INVESTIGATION OF THERMOCHEMICAL CHARACTERISTICS OF MIXTURES OF DISPERSED MATERIALS BY DIFFERENTIAL THERMAL ANALYSIS METHODS*

V.N. SHLEPAKOV and **A.S. KOTELCHUK**
E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

It is shown that formation of melts as early as at a stage of heating of the powder core up to melting of the sheath of a flux-cored wire and evolution of the gaseous products (H_2O, CO_2, SiF_4) determine shielding functions of an electrode material and exert a substantial effect on the course of metal to gas interaction reactions at the drop and pool stages. Temperature ranges of thermochemical reactions accompanying the heating process overlap, and their thermal effects superimpose on one another, thus stimulating development of some processes and slowing down the other ones. Control of these reactions by varying composition of a mixture allows regulation of the rate of melting of the core to achieve favourable characteristics of melting of the flux-cored wire and transfer of the electrode metal into the weld pool.

Keywords: *electric arc welding, flux-cored wire, core composition, thermochemical processes, thermal analysis, thermogravimetry, differential scanning calorimetry*

The flux-cored wire sheath or electrode rod is heated during welding primarily due to the heat released by the electric current flow and heat of the active spot of the welding arc. In this case a temperature field close to the quasi-steady one is formed at the extension (region of the wire ranging from the contact tube or holder to the arc) [1–3]. As shown by the earlier calculations [3], the electrode rod or flux-cored wire sheath can be heated at the extension to a temperature above 1000 °C. The powder composite of the wire core or electrode covering at a high melting rate is heated mostly due to the heat transferred from the arc and, to a lesser degree, from the rod or sheath. As thermal conductivity of the powder composite is dozens of times lower than that of metal, at high melting rates the heat transferred to the electrode wire tip from the arc propagates to a considerably smaller distance [3]. This allows the flux-cored wire core or electrode covering to be modelled as an infinite-length cylinder (solid or hollow) heated from the surface (external or internal) and tip to make corresponding calculations [1, 3]. However, practical application of the calculations for estimation of the extent of the reactions developing in the powder composite is hampered by the need to find relationships and coefficients that are also determined by the extent of development of the reactions. Therefore, physical modelling is a well justified approach for experimental estimation of development of the processes of evaporation, dissociation, thermal destruction and oxidation of components of the flux-cored wire core or electrode covering, which accompany heating and melting of the powder composites during welding [4–6].

The above processes can be successfully studied by the methods and procedures of thermal analysis of powder materials and composites: differential thermal analysis, thermogravimetric (TG) analysis, differential thermogravimetric analysis and differential scanning calorimetry (DSC) [1, 2, 5, 6]. These methods of thermal analysis are supplemented by mass-spectral analysis of the gas phase formed in heating and melting of the materials investigated.

Investigation procedure. Complex thermal analysis for the solid, liquid and gas phases allows investigation of reactions of the following types (the «prime» mark means allotropic transformation):

$$A_s \leftrightarrow A'_s; \quad A_s \rightarrow A_l; \quad A_s \rightarrow A_g, \tag{1}$$

$$A_s + B_g \leftrightarrow C_s; \quad A_s + B_g \leftrightarrow C_g, \tag{2}$$

$$A_s \rightarrow B_s + C_g; \quad A_l \rightarrow B_l + C_g, \tag{3}$$

$$A_s + B_s \leftrightarrow C_s + D_g; \quad A_s + B_g \rightarrow C_s + D_g. \tag{4}$$

Equations (1) through (4) are well suited to describe the processes of evaporation, oxidation, dissociation and reduction, as well as other phase transformations characteristic of the welding processes [1, 2]. Investigations of such processes were carried out by using thermoanalyser TGA/DSC Q600 STD (TA Instruments, USA) combined with mass-spectrometer VG Prolab (Thermo Scientific Fisher, Great Britain) (Figure 1). Thermoanalyser TGA/DSC Q600 STD is an analytical instrument allowing simultaneous investigations by the DSC and TG methods. It is used to measure the heat flow and mass variations that accompany phase transformations and reactions in the

---

*Based on the paper presented at the VI International Conference on Welding Consumables of the CIS Countries «Welding Consumables. Development. Technology. Production. Quality. Competitiveness» (Krasnodar, 2011), P. 91–97.

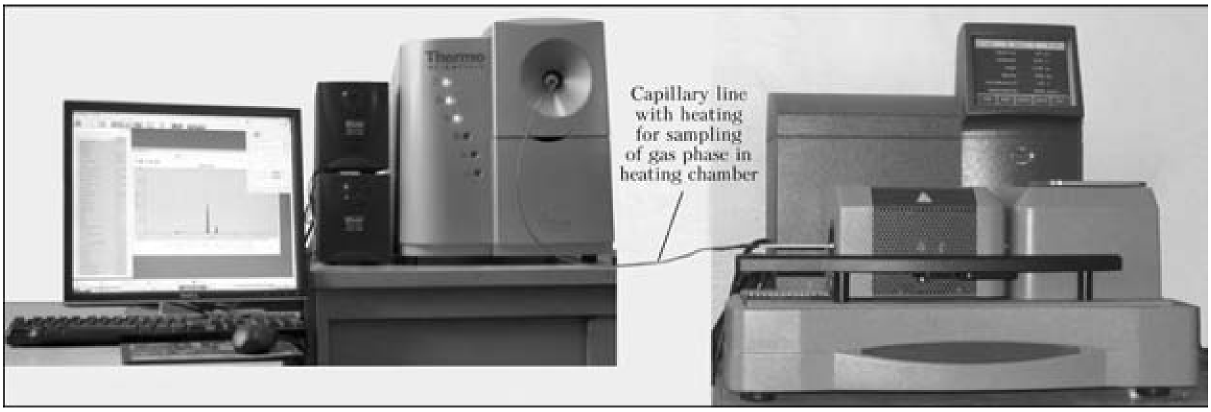

Figure 1. Thermoanalyser TGA/DSC Q600 STD (*to the right*) combined with mass-spectrometer VG Prolab (*to the left*) for monitoring and analysis of gas phase composition in heating chamber

materials investigated. The data obtained enable distinguishing the endothermic and exothermic processes that do not lead to changes in mass (e.g. melting and solidification) from the processes of interaction with the gas phase that cause a change in mass of a sample (e.g. dissociation or oxidation). Simultaneous calorimetric and thermogravimetric analyses of the same sample make it possible to decrease the experimental and sampling errors.

Specifications of thermoanalyser TGA/DSC Q600 STD, as well as of the employed crucibles, scales, heating chamber and purging gases are given below [7]:

Thermocouples	platinum-platinum + 13 % rhodium, type R
Temperature range for investigations, °C	5–1500
Heating rate, °C/min	up to 100 (to 1000 °C) up to 25 (to 1500 °C)
Type of crucibles	platinum, ceramic (Al_2O_3)
Capacity of crucibles	platinum: 40 and 110 μl aluminium oxide: 40 and 90 μl
Accuracy of measurements of heat flow (DSC) for pure metals, %	≤ ±2
Frequency of measurements of heat flow (DSC) for pure metals, %	≤ ±2
Accuracy of measurements of temperature for pure metals, °C	±1
Frequency of measurements of temperature for pure metals, °C	±0.5
Sensitivity to temperature difference (DTA), %	0.001 (200–1300)
Sensitivity in determination of mass, μg	0.1
Mass measurement accuracy, %	±1
Primary purging gases	He, N_2, air, Ar
Primary purging gas flow rate, ml/min	20–1000
Secondary purging gases	O_2, air, CO, CO_2, N_2, He, Ar
Secondary purging gas flow rate, ml/min	10–100

The secondary purging system is intended to provide the low concentration of a reagent gas fed to the chamber with a sample. The gas flow rate is set by the control computer and adjusted by the flow meter, which also provides a switch-over of gases [7].

Experimental investigations by using the thermoanalyser are carried out by one common scheme, which includes selection of modes and signals for registration, setting of gas flow rates for primary and secondary purging, setting of temperature conditions for an experiment, selection and mounting of empty crucibles on arms of microscales, calibration of a mass signal, weighing of the required amount of a sample, closing of the heating chamber, starting up of the experiment, removal of the sample remainders after the experiment, and processing and analysis of the data obtained. Most of the operations are performed by using control software of the external control computer. To achieve the required accuracy, the instrument is preliminarily calibrated by the signals of mass, temperature, heat flow and difference in temperatures of the sample and standard.

Composition of the gas phase in the thermoanalyser heating chamber is monitored by using quadrupole mass-spectrometer VG Prolab, the system of which is designed to analyse gases under a pressure close to the atmospheric one (from 100 to 1500 mbar) and a low flow rate (not higher than 20 ml/min) [8]. Sampling of gas is done by using a quartz capillary line with heating. The frequency of analysis of samples is up to 1 ms, the mass of fixed ions being up to 300 amu. The mass-spectrometer comprises a closed contamination-resistant ion source, the sensitivity of which is not lower than $5 \cdot 10^{-5}$ A/Torr (for nitrogen using the Faraday detector). The limit of detection by using the Faraday detector is not lower than 10^{-5}, and that by using the electronic multiplier is not lower than 10^{-6} [8]. The software package for control of the mass-spectrometer and processing of its data contains the library of spectra to ensure quality analysis of an unknown composition of the gas phase.

Investigation of thermochemical processes in heating and melting of mixtures by an example of compositions of flux-cored wire cores. Objects for our investigations were powder composites, the compositions of which corresponded to two types of self-shielding flux-cored wires: having cores of the fluoride-oxide (system $MgO-BaF_2-LiF$) and carbonate-fluorite ($CaCO_3-CaF_2-Li_2O \cdot TiO_2-CaO \cdot SiO_2$) types with the oxidising and alloying system on the Al–Mn–Ni–Zr base. Properties of such composites were studied on samples with a mass of 20.0±0.2 mg placed

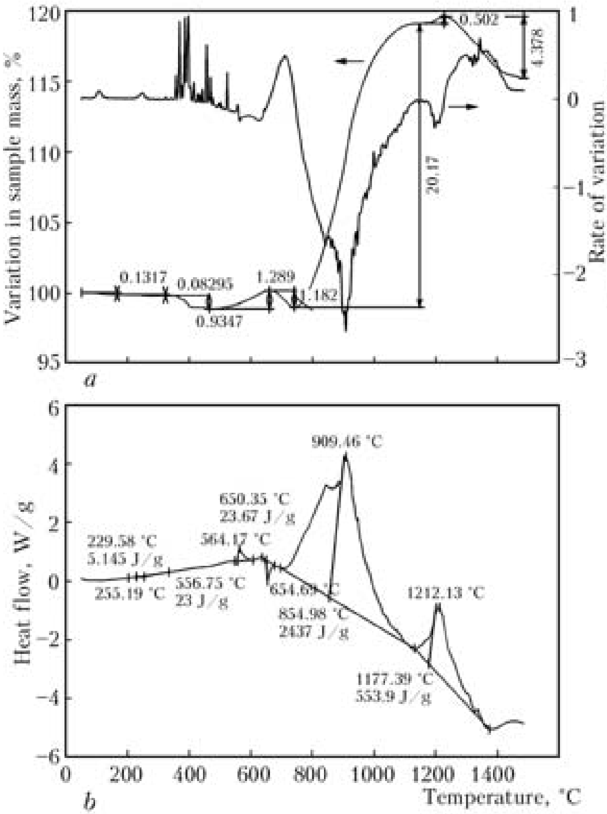

Figure 2. Results of analysis of a sample of flux-cored wire charge of the carbonate-fluorite type by the TG (*a*) and DSC (*b*) methods

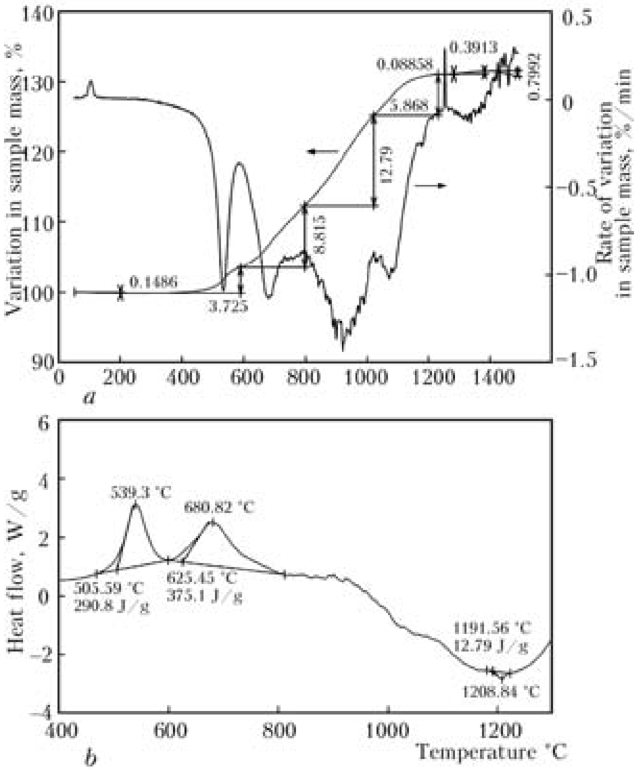

Figure 3. Results of analysis of a sample of flux-cored wire charge of the oxide-fluoride type by the TG (*a*) and DSC (*b*) methods

in aluminium oxide crucibles during dynamic heating to 1500 °C in air at its flow rate of 100 ml/min.

Figure 2, *a* shows typical results of TG analysis of the flux-cored wire charge of the carbonate-fluorite type containing calcium, magnesium and sodium carbonates, as well as sodium hexafluosilicate. Characteristic ranges of removal of absorbed moisture at a temperature of approximately up to 150 °C, thermal dissociation of sodium hexafluosilicate to evolve SiF_4 in a temperature range of 380–450 °C and that of carbonates (700–1450 °C) to evolve CO_2 can be seen in the sample mass variation curve. Evolution of the said gases was confirmed by mass-spectral monitoring of composition of the gas phase in the heating chamber. At a temperature above 450 °C the processes of thermal destruction to evolve gaseous products were superimposed by a growth of mass of a sample due to development of oxidation of the iron powder, ferroalloys and alloying components. Upon reaching a temperature of 700 °C the increase in mass of the sample was replaced by its decrease, and the intensity of current of the carbon dioxide ions increased in the mass spectrometer, this evidencing the intensification of thermal destruction of the carbonates.

Figure 2, *b* shows results of analysis of the same charge sample by the DSC method and calculations of the total thermal effects of the overlapping reactions. The process of heating of the carbonate-fluorite type mixtures was accompanied by the exothermic effects of a low intensity in a temperature range of 600–800 °C. Further heating was accompanied by alternation of the exothermic and endothermic effects, from which it is possible to determine the simultaneous course of the processes of destruction of mineral components and oxidation of metallic components. Concerning self-shielding flux-cored wires of the carbonate-fluorite type, the experimental investigations, the results of which are presented in study [9], made it possible to establish that the highest efficiency of the gas shielding is provided by using compositions of the core for which the gas evolution processes extend from 400 °C to the melting temperature of steel. In other words, the strongest gas shielding is formed in welding using wires with the cores that generate shielding gases at all stages of their heating and melting.

Figure 3, *a* shows typical results obtained by the method of TG analysis of the flux-cored wire charge of the oxide-fluoride type containing aluminium-base master alloys (in particular, Al·Li and Al·Mg master alloys), and Figure 3, *b* shows results of analysis of the same sample by the DSC method and calculation of the total thermal effects of the reactions.

The process of heating of the flux-cored wire charge of the oxide-fluoride type was characterised by the exothermic effects at temperatures of about 600 and 800 °C, as well as by a much higher intensity compared to the wire charge of the carbonate-fluorite type, which were accompanied by increase in mass of a sample and decrease in the content of oxygen in the gas phase of the heating chamber, this being indicative of the processes of oxidation of the aluminium and magnesium powders, iron powder and ferroalloys. The slag melt was formed at a temperature close to 1200 °C. This was accompanied by a marked exothermic effect reaching its maximum at the said temperature.

Discussion of results and conclusions. Investigations of physical-chemical properties of powder materials and their mixtures modelling the flux-cored wire core, which were carried out by the methods of complex thermal analysis and mass-spectroscopy of the gas phase in dynamic heating from 30 to 1500 °C, make it possible to establish the temperature ranges, extent of development and consumption of heat for the reactions of thermal destructions to evolve gases, oxidation of components, and melting of mixtures to form the primary melt of the metal and slag phases. Formation of the melts as early as at a stage of heating of the powder core up to melting of the wire sheath and evolution of the gaseous products (H_2O, CO_2, SiF_4) determine shielding functions of the electrode material and exert a substantial impact on the course of the metal to gas interaction reactions at the drop and pool stages. Temperature ranges of the thermochemical reactions (endothermic processes of removal of moisture, destruction and melting, and exothermic processes of oxidation and complex formation) accompanying the heating process overlap, and their thermal effects superimpose on one another, thus stimulating development of some processes and slowing down of the other ones. Therefore, control of these reactions by varying composition of a mixture allows regulation of the rate of melting of the core to achieve favourable characteristics of melting of the flux-cored wire and transfer of the electrode metal to the weld pool. Values of the heat flow in heating of powder composites enable estimation of the consumption of heat for their heating and melting, allowing for the mutual effect of the exothermic and endothermic reactions occurring in the material investigated.

1. Pokhodnya, I.K., Suptel, A.M., Shlepakov, V.N. (1972) *Flux-cored wire welding*. Kiev: Naukova Dumka.
2. Pokhodnya, I.K., Yavdoshchin, I.R., Paltsevich, A.P. et al. (2004) *Metallurgy of arc welding: interaction of metal with gases*. Ed. by I.K. Pokhodnya. Kiev: Naukova Dumka.
3. Erokhin, A.A. (1973) *Principles of fusion welding. Physical-chemical mechanisms*. Moscow: Nauka.
4. Killing, R. (1980) Welding with self-shielded wires — the mechanism of shielding and droplet transfer. *Metal Constr.*, 12(**9**), 433–436.
5. Shlepakov, V.N. (1990) *Kinetics of processes of interaction between metal and gases in flux-cored wire welding*. Kiev: Naukova Dumka.
6. Shlepakov, V.N., Suprun, S.A., Kotelchuk, A.S. (1987) Kinetics of gas generation in flux-cored wire welding. *IIW Doc. XII-1046–87*.
7. (2003) *Combined DSC-TGA Q600*: User's manual. Moscow: Intertech Corp.
8. (2008) Prolab: Operation manual. *Thermo Sci., Ion Path*, Issue 7, July.
9. Shlepakov, V.N., Suprun, S.A., Kotelchuk, A.S. (1990) Estimating of the characteristics of flux-cored wire welding under the wind flow effect. In: *Proc. of Int. Conf. on Welding under Extreme Conditions* (Helsinki, Sept. 4–5, 1989). Oxford; New York: Pergamon Press, 171–179.

CONTROL OF PROPERTIES OF THE WELD METAL BY REGULATING THE LEVEL OF OXIDATION OF THE WELD POOL IN GAS-SHIELDED WELDING

S.T. RIMSKY
E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Activity of oxygen dissolved in the weld pool metal was determined directly in the process of welding of low-alloy steel in the oxidising shielding gas atmosphere by using the electrochemical method. Prediction of mechanical properties of the weld metal depending on the activity of oxygen in molten metal and welding heat input was substantiated.

Keywords: *arc welding, consumable electrode, oxidising shielding gases, weld pool, electrochemical method, oxygen activity, heat input, weld metal, structure and mechanical properties*

Structure and properties of the weld metal on low-alloy steels are known to depend to a considerable degree on its oxygen content [1, 2]. Oxygen contained in molten metal of the drops and weld pool in arc welding of steel in oxidising shielding gases may be in different states: in a dissolved or chemically combined state in the form of suspended particles of oxides and complex inclusions. Metal-soluble oxygen $[O]_s$ or oxygen activity a_o determines the course of the processes of deoxidation, refining and secondary oxidation and affects the final composition of the weld metal, its structure formation and properties.

The methods applied in practice for analysis of the oxygen content of the weld metal allow evaluation of its total concentration, i.e. the total content of oxygen $[O]_t$, both active and combined into chemical compounds. It takes several hours to perform this operation, including sampling, preparation of a sample, its transportation to a laboratory and analysis by the vacuum melting method.

At the same time, large-scale metallurgy uses to an increasing extent the method of evaluation of the activity of oxygen in iron-based melts, which consists in measuring the electromotive force (emf) generated in a concentration cell based on solid oxide electrolyte