PHASE EQUILIBRIA IN THE SYSTEM Fe–Mo–Cl–H–O

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To alloy the surface of structural components, processes of diffusion transfer of alloying elements through a chloride phase are widely used; these processes are based on the chlorination of metallic solutions or metal oxides. In the present work we determine the thermodynamic conditions of chlorinating an alloy in the system Fe–Mo–Cl–H–O at 1273-1373 K.

According to [1], the oxides FeO, MoO_3 are stable in the system Fe–Mo–O at 1273-1373 K. We determined the conditions of equilibrium of oxide phases with the solid solution [Fe–Mo]_s dealing with the chemical interactions:

\[
[\text{Fe}_s + \frac{1}{2} \text{O}_g] = \text{FeO}(s); \quad K_1 = \frac{1}{a_{\text{Fe}} \cdot P_{O_2}};
\]

\[
[\text{Mo}_s + \frac{3}{2} \text{O}_g] = \text{MoO}_3(s); \quad K_2 = \frac{1}{a_{\text{Mo}} \cdot P_{O_2}^3};
\]

\[
[\text{Mo}_s + 2 \text{O}_g] = \text{MoO}_2(s); \quad K_3 = \frac{1}{a_{\text{Mo}} \cdot P_{O_2}}.
\]

We calculated the temperature dependences of the constants of equilibrium of the reactions according to the data of [1], and also by taking the following balance equation into account:

\[
x_{\text{Fe}} + x_{\text{Mo}} = 1.
\]

The activity of molybdenum in the solid solution was determined with the aid of the experimental data of [2, 3]:

\[
\log a_{\text{Mo}} = \log x_{\text{Mo}} + \frac{1305}{T} (1 - x_{\text{Mo}}^2).
\]

With T = const, no more than two oxide phases can be simultaneously in equilibrium with the solid solution and with the gas phase (number of degrees of freedom C = 0). The parameters of four-phase equilibria are unambiguously determined. If one oxide phase is in equilibrium with the solid solution and the gas phase, the composition of the solid solution is determined by the partial pressure of oxygen. We calculated the composition of the equilibrium phases by solving Eqs. (1)-(5). The results of the calculation are presented in the form of a diagram of the phase equilibrium of the system Fe–Mo–O (Fig. 1). The line ABC is the geometric locus of the points of equilibrium [Fe–Mo]_s–FeO(s)–MoO_2(s)–O_2(g) at different temperatures; to the right of the line are the isotherms of equilibrium [Fe–Mo]_s–MoO_3(s)–O_2(g), to the left [Fe–Mo]_s–FeO(s)–O_2(g). Equilibrium of the solid solution with the oxide MoO_3 in the presence of iron is not attained. It follows from the calculations that with all compositions of the alloy \(x_{\text{Mo}} < 0.1455\) (1373 K) the stable oxide phase is wustite. Under the conditions we deal with, the molybdenum oxides are reduced, and Mo passes into the solution. The same conclusions were arrived at in [2, 4].

According to the data of [5], in the system Fe–Mo–Cl at 1273-1373 K the stable gaseous chlorides FeCl_2, MoCl_5 are in equilibrium with the metallic solution. Having analyzed the chemical reactions of the formation of chlorides and the corresponding balance equations, and
with a view to the results of [6] we determined the parameters of equilibrium solid solution-gas phase. It follows from Table 1 that when the alloy iron-molybdenum is chlorinated, iron chloride predominates in the gas phase. Pure molybdenum interacts with chlorine but when even a small amount of Fe is introduced into the system, chlorination of Mo ceases in fact. Introduction of hydrogen into the system has a greater effect on the process of chlorination of the alloy. Figure 2 shows the dependence of the partial pressure $P_{FeCl_2}$ on the composition of the alloy and on the hydrogen content of the gas phase. We can see that an addition of hydrogen reduces the pressure of the iron chloride and impairs the conditions of chlorination of iron from the alloy Fe-Mo.

When molybdenum interacts with chlorine in the presence of oxygen, it is possible that in addition to chlorides, oxychlorides [6] form, too. However, there are insufficient thermodynamic data available for taking these compounds into account. Since molybdenum is practically not chlorinated in the presence of iron, and the stable oxide phase is wüstite, we dealt with the equilibrium of the solid solution, of wüstite, and of the gas phase in the system Fe-Mo-Cl-H-O. We calculated the parameters of equilibrium for $P_{tot} = 100$ kPa and $T = 1373^\circ K$. The composition of the solid solution and the partial hydrogen pressure were determined by the equation

$$
\text{TABLE 1. Parameters of Equilibrium of the System [Fe-Mo],-Gas Phase}
$$

<table>
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<tr>
<th>T, $^\circ K$</th>
<th>$x_{Mo}$</th>
<th>$x_{Mo}$</th>
<th>$P_{FeCl_2}$, kPa</th>
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