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THERMODYNAMIC ANALYSIS OF THE INTERACTION BETWEEN STEELS AND ALLOYS AND SULFUR DIOXIDE

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Contact between metals and sulfur dioxide SO_2 (for example, during heat treatment) under certain conditions leads to oxidation and sulfur enrichment of the metals in accordance with the reactions:

$$(2mx+yz)\,M+ymSO_2=2mM_xO_y+yM_zS_m; \quad (1)$$

$$2xM+ySO_2=2M_xO_y+yS; \quad (2)$$

$$zM+mS=M_zS_m, \quad (3)$$

where S is the sulfur in the solid solution of the metal or in the free state. It is established as a result of metallographic and electron-microscope studies and microanalysis that during interaction of SO_2 and nickel [1, 2], iron [3], iron–nickel [4], nickel–silicon [5], and iron–chromium [6] alloys, a sulfur-enriched layer forms under the oxide layer.

Analysis of experimental data available in the literature does not permit a quantitative estimate of the stages of oxidation with simultaneous sulfur enrichment of metals, steels, and alloys.

In our study, we thermodynamically analyzed the interaction between Fe, Cr, Ni, Si, Mo, Mn, and Ti (with allowance for their thermodynamic activity a_M in steels and alloys) and atmospheres containing various amounts of SO_2 and determined the equilibrium conditions of reactions (1)-(3) (Figs. 1-3). Values of the energy of formation of oxides and sulfides, which are given in [7], were used for the computations.

For all metals investigated, the oxidation-sulfidation reaction (1) proceeds at a lower partial pressure (P_{SO_2}) of sulfur dioxide than reaction (2) involving the formation of free sulfur ($a_S = 1$) (Fig. 1).

It should be noted that when $a_S = 1$, reaction (2) for titanium proceeds at low P_{SO_2} values close to the P_{SO_2} for silicon and chromium (Fig. 2a), and reaction (1) takes place at even lower P_{SO_2}.

If the partial pressure of SO_2 in the gaseous atmosphere is insufficient for reactions (1) and (2) when $a_S = 1$, reaction (2) ($a_S < 1$) during which the oxidation process is accompanied by the conversion of sulfur to the solid solution takes place. Equilibrium of reaction (2) ($a_S < 1$) is described by the ratio

$$\frac{a_S}{P_{SO_2}}=f\,(a_S, a_M, P_{SO_2}, T)\ \text{(Figs. 2b and 3).}$$

Nikopol' Southern Pipe Plant. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 10, pp. 4-7, October, 1984.

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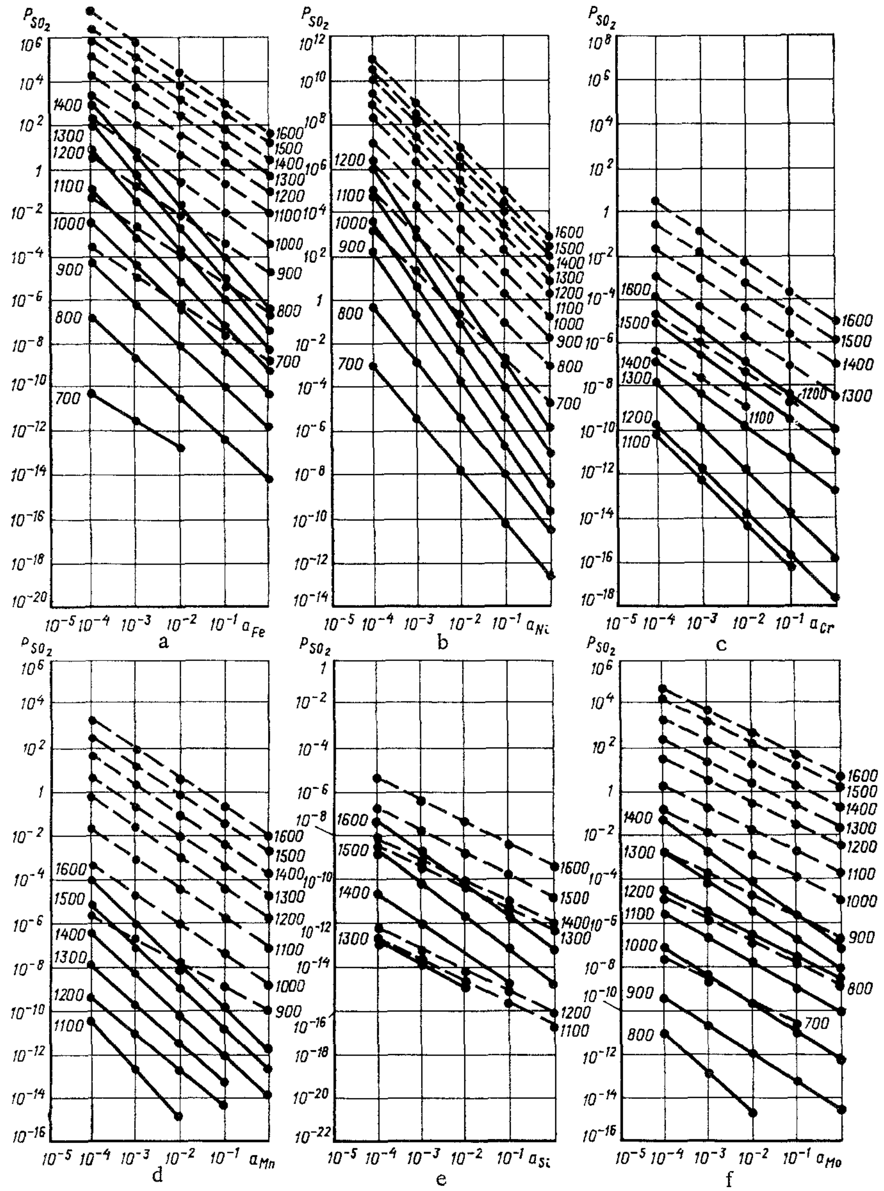

Fig. 1. Relationship between equilibrium values of partial pressure P_{SO_2}, atm, and thermodynamic activity of metals a_M and temperature (figures near curves, °K) for reaction (1) (solid lines) and reaction (2) when $a_S = 1$ (broken lines) involving formation of oxides and sulfides of different metals: from reaction (1): a) Fe_2O_3, FeS; b) NiO, NiS; c) Cr_2O_3, Cr_2S_3; d) Mn_2O_3, MnS; e) SiO_2, SiS_2; f) MoO_2; Mo_2S_3; from reaction (2): a) Fe_2O_3; b) NiO; c) Cr_2O_3; d) Mn_2O_3; e) SiO_2; f) MoO_2.

Thus, the ratio a_S/P_{SO_2} is a characteristic process that takes place at absolute P_{SO_2} values lower than those for reactions (1) and (2) when $a_S = 1$ (the area under the curve in Fig. 1). If the initial a_S value of the sulfur in the solid solution of the metal being heated is greater than a certain magnitude, and P_{SO_2} is so low that the a_S/P_{SO_2} ratio is greater than the ratio of these characteristics in the equilibrium state (Figs. 2b and 3), the process of the metal's oxidation and sulfur enrichment in accordance with reaction (2) is suppressed when $a_S < 1$.

The sulfur that forms as a result of reaction (2) when $a_S \leqslant 1$ interacts with the metal via reaction (3). The product $a_M^z a_S^m$, where z and m are the coefficients before the metal and sulfur in the sulfide, respectively, is a thermodynamic characteristic of the equilibrium of reaction (3). The temperature dependence of this product is given in Table 1 for certain metals. If the condition

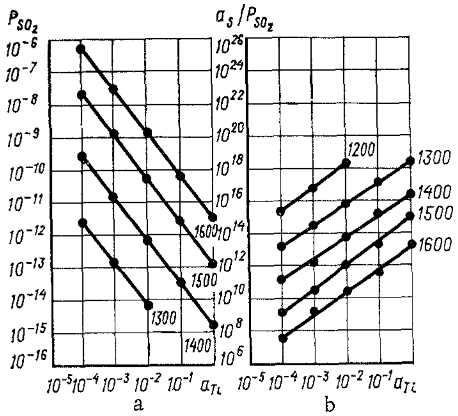

Fig. 2. Relationship between equilibrium values of P_{SO_2} in atm (2) and ratios of a_S/P_{SO_2} (b) and thermodynamic activity of titanium a_{Ti} and temperature (figures near curves in °K) for reaction (2) of Ti_2O_3 formation when $a_S < 1$.

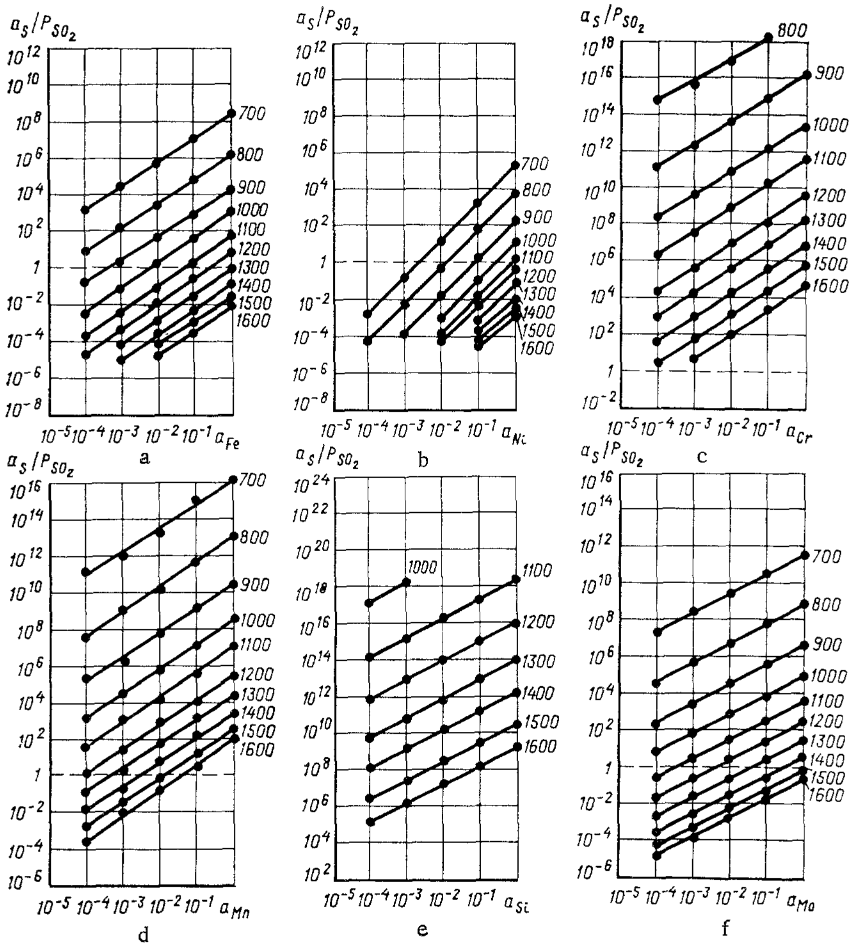

Fig. 3. Dependence of equilibrium ratios a_S/P_{SO_2} on thermodynamic activity of metals a_M and temperature (figures near curves in °K) for reaction (2) (when $a_S < 1$) of oxide formation: a) Fe_2O_3; b) NiO; c) Cr_2O_3; d) Mn_2O_3; e) SiO_2; f) MoO_2.

TABLE 1

Sulfide	T, °K	$a_M^z\ a_S^m$
FeS	1200	$2,9\ 10^{-8}$
	1300	$6,4\cdot 10^{-8}$
	1400	$1,2\cdot 10^{-7}$
	1500	$2,2\cdot 10^{-7}$
	1600	$3,6\cdot 10^{-7}$
NiS	1200	$1,3\ 10^{-7}$
	1300	$2,8\cdot 10^{-7}$
	1400	$5,2\cdot 10^{-7}$
	1500	$8,9\cdot 10^{-7}$
	1600	$1,4\cdot 10^{-6}$
SiS	1200	$6,7\ 10^{-7}$
	1300	$3,6\cdot 10^{-8}$
	1400	$1,7\cdot 10^{-8}$
	1500	$9,7\cdot 10^{-9}$
	1600	$5,7\cdot 10^{-9}$
MoS_2	1400	$1,0\cdot 10^{-12}$
	1500	$7,0\cdot 10^{-12}$
	1600	$2,8\cdot 10^{-11}$

$$\left(a_M^z a_S^m\right)_{\text{steel}} > \left(a_M^z a_S^m\right)_{\text{tabulated}}$$

is satisfied in the steel (or alloy) at the corresponding temperature, the process of sulfide formation of the corresponding metal will take place.

If the metal contained in the steel possesses a low affinity for oxygen and does not form oxides in accordance with reactions (1) and (2), but exhibits a rather high affinity for sulfur, it may form a sulfide while interacting in accordance with reaction (3) with the sulfur obtained from reaction (2) into which a metal having an increased affinity for oxygen enters.

For example, the partial pressure $P_{SO_2} = 0.01$ does not give rise to the oxidation of nickel in Fe—Cr—Ni steel ($a_{Ni} \cong a_{Fe} \cong 0.1$) at 1500°K in accordance with reactions (1) and (2) (see Fig. 1b); this P_{SO_2} value is sufficient, however, to support oxidation of the chromium component of the steel in accordance with reaction (2). Free sulfur with $a_S = 1$ is formed in this case (see Fig. 1c); $(a_{Ni}a_S) = (0.1\cdot 1) > (a_{Ni}a_S)_{\text{tabulated}}$; this suggests the possibility of the formation of nickel sulfide under the given conditions. Iron sulfide may form under the given conditions both as a result of the oxidation-sulfidation reaction of iron (1) (see Fig. 1a) and reaction (3) wherein the iron interacts with the sulfur obtained as a result of reaction (2) between SO_2 and Cr when $a_S = 1$ (Fig. 1c).

The laws under consideration agree with the experimental data of [4, 8] in which it is established that on heating in atmospheres containing SO_2, the oxidation and sulfidation reactions take place simultaneously in Fe—Cr—Ni steels.

Thus, complete analysis of the processes involving the interaction between a steel (or alloy) of complex composition and gaseous atmospheres containing SO_2 can be achieved only when the behavior of each of the steel (or alloy) components is considered in conformity with reactions (1)-(3).

Analysis of the data obtained in this study and data that we had derived earlier [9] makes it possible to point up the increased aggressiveness of SO_2 toward metals as compared with CO_2 under the same conditions.

For equal contents of sulfur and carbon dioxides ($P_{SO_2} = P_{CO_2} = 0.01$) in the gaseous atmosphere of the furnace unit, for example, oxidation and sulfidation of iron—nickel steel take place in accordance with reaction (1) for iron as it is heated to 1500°K. Similar oxidation-carbonizing reactions do not occur in this case.

Thus, the laws that we have derived make it possible to describe processes involving the interaction between complex-alloy steels and alloys and atmospheres containing sulfur dioxide.

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PHASE TRANSFORMATIONS AND ANOMALIES OF DUCTILITY IN STEEL 03Kh11N10M2T

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Gulyaev [1] made a detailed examination of subcritical superplasticity and showed that steels have high ductility when heated to temperatures below the critical point and that is characteristic of all steels that undergo polymorphous $\alpha \rightleftarrows \gamma$ transformation. It is assumed that subcritical superplasticity is due to the special state of the solid solution near the phase transitions, i.e., the pretransformation state.

It was shown [2, 3] that when martensite-aging Fe–Cr–Ni steels are subject to deformation, an anomalous increase of relative elongation is encountered in the temperature range of the $\alpha \rightleftarrows \gamma$ transformations which is believed to be connected with the onset of these transformations. However, when such steels are heated, we find in a broad temperature range (up to the onset and in the process of $\alpha \rightarrow \gamma$ transformation) that there is interaction of the impurity atoms with defects; we find lamination along the chromium, the formation of intermetallides, etc. [4]. These processes are accompanied by a change of the internal energy of the system, of the state of the crystal lattice, of the properties of the alloys, and all this is bound to exert an effect on the nature of the temperature dependence $\delta = f(t)$.

The present work examines the phase and structural transformations when the martensite-aging steels 03Kh11N10M2T (ÉP678) and 03Kh11N10M2 (ÉP842) are heated from normal temperature to the temperature of the end of the $\alpha \rightarrow \gamma$ transformation, and an attempt is made to determine the factors causing the anomaly of the temperature dependence of relative elongation.

The chemical composition and the critical points of martensitic transformations of steels in both directions are presented in Table 1.*

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*Table 1 missing in Russian original — Publisher.

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