05
Crater slopes (dark areas)	14.9	1.00
	14.2	0.92
	8.5	0.53

compression of the powder charge certain amount of air is entrained together with it, it is quite possible that during heating of the insert aluminium and barium are oxidized to Al_2O_3 and BaO .

In second zone charge components are in the form of quasi-homogeneous alloy in liquid state. Solid aluminium and barium oxides transit from third zone into the second one without changes. At increased temperature in the second zone formation of solid zirconium nitride is possible. Copper in this zone transits into gas phase and is evaporated or partially retained in formed by it bubbles.

In the first zone homogeneous oxide alloy of zirconium and barium oxides with a certain share of aluminium oxide are formed as a result of interaction of the charge components. In this alloy barium monozirconate is also formed in liquid phase. Just insignificant amount of solid zirconium nitride, which passed from the second zone, may preserve in oxide melt. Thermo-dynamical analysis shows that probability of ZrN formation from the air nitrogen is rather low in comparison with formation of Al_2O_3 . High temperature of the first zone and electrolysis of the oxide melt cause disturbance of stoichiometry of oxides both in liquid solution BaO in ZrO_2 and in liquid chemical compound BaZrO_3 .

Zirconium dioxide transits into the gas phase, which is equilibrium with oxide melt of the first zone, with partial dissociation and formation of ZrO and O , and Al_2O_3 with formation of AlO , Al_2O , Al , and O . Barium oxide, in its turn, disintegrates into Ba and O .

If we take into account that air in the arc column at comparatively low temperatures, which is peculiar for arc discharge with oxide cathode, will be present in the form of completely dissociated oxygen and partially dissociated nitrogen, N_2 , N and O have to be added to the gas atmosphere. Copper practically does not change its composition when transiting into the gas phase, just certain aggregation of separated particles is possible [6].

By means of missile technology development thermodynamics of high-temperature oxide systems was thoroughly studied and presented in known publications JANAF Tables as well as in [7]. Results of calculation of partial pressures of the gas phase separate components are presented in [8].

So, gas phase above emission film of the cathode represents a multi-component system similar to the one presented in Figure 6.

Barium compounds in the emission film reduce electron work function from oxide cathode and thus

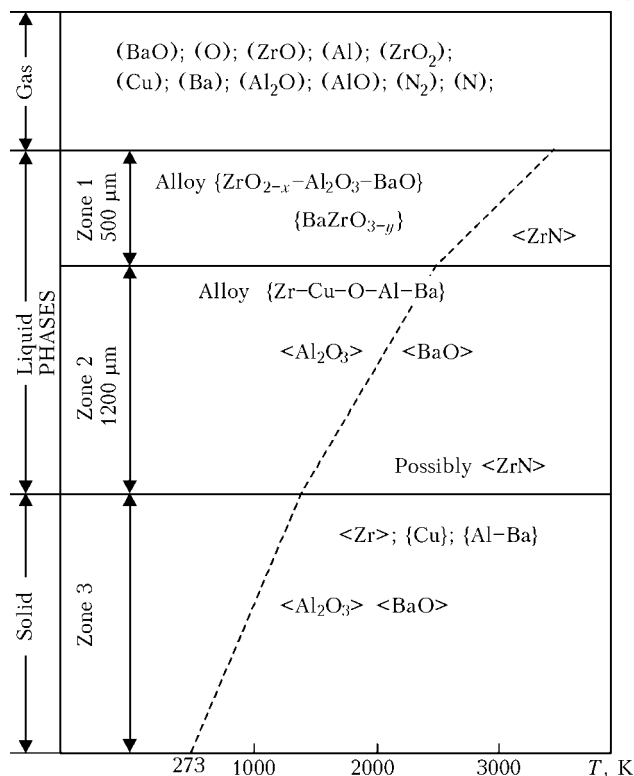


Figure 6. Scheme of temperature distribution (dash line) and forms of existence of oxide cathode chemical components in process of arc discharge work: corner brackets — solid, curly brackets — liquid, and parentheses — gas-vapor phases

increase thermal coefficient of efficiency of the arc, which acts as converter of electric energy into heat one. Voltaic equivalent in these cathodes does not exceed 2 V, and presence of barium in the arc atmosphere increases stability of the arc discharge burning and reduces gradient of electric voltage in the arc column.

1. Lakomsky, V.I., Taran, A.Ya. (1990) Structure and composition of emission film of self-sintering thermochemical cathodes. *Avtomatch. Svarka*, **8**, 23–27.
2. Zhukov, M.F., Kozlov, N.P., Pustogarov, A.V. et al. (1982) *Near-electrode processes in arc discharges*. Novosibirsk: Nauka.
3. Nikolaenko, V.A., Karpukhin, V.I. (1986) *Measurements of temperature using the irradiated materials*. Moscow: Energoatomizdat.
4. Lakomsky, V.I. (1997) *Oxide cathodes of electric arc*. Zaporozhie: Internal.
5. Leonov, A.I., Kostikov, Yu.P., Strykanov, V.S. (1988) Influence of surface microstructures on physical-chemical properties of oxides. *Uspekhi Khimii*, **57**(8), 1233–1252.
6. Suvorov, A.V. (1970) *Thermodynamical chemistry of vaporous state*. Leningrad: Khimiya.
7. Kulikov, I.S. (1966) *Thermal dissociation of compounds*. Moscow: Metallurgiya.
8. Lakomsky, V.I., Taran, A.Ya. (1990) On composition of gas-vapor phase on the thermochemical cathode surface. *Avtomatch. Svarka*, **8**, 20–23.



THESES FOR A SCIENTIFIC DEGREE



Rudoj Yu.E. Development of Gradient Thermal Barrier Coatings and Electron Beam Technology for Deposition thereof on Gas Turbine Blades

Thesis for scientific degree of candidate of technical sciences in speciality «Metallurgy of high-purity metals and special alloys».

E.O. Paton Electric Welding Institute of the NAS of Ukraine, Kiev 2005. Date of the thesis defending is 1st of March 2006.

Conditions of deposition of the thermal barrier coating on substrate with a gradient of chemical composition and structure over its thickness with outer ceramic layer, which include electron beam heating and evaporation of a mixture of metals (alloys) and oxides (in the form of a compressed pallet, located on end of a ceramic ingot from stabilized zirconium dioxide), having different pressure of vapor at evaporation temperature, are determined.

Structure and functional properties of gradient thermal barrier coatings metal–ceramics with a transition zone on bases of the Al–ZrO₂(Y₂O₃), Al–Pt–ZrO₂(Y₂O₃) and Al–Y–ZrO₂(Y₂O₃) systems, produced by a single-stage process of application, are investigated. Possibility of regulating structure of gradient coatings by means of chemical composition change of the mixtures being evaporated is shown. Optimization of chemical composition of a pallet being evaporated allows producing a long-lasting gradient thermal barrier coating with long thermal-cycle working life in air.

Regularities of chemical composition and structure change of transitional zones metal–ceramics of deposited gradient coatings as a function of the deposition process technological parameters are studied.

The mechanism of formation of gradient structures produced by electron beam evaporation of the zirconium dioxide based composite ceramic ingot is considered. Results of investigations of chemical composition, structure and properties of recommended thermal barrier gradient coatings NiCoCrAlY + AlCr / ZrO₂(7Y₂O₃) and Me_xC_y + NiAl / ZrO₂(7Y₂O₃) deposited from vapor phase on surface of high-temperature alloys are presented.

Single-stage electron beam technology based on evaporation of a composite ceramic ingot allows depositing gradient thermal barrier coatings on gas turbine blades with higher level of reliability and longer service life and at lower cost in comparison with existing multi-stage technological processes of producing thermal barrier coatings.



Teslevich S.M. New Technologies and Equipment for Producing Titanium Sponge and its Remelting into the Ingot

Thesis for scientific degree of candidate of technical sciences in speciality «Metallurgy of high-purity metals and special alloys».

E.O. Paton Electric Welding Institute of the NAS of Ukraine, Kiev 2006. Date of the thesis defending is 15th of March 2006.

Issues of improving quality of spongy titanium and its remelting, as well as development of principally new installation for production of spongy titanium with cycle output 3.8 t are considered in the thesis.

Methodology of multiple increase of the reaction rate of titanium reduction from its tetrachloride by magnesium on a periodically renovated surface of Ti-containing melt is developed.

Temperature parameters for unconstrained transportation of the products of titanium reduction reaction over steam conduit from the reduction retort into the condenser-retort are determined.

On the basis of a complex of heat engineering and engineering-technological investigations new technologies for reduction of titanium from titanium tetrachloride by magnesium and vacuum separation of formed in the process of the reduction reaction mass with production of spongy titanium of the highest grades have been developed for the new apparatus.

Comprehensive investigations of the technology for production of high-quality spongy titanium on laboratory and pilot installations have been carried out. Conditions of controlled removal of residual chlorine in vacuum separation of spongy titanium are determined. Experimental check of distribution of impurity elements over volume of the spongy titanium block, having mass up to 3.8 t, is carried out.

Special specimens are prepared, containing 0.08–0.45 wt.% of residual chlorine, to be subjected to remelting in induction and plasma-arc furnaces. The investigations showed that hydrogen and moisture are present in gas phase. Correlation dependence between increase of residual chlorine content in spongy titanium and amount of hydrogen in gas phase above the melt is established. It is shown that content of hydrogen in metal in induction melting exceeds the equilibrium one 1.2–1.3 times.

For the first time technology for melting ingots from spongy titanium with increased (0.08–0.45 wt.%) content of chlorine, which includes first remelting of spongy titanium in an induction furnace with a sectional mould, due to which excessive chlorine is removed. Second remelting may be performed in vacuum-arc, electron-beam or plasma-arc furnaces for reducing content of hydrogen down to the level required by GOST 19807–91.

Spongy titanium of new quality, produced in super-size apparatuses for reduction and separation, was remolten in the VD-11 vacuum-arc furnace. Ingots of 5 t mass and 780 mm diameter, which meet requirements of standards for the alloy of VT1-0 grade, were manufactured.

In addition to development of commercial production of ingots from spongy titanium of new quality, experiments, connected with manufacturing of shaped titanium castings using a combined consumable electrode, consisting of two pressed and one cast billet in renovated foundry skull furnaces with non-water-cooled titanium crucible of new design, were carried out.