Dephosphorization of Complexly Alloyed Nickel Melts under Vacuum Induction Melting Conditions: I. Thermodynamics of Dephosphorization

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Abstract—A thermodynamic computer simulation of the oxidation potential of a gas–melt–ceramic (80 wt % MgO, 20 wt % Al\textsubscript{2}O\textsubscript{3}) system under vacuum induction furnace conditions is used to find that the major contribution to this potential at temperatures ranging from 1673 to 2273 K is made by a nickel melt with additives of nickel protoxide. This provides the possibility of oxidative dephosphorization of the metallic melt. The computation of the saturated vapor pressure of phosphorus compounds with the IIA group elements shows that the data obtained for magnesium, calcium, and barium metaphosphates and europium orthophosphate at 1873 K indicate the principal possibility of melt dephosphorization by the evaporation of these compounds under oxidative conditions.

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INTRODUCTION

The oxidation period of melting of carbon-free complexly alloyed nickel melts in a vacuum induction furnace (VIF) starts after the melting of a charge and is characterized by the oxidation potential of a system formed due to the oxidation potentials of ceramic, liquid metal, and additives of oxide components, in particular, nickel protoxide, to a liquid metal. The most important refining processes of this period are the removal of carbon as carbon monoxide and related nitrogen desorption, the removal of phosphorus in the course of native slag phase formation, and sulfur removal to a gas phase [1]. Since the phosphorus content significantly affects the service properties of nickel-based superalloys [2], it is important to develop methods for the dephosphorization of complexly alloyed nickel melts in a VIF with allowance for the restricted possibilities of metal refining by vacuum melting [3]. Therefore, the purpose of the first part of this work is a thermodynamic estimation of the possibilities of dephosphorization under the oxidative and reductive conditions of melting of a complexly alloyed nickel melt in vacuum using computer simulation.

THERMODYNAMIC SIMULATION OF THE DEPHOSPHORIZATION OF NICKEL MELTS WITH THE TRANSITION OF P\textsuperscript{5+} TO SLAGS BASED ON CALCIUM AND BARIUM OXIDES

The study of the physicochemical processes of the dephosphorization of iron-based melts [4] shows that phosphorus can be removed from a melt by two methods. This first method is valid under oxidative conditions (at $p_{O_2} = 10^{-1} - 10^{-17}$ MPa) with the transition of phosphorus in oxidation state P\textsuperscript{5+} to a slag phase and the formation of stable compounds of the 4CaO·P\textsubscript{2}O\textsubscript{5} or 3BaO·P\textsubscript{2}O\textsubscript{5} type in this phase [5]. The second method is valid under reductive conditions (at $p_{O_2} = 10^{-17} - 10^{-21}$ MPa) with the transition of phosphorus P\textsuperscript{3–} to a slag or gas phase and the formation of phosphate components in the slag. Similar studies for nickel melts are lacking. However, an analogy in the behavior of phosphorus can be found even when taking into account stronger bonds of phosphorus with nickel than its bonds with iron [6].

Oxidation Potential of the Gas–Oxide Ceramic MgO–Al\textsubscript{2}O\textsubscript{3} System at 1673–2273 K

To estimate the values of $p_{O_2}$ in the gas phase under VIF conditions, the IVTANTERMO program package [7] was used in computation with the following initial parameters: the composition of the lining material was 80 MgO and 20 Al\textsubscript{2}O\textsubscript{3}, the temperature range from 1673 to 2273 K, and the pressure range $p_{tot} = 10^{-5} - 10^{-9}$ MPa. According to the calculation results, the major components of the gas phase are Mg, O, and O\textsubscript{2}. As the pressure in the system decreased, the ratio of

\footnotesize{$^1$ Hereafter, the content is given in wt %}
the components and the temperature of the appearance of a significant number of moles of the gas-phase components decreased. Temperatures of 1680 and 1580 K and $p_{O_2,\text{max}} = 2.2 \times 10^{-9}$ and $2.2 \times 10^{-10}$ MPa corresponded to pressures $p_{\text{tot}} = 1 \times 10^{-8}$ and $1 \times 10^{-9}$ MPa, respectively. Evidently, the lining of these compositions is a source of gas components with a significant oxidation potential.

**Oxidation Potential of Ni–O and Ni–O–Cr Melts at 1873 K**

The following melt composition was chosen for the thermodynamic calculation of oxygen dissolution and chromium oxidation in nickel-based melts in vacuum: 77 Ni, 10 Co, 6 Cr, 4 W, 1 Mo, and 2 Re. The equilibrium oxygen content in a melt was calculated for the equation

$$\text{NiO}_s = [\text{Ni}] + [\text{O}],$$

$$\Delta G^o_T = 196717 - 103.45T, \text{ J [8].}$$

In this case, we have $K_{\text{eq}} = a_{[\text{Ni}]}a_{[\text{O}]} / a_{\text{NiO}_s}$ and $\log[O] = \log K_{\text{eq}} - \log a_{[\text{Ni}]} - \log f_{[\text{O}]}$. For 1873 K, $\log K_{\text{eq}} = -8.2 \times 10^{-2}$ was obtained. Presenting the expressions for $\log f_{[\text{Ni}]}$ and $\log f_{[\text{O}]}$ through the interaction parameters for dilute solutions of nickel $e_{\text{Ni}}^{\text{Co}} = 0$, $e_{\text{Ni}}^{\text{Cr}} = 0.0013$, $e_{\text{Ni}}^{W} = 0.011$, $e_{\text{Ni}}^{\text{Mo}} = 0.0097$, and $e_{\text{Ni}}^{\text{Re}} = 0$ [8], the following values were calculated: $\log f_{[\text{Ni}]} = 1.7 \times 10^{-1}$ and $\log a_{[\text{Ni}]} = 1.99$. The value of $\log f_{[\text{O}]}$ was calculated accepting that $e_{\text{O}}^{\text{Ni}} = 0$, $e_{\text{O}}^{\text{Co}} = -0.0088$, $e_{\text{O}}^{\text{Cr}} = -0.19$, $e_{\text{O}}^{W} = -0.024$, $e_{\text{O}}^{\text{Mo}} = -0.004$, and $e_{\text{O}}^{\text{Re}} = 0$ [8]. Then, we have $\log f_{[\text{O}]} = -1.223$ and $\log a_{[\text{O}]} = -0.938$, or $[\text{O}] = 0.115\%$.

The value of $p_{O_2}$ above the metal was calculated to compare the oxidation potentials of the lining and melt. For this purpose, the following equation was used:

$$1/2O_2 = [\text{O}]^{\text{Ni}}_{1%},$$

$$\Delta G^o_T = -55956 - 8.79T, \text{ J [8],}$$

with the equilibrium constant $K_{\text{eq}} = a_{[\text{O}]} / p_{O_2}^{1/2}$. At 1873 K, we have $\log K_{\text{eq}} = 2.019$. Then, we determined $\log p_{O_2} = 2(\log a_{[\text{O}]} - \log K_{\text{eq}})$ and obtained $p_{O_2} = 1.2 \times 10^{-7}$ MPa after the known values were substituted. Evidently, the oxidation potentials of both the furnace lining and the nickel melt with NiO additives are sufficient for possible oxidative dephosphorization of the metallic melt, as will be shown further. Note that oxygen dissolved in the metal interacts with other components of the melt, particularly, with chromium and cobalt (data on the interaction with W, Mo, and Re are absent [9]) simultaneously with the oxidation of carbon present in the melt. The equilibrium content of oxygen that provides the appearance of an oxide Cr$_2$O$_3$ film was calculated using the equation $[\text{Cr}]_{\text{Ni}} + [\text{O}]_{\text{Ni}} = \text{Cr}_2\text{O}_3$. Since the values of the interaction parameters of chromium with the melt components are unknown, the solubility of oxygen was determined for a Ni–Cr–O melt at 1873 K and $\log[O] = -2.472 - 2/3\log[\text{Cr}] + 0.183[\text{Cr}]$ [9]; it was found to be 0.012%. Thus, the appearance of an oxide refractory film that would prevent dephosphorization is thermodynamically probable at this oxygen content on the melt surface.

**Oxidation Potential of the Dephosphorization of a Nickel Melt with Calcium and Barium Oxides at 1873 K**

To perform a thermodynamic analysis of the dephosphorization of a nickel melt, we sum up the reactions:

$$3\text{CaO} \cdot P_2\text{O}_5 = 3\text{CaO}_s + P_2\text{gas} + 5/2\text{O}_2,$$

$$\Delta G^o_T = 2315411 - 556.9T, \text{ J [10],}$$

$$P_{2\text{gas}} = 2[\text{P}]_{\text{Ni}},$$

$$\Delta G^o_T = -430152 - 2.72T, \text{ J [8],}$$

$$3\text{BaO} \cdot P_2\text{O}_5 = 3\text{BaO}_s + 2[\text{P}]_{\text{Ni}} + 5/2\text{O}_2,$$

$$\Delta G^o_T = 1885259 - 559.62T, \text{ J.}$$

For 1873 K, we have $\Delta G^o_T = 837090 \text{ J}$ and $\log K_{\text{eq}} = -23.34$. Assuming that $[\text{P}] = 0.002\%$, we determined $p_{O_2} = 6.6 \times 10^{-9}$ MPa.

The following reactions were similarly summed up:

$$3\text{BaO} \cdot P_2\text{O}_5 = 3\text{BaO}_s + P_2\text{gas} + 5/2\text{O}_2,$$

$$\Delta G^o_T = 2443600 - 284.8T, \text{ J [10],}$$

$$P_{2\text{gas}} = 2[\text{P}]_{\text{Ni}},$$

$$\Delta G^o_T = -430152 - 2.72T, \text{ J [8],}$$

$$3\text{BaO} \cdot P_2\text{O}_5 = 3\text{BaO}_s + 2[\text{P}]_{\text{Ni}} + 5/2\text{O}_2,$$

$$\Delta G^o_T = 2013448 - 287.52T, \text{ J.}$$

For 1873 K, $\Delta G^o_T = 1474923 \text{ J}$ and $\log K_{\text{eq}} = -41.125$. Assuming that $[\text{P}] = 0.002\%$, we determined $p_{O_2} = 5.1 \times 10^{-16}$ MPa.

Note that the value obtained is approximate, because the exact value of the entropy of formation of $3\text{BaO} \cdot P_2\text{O}_5$ is unknown. The parameters of the interaction of phosphorus with the components of the melts in dilute solutions at high temperatures are also unknown. In spite of this fact, it can rather reliably be considered that $p_{O_2}$ for the dephosphorization of nickel melts with calcium and barium oxides is consid-