THERMODYNAMIC ANALYSIS OF SLAG MELTS IN MANUFACTURE OF FUSED WELDING FLUXES

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Applicability of equilibrium thermodynamic laws for analysis of physico-chemical reactions was established proceeding from analysis of temperature-time conditions of melting of welding fluxes in arc and open gas furnaces. Thermodynamic analysis of reactions of charge components used in welding flux manufacture was conducted. Techniques to control the process of slag melt refining are determined.

Keywords: *fused welding fluxes, slag melt, sulphur, phosphorus, thermodynamic analysis*

Ukraine today is a leading manufacturer of fused welding fluxes. Such leading scientists as E.O. Paton, K.V. Lyubavsky, B.E. Paton, V.I. Dyatlov, I.I. Frumin, V.V. Podgaetsky, I.K. Pokhodnya and many others participated in development of flux compositions and their manufacturing technology. In connection with depletion of deposits of mineral raw materials traditionally applied in fused flux manufacture, the problem of ensuring the required flux composition and their quality, respectively, became much more acute.

Conducted analysis of charge materials showed that in most of the cases the content of impurities in them is specified by the normative documents (GOST, DSTU, TU). Technical documentation predominantly specifies the content of the main component in the raw material, and in a number of cases does not limit the content of impurities — sulphur, phosphorus, and iron oxides. At the same time, their content in the fluxes is limited. On the other hand, statistical data of incoming inspection of the raw materials are indicative of wide ranges of variation of their impurity content.

The most contaminated are manganese ore and fluorospar concentrates, in which sulphur and phosphorus content reaches 0.3 % in some cases. These materials make up almost half of the charge in manufacture of the most widely accepted fluxes of AN-348-A, OSTs-45 grades. Therefore, it is possible to keep their sulphur and phosphorus content only at the upper admissible level by the technical requirements. Forced application of low-grade ore materials leads to increase of the amount of impurities contributed by them to the melt that in its turn reduces the technological margin on impurities in flux melting.

Therefore, work on investigation of processes running in flux-meting furnaces is urgent for development of recommendations on lowering the impurities in the slag melt.

Fused welding fluxes are made in open gas and arc furnaces [1]. These melting units differ by temperature conditions, lining type, volume, mixing conditions and time of slag melt existence. For open gas furnaces these are: up to 1450 °C temperature, up to 60 t melt volume, and up to 6 h melting time. In the case of arc furnaces slag melt temperature is higher on average and can reach 1800–1900 °C. Melt volume for various types of furnaces can be in the range from 50 kg up to 5 t, and melting time is from 1 up to 2 h. Intensive processes of slag melt mixing proceed in arc furnaces under the impact of the magnetic field and temperature gradient. Thus, equilibrium conditions are in place in both the cases, which are characterized by long-time existence of the melt, large volume and uniformity in local melting regions. All that allows applying the principles and laws of chemical equilibrium thermodynamics for assessment of physico-chemical processes in flux-melting furnaces.

In the general case the melting space of a furnace can be regarded as a closed thermodynamic system that is related to features of mass exchange with the environment. In flux melting by a traditional schematic, uniformly blended charge is fed into the furnace and, as a rule, there is no further adding of charge components to the furnace volume. Mass transfer can be performed only as a result of gas removal from the melting space and transition of compounds from slag into the metal phase.

Melting space, in which charge material components are present in the form of solid and partially molten particles of the slag melt, shot iron and lining, is a heterogeneous system. To perform analysis of such a complex heterogeneous thermodynamic system, the melting space should be separated into certain homogeneous systems (zones), in which chemical reactions will be considered. Zone interaction is performed through interfaces. It is understandable that such a division is conditional, and does not reflect all the diversity of high-temperature processes in the furnace melting space, in particular, kinetics of slag melt homogenizing, hydrodynamic conditions of its existence, process of gas removal from the melt and impact of the electromagnetic field (in flux melting in electric arc furnaces).

Traditionally [2] the process of flux melting is divided into three stages: reaction in the solid state, flux formation and slag melt homogenizing. As a result, the following phases can be singled out in the flux volume:

- solid, in which thermal dissociation and interaction of charge particles take place;
- partially molten dispersed solid-liquid phase, arising as a result of charge heating, eutectic and contact melting;
- slag melt with a certain degree of homogenizing;
- metallic phase (shot iron) forming as a result of chemical reactions in the slag melt;
- gas phase forming as a result of thermal dissociation of charge components and chemical reactions with formation of gaseous products, which float to the slag melt surface in the form of bubbles.

Interfaces are well developed, rather blurred, particularly in the presence of dispersed particles at the beginning of slag melt formation. A certain temperature interval corresponds to each phase in flux manufacture.

The objective of this work was analysis of thermodynamic probability of chemical reaction running in the flux-melting furnace volume, and precising the mechanism of sulphur and phosphorus removal from the slag melt to lower the content of these impurities in the finished flux composition. A characteristic of the probability of reaction running was dependence of Gibbs energy ΔG on temperature. In metallurgy in most of the cases a simplified Gibbs equation is used, which allows for the change of enthalpy and entropy of the reaction, depending on temperature. Heat capacity of initial materials and reaction products in this case is neglected. This is related to the fact that heat capacity contribution to ΔG value at up to 800–1000 K temperatures is negligible. At temperature rise heat capacity value rises by a logarithmic dependence, and it can change the heat capacity of elements 2 times. One of the calculation methods of allowing for the change of heat capacity value, depending on temperature, is application of Uhlich function

$$M_0 = \ln \frac{T}{298.15} + \frac{298.15}{T} - 1. \tag{1}$$

As a result, equation for calculation of the change of Gibbs energy becomes

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - \Delta Cp_{298}^0\, TM_0, \tag{2}$$

where

$$\Delta H_{298}^0 = \sum H_{298\ \mathrm{prod}}^0 - \sum H_{298\ \mathrm{in}}^0; \tag{3}$$

$$\Delta S_{298}^0 = \sum S_{298\ \mathrm{prod}}^0 - \sum S_{298\ \mathrm{in}}^0; \tag{4}$$

$$\Delta Cp_{298}^0 = \sum \Delta Cp_{298\ \mathrm{prod}}^0 - \sum \Delta Cp_{298\ \mathrm{in}}^0; \tag{5}$$

ΔH_{298}^0, ΔS_{298}^0, ΔCp_{298}^0 is the variation of values of thermodynamic characteristic functions of the participants (products and initial materials) of the chemical reaction under standard thermodynamic conditions (at temperature of 298 K and atmospheric pressure of 1 atm ($9.80665 \cdot 10^4$ Pa)).

One of the main problems, arising during thermodynamic metallurgical calculations, is finding the values of enthalpy, entropy and heat capacity of the initial materials and reaction products. Unfortunately, the most fundamental works [3, 4] do not include the data on complex compounds, so that we assumed them on the basis of processing the experimental equations, used in metallurgical calculations [5].

In manufacture of fused welding fluxes for steel welding, the most often used raw materials are manganese ore concentrates, quartz sand, alumina, periclase powders, lime, marble, fluorite, fluorspar, rutile, zirconium concentrates, etc., which contain such chemical compounds as SiO_2, MnO_2, Mn_2O_3, MnO, Fe_2O_3, CaO_3, $MgCO_3$, TiO_2, FeS_2, MnS, Mn_nP, CaF_2, P_2O_5, $Ca_5(PO_4)_3(F, Cl, OH)$. In ores phosphorus is mostly present in the form of phosphorus-calcium salt, included into the composition of apatite minerals [6]. In addition, material of the electrodes and lining — carbon (for arc furnaces) and firebrick (for open gas furnaces) — will participate in the interaction reactions.

At consideration of the first stage, analysis of chemical reactions in the solid state — gaseous compounds formation and removal — is traditionally performed. This is exactly the stage at which melting of the flux charge proceeds, i.e. charge transition from the solid into the liquid state. The charge, which later on forms the slag melt, is first present in the form of separate components, the melting temperature of which is much higher than that of the melting space. The charge melting process proceeds at the expense of contact melting of charge particles with simultaneous thermal dissociation of carbonates and higher oxides.

In the contacting surfaces of flux charge particles interdiffusion takes place, which results in formation of a eutectic layer and contact melting at temperatures below the melting temperature of individual charge materials. This results in formation of partially molten dispersed phase, which promotes further charge melting at melting space temperatures, and flux forming process takes place. The lowest-melting eutectics can form as a result of contact interaction of flux charge particles already at temperatures of 900–1100 °C [7, 8].

Processes of thermal dissociation of charge components are accompanied by intensive gas evolution, thus leading to increase of charge melting rate due to mixing of the forming liquid phase. It should be noted that formation of gaseous compounds should influence the kinetic features of charge material interaction, and can change the concentrational conditions of the reactions between the components in the solid and semi-liquid state.

At the first stage reactions of carbonate decomposition with carbon dioxide gas evolution, as well as reduction of higher manganese oxides (Figure 1, *a*) with formation of gaseous oxygen, take place. Manganese, calcium and magnesium sulphides do not decompose (Figure 1, *b*). Interaction of oxygen with sulphides results in appearance of gaseous sulphur oxide SO_2, which is removed from the melting space (Figure 2, *a*). Therefore, it is believed that for maximum removal of sulphur at the first stage of melting it is necessary to create oxidizing conditions, which can be formed due to dissociation of higher oxides, for instance MnO_2 (see Figure 1, *a*). Besides oxygen, sulphur can be removed from the compounds as a result of interaction of calcium sulphide with higher manganese oxide (Figure 2, *a*).

Manganese phosphides can decompose with formation of solid and gaseous phosphorus (see Figure 1, *b*). The thus formed manganese can here interact with phosphorus oxide also with formation of solid and gaseous phosphorus, which can also be reduced by other metals, for instance, silicon (Figure 2, *b*). However, their presence at the first stage of melting is improbable. Reaction of phosphorus oxidation at interaction with silicon oxide is more probable. Reduction of phosphorus oxide by iron at this melting stage is improbable (see Figure 2, *b*).

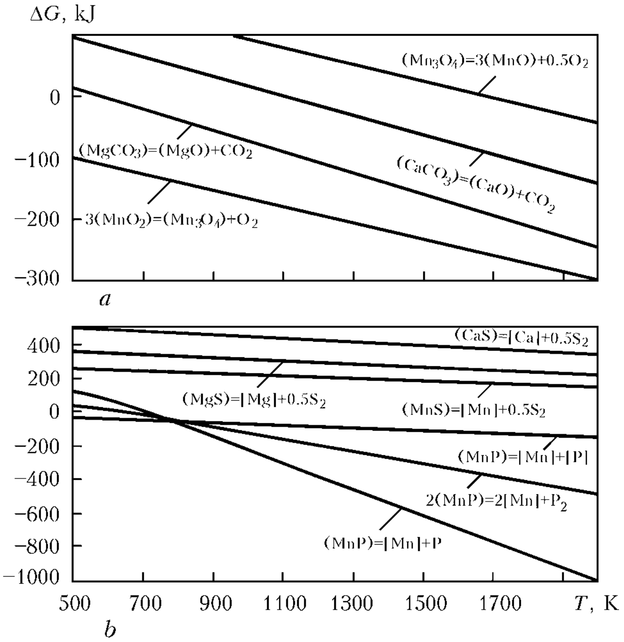

Figure 1. Change of Gibbs energy for reactions of dissociation of carbonates, higher oxides of manganese (*a*), phosphides of manganese and sulphides (*b*)

Proceeding from the calculation data, it can be anticipated that phosphorus, similar to sulphur, should be removed already at the first stage of melting. This process, however, is prevented by two interrelated factors: under oxidizing conditions sulphur is removed at the first melting stage during a reaction of interaction of solid and gaseous phosphorus with formation of P_2O_5, which, in its turn, comes into a reaction with calcium and magnesium oxides, forming the respective phosphates (Figure 3, *a*). At the same

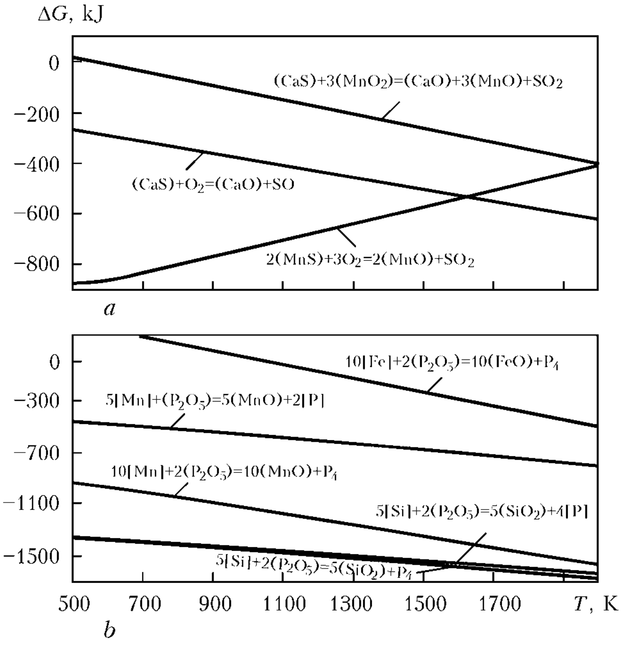

Figure 2. Change of Gibbs energy for reactions of formation of sulphur oxide (*a*) and phosphorus precipitation (*b*)

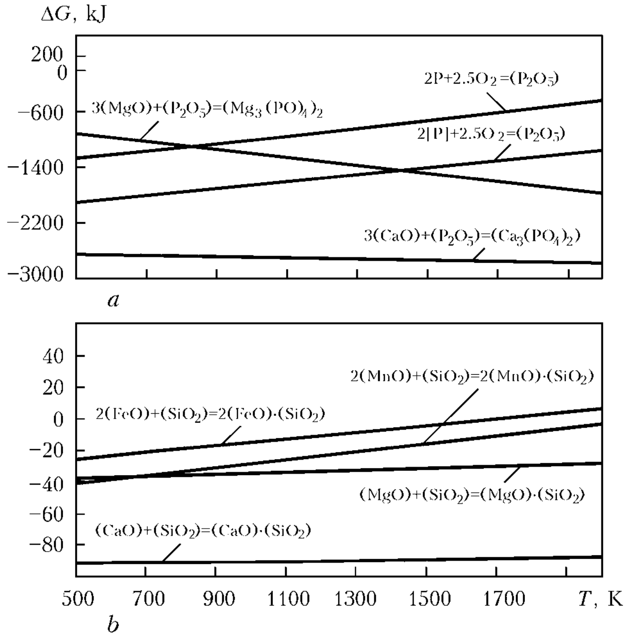

Figure 3. Change of Gibbs energy for reactions of formation of phosphorus oxide and complex compounds with phosphorus oxide (*a*) and silicon oxide (*b*)

time, these oxides can form complex compounds based on silicon oxide. The known property of silicon oxide to form silicon-oxygen chains in the melt leads to phosphorus oxide being bound into extremely strong aggregated complex compounds, which further on at high contents of silicon oxide in the melt are built into the silicon-oxygen lattice of the slag melt and can be removed from the melt only when reducing conditions are created. The probability of these reactions is higher (Figure 3, *b*). Temperature, at which this melting stage is over, can be conditionally taken to be equal to about 1000–1200 °C (±50 °C). The process of charge melting is determined by the kinetics of the processes of gas evolution and contact melting of charge particles. It is exactly the kinetics of these processes at this stage that determines the completeness of removal of gaseous products from the melt, namely phosphorus and sulphur oxides. The main factor, determining the completion of this melting stage, is removal of oxygen and carbon dioxide gas from the melt.

The flux forming (slag forming) stage is characterized by that all the charge mass turns into the melt as a result of interaction of eutectics formed at contact melting with the charge bulk. Charge homogeneity is not achieved [2]. Its mass contains a large number of gas bubbles and has a non-uniform structure. At traditional conducting of the melting process, formation of thermodynamically stable complex compounds — calcium, magnesium, manganese, iron and phosphorus silicates goes on at this stage in the presence of silicon oxide in the charge (see Figure 3, *b*). Calculation results show that due to known property of silicon oxide, mentioned above reactions proceed in the entire temperature range characteristic for the flux melt, i.e. complex formation accompanies the entire process of flux melting. These are exactly the complex compounds that do not allow phosphorus to be removed from the flux melt in the process of flux melting. Note the fact that the probability of $CaO{\cdot}P_2O_5$ formation rises with temperature, thus making phosphorus removal from the slag melt difficult.

The objective of phosphorus removal from the melt can be implemented by creation of certain concentrational conditions, in which complex formation will be limited, for instance, by addition of silicon oxide (or part of it) separately from the other charge components.

The main outcome of the second stage, which corresponds to temperature interval of 1200–1270 °C (±50 °C), is charge transformation into the slag melt, in which unmolten charge particles are absent.

At the third stage the processes of slag melt homogenizing and degassing proceed. An important requirement to oxide fluxes for steel welding is lowering of their oxidizing ability relative to metal in the reaction welding zone. Therefore, during their manufacture the slag melt is further oxidized through reactions of carbo-thermal reduction of the melt components with the carbon of the lining (in the case of arc furnaces) or coke breeze additives (in the case of open gas furnaces). As a result, oxidizing conditions in the furnace are replaced by reducing conditions, flux components interact with carbon, forming the metal phase, containing iron, manganese and silicon (Figure 4). Appearing metals interact with phosphorus oxide with formation of gaseous and solid phosphorus (see Figure 2, *b*), taking it out of the slag melt.

Thus, the most important in terms of slag melt dephosphorization is the reaction of phosphorus transfer into the metal phase, which is realized exactly at this stage of the process. Phosphorus reduced by metals goes into the metal phase together with other metals and precipitates on the furnace bottom plate. Temperature and concentrational conditions of this process running have the main role here. On the one hand, reactions of intermediate manganese oxides of Mn_2O_3 type are highly probable, and on the other — probability of the reactions of iron oxide reduction exceeds the possibility of MnO reduction. This enables controlling the processes of manganese loss as a result of its transition into the metal phase. In particular, such a lowering can be achieved due to complete transfer of higher oxides into the lower (MnO) oxide at the first and second melting stages.

In addition, carbon reduces phosphorus from complex compounds based on calcium and man-

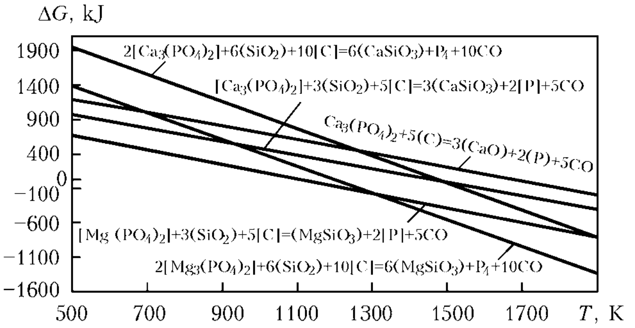

Figure 4. Change of Gibbs energy for reactions of oxide reduction by carbon

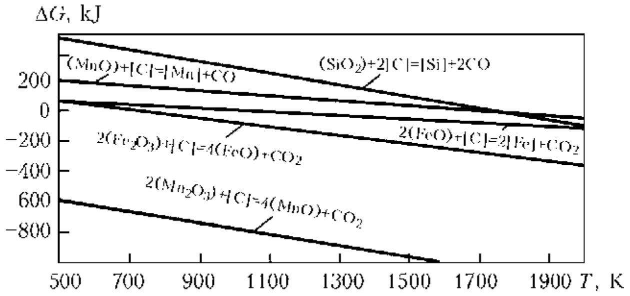

Figure 5. Change of Gibbs energy for reduction of phosphates by carbon and silicon oxide

ganese oxides in the presence of silicon oxide (Figure 5). However, some of these reactions start running only after 1200 °C, and their bulk — after 1500 °C, i.e. at the final stage of melting. The thus formed phosphorus precipitates on furnace bottom. In arc furnaces the probability of the reactions is enhanced in near-electrode regions. The simultaneously precipitating carbon oxide promotes homogenizing of the slag melt.

Completeness of phosphorus oxide removal from the slag melt is determined by the presence of the metal phase. Melting conditions can be selected so that it will mainly consist of iron, whereas silicon and manganese transition will be minimum. Temperature range of the last melting stage is determined by technological capabilities of arc furnaces. For open gas furnaces it is over at the temperature of 1470 °C (±10 °C), and for flux melting — at 1800–1900 °C.

CONCLUSIONS

1. Proceeding from analysis of temperature-time conditions of welding flux melting in arc and open gas furnaces, the possibility of application of the laws of equilibrium thermodynamics for analysis of physico-chemical reactions was determined. Here the heat capacity of the elements and their compounds should be taken into account, and the calculation proper should be performed by Uhlich formula.

2. As a result of thermodynamic analysis of the reactions of charge components used in welding flux manufacture it is established that:

- reactions of sulphide decomposition do not proceed, and their removal requires the presence of oxidizing conditions;
- reactions of phosphide decomposition run in the entire temperature range, but under oxidizing conditions phosphorus oxide forms, which goes into difficult to remove complex compounds;
- in the presence of carbon, exchange reactions proceed in the melt, which result in formation of metals reducing phosphorus from the oxide up to the metallic and gaseous state, and oxides of the same metals, i.e. this group of reactions are interrelated and should be regarded as one thermodynamic system;
- as a result of exchange reactions with participation of carbon, silicon oxide and phosphates, which are present in complex compounds, reactions of phosphorus reduction with simultaneous formation of carbon oxide run at the third stage of melting. There are ten CO molecules for one P_4 molecule that should promote removal of gaseous phosphorus from the melt. Carbon monoxide further oxidizes in the slag melt, promoting lowering of oxidizing ability of the ready flux.

3. Methods to control the processes of slag melt refining are as follows:

- creating oxidizing conditions at the initial melting stage by adding higher oxides of variable valency for sulphur transfer into gaseous oxides;
- separate addition of charge components, in particular silicon oxide, separately from the rest of the charge bulk to prevent formation of complex compounds in the slag melt, hindering phosphorus removal;
- mandatory simultaneous addition of carbon and silicon oxide at the final stage of melting process for decomposition of phosphates present in the complex compounds;
- mandatory presence of the metal phase, forming through reactions of reduction of iron, manganese and silicon oxides by carbon, to remove solid phosphorus from the slag melt. It is possible to create such concentration and temperature conditions, under which the metal phase will consist mainly of iron and phosphorus, and manganese transition into it will be minimum.

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