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ON THE OXIDATION PROCESSES OF HIGH-NITROGEN, HIGH-CHROMIUM, NICKEL-FREE ALLOYS

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ABSTRACT

In a previous paper [1] we have studied the quantitative relationships of high-temperature oxidation of the new chromium (18–21%Cr) high nitrogen (0.4–1.2%N) nickel free alloys.

The present work is dedicated to the qualitative relations using chemical analysis data, metallography, electron-diffraction pattern, layer X-ray analysis, etc. It is suggested that the oxidation processes of the alloy are generally governed by diffusion of chromium and iron ions in the surface layers and the diffusion of these elements is hampered by the Cr_2O_3, which is especially strongly expressed at temperatures $T \leq 900\,^{o}C$ and times ≤ 1000 min.

Keywords: high nitrogen nickel-free alloys, high-temperature oxidation.

INTRODUCTION

The technology of manufacturing of many elements, including orthopedical and traumatological implants of the new high nitrogen iron-chromium alloys, consists of high-temperature heating in air during the process of hot plastic processing or thermal treatment. During these processes a number of changes take place in the surface properties and dimensions of the treated items. The objective of the present work is to investigate the high-temperature oxidation of high-nitrogen high-chromium nickel-free alloys.

EXPERIMENTAL

The high-nitrogen high-chromium nickel-free alloys were obtained in IMet-BAS using the big steel bath (BSB) method [2,3] and the sheet ingots were cast with weight of 8 kg and thickness of 40 mm. The alloy parameters were obtained in IMet-BAS and IMET-RAN for specimens made of hot-rolled sheets with a thickness of 12mm. The chemical composition [4] is given in Table 1.

The scale resistance tests were carried out by the method of the specific weight increment recording for cylindrical specimens with a diameter of 8 mm at temperatures 500-1000^{o}C and oxidation time from 10 to 1.10^3 min in air atmosphere. The degreased with alcohol specimens were placed in corundum crucibles, preliminarily annealed to constant weight and then weighed. The samples were loaded in furnaces, heated to the test temperature. The temperature in the furnaces was automatically maintained constant with an accuracy of $\pm 2^{o}$C. After the test, the specimens were weighed using an analytical balance with an accuracy of $\pm$ 0.0001g.

The specific weight increment in scale resistance tests (Δm) is calculated according to the formula:

$$\Delta m = (m_0 - m_i) / S$$

where: m_0 is the mass of the specimen before testing, g;
m_i – the mass of the specimen after the test, g;
S – the area of specimen, m^2.

Table 1. Chemical composition of the investigated alloys.

Steel brand	Chemical composition, mass %						
	C	Si	Mn	Cr	N	Ni	др.
0Cr18N0.4	0.030	0.40	0.21	18.20	0.42	-	-
0Cr18N0.7	0.030	0.40	0.20	18.24	0.67	-	-
0Cr15N1.0	0.030	0.24	0.77	14.93	0.96	-	-
0Cr21N1.0	0.020	0.42	0.19	21.45	1.02	-	-
0Cr18N1.2	0.035	0.40	0.42	18.48	1.22	-	-
Analogous							
0Cr18Ni2N1.0	0.03	0.41	0.42	18.10	1.02	-	-
95Cr18	0.90÷1.00	≤ 0.80	≤ 0.80	17.00÷19.00	-	≤ 0.60	Ti≤ 0.20
Cr23Ni18	≤ 0.14	≤ 2.00	≤ 2.0	21.00÷25.00	-	16.00÷20.00	-

The oxidation rate V, g/m^2 h is determined from the relation:

$$V = \Delta m / \tau$$

where τ is the time of holding at the oxidation temperature, h.

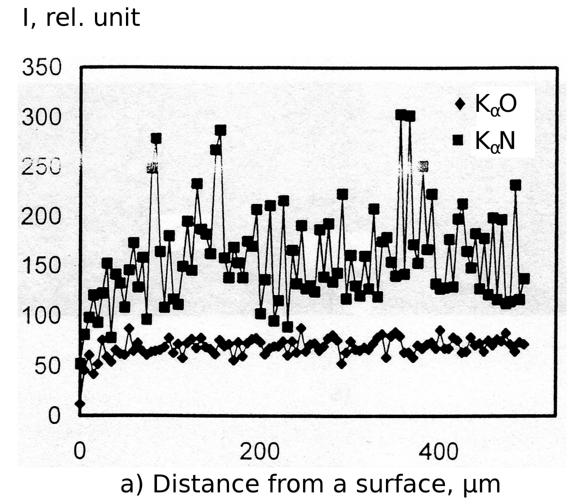
RESULTS AND DISCUSSION

In order to evaluate the effect of cold plastic deformation (compression of 30 %) the alloy 0Cr18N1.2 was tested at 1000°C. Significant increase of scale resistance was observed for the deformed metal compared to the annealed one. This may be due to the higher diffusion rate of chromium in the metal, saturated with defects of the crystalline structure as a result of the rolling process.

In contrast to chromium steel 95Cr18 and high nitrogen alloys with nitrogen content less than 1%, the scale on the new high nitrogen (N>1%) alloys 0Cr18N1.2 and 0Cr21N1.0 for all oxidation regimes was not cracked and delaminated. The observation of the surface and microstructure of the specimens showed formation of dense non-porous scale with good adhesion to the matrix. According to the micro- X-ray analysis the composition of the scale on 0Cr18N1.2 alloy is 75 at. % oxygen, 3 at. % chromium and 21 at. % iron. This is an indication that the predominating phase in the surface scale layer in this case is a phase of Fe_2O_3 type. Large (up to 10 μm) particles of SiO_2, containing 65 at. % of oxygen and 35 at. % of silicon are also found in the scale. The layer under the scale exhibits sections with erosion at high temperatures and long holding times. The content of chromium in this layer is 25 wt. %, which is somewhat higher than the average chromium content in the alloy matrix (18-20 wt. %). Separations of nitrides of Cr_2N type were observed in the ferritic matrix, which were formed during the process of nitrogen austenite decomposition with formation of lamellar colonies. These nitride formations become bigger and acquire more rounded shape with increasing duration of thermal treatment.

The distribution of nitrogen and oxygen when scanning with a narrow sound (diameter of 2 μm) in the 0Cr18N1.2 alloy specimens after oxidation at 700°C (a) and 1000°C (b) with duration of 1000 min is shown in Fig. 1. The inhomogeneity of nitrogen distribution is provoked by the presence of chromium nitrides of Cr_2N type in the structure, their size being compatible to the sound dimensions. The sharp rise of oxygen content caused by its diffusion penetration and the decrease in nitrogen concentration related with the high temperature denitrogenation is observed in the surface layer with a thickness of about 60-70 μm (Fig. 1b).

The electron-diffraction patterns of the oxidized specimens of the high nitrogen alloy 0Cr18N1.2 are obtained at different temperatures. Diffraction maximums are present in the electron-diffraction pattern, which correspond to the phase of Cr_2O_3 type (a = 4.96 Å), together



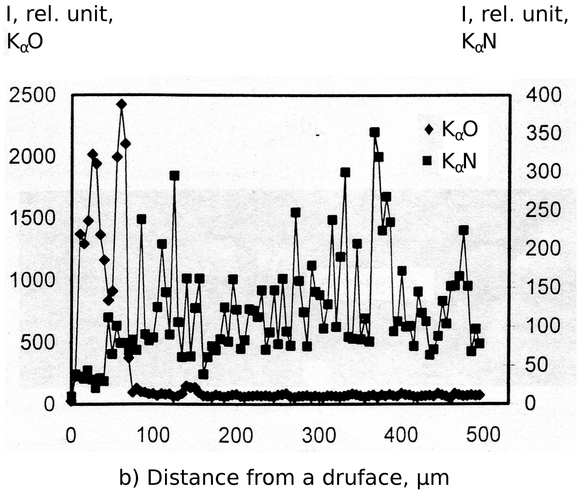


Fig. 1. Distribution of nitrogen and oxygen in the 0Cr18N1.2 alloy after oxidation at 700°C, 1.10^4 min (a) and 1000°C, 1.10^4 min (b).

with slight austenite reflections. The presence of thermodynamically stable phase Cr_2O_3 determines the high scale resistance of the alloy. The phase composition of the scale more complicated after oxidation at 600°C wuestite FeO (a = 4.30 Å) and spinel chromite $FeCr_2O_4$ (a = 8.31 Å) appear in the alloy scale as well as traces of ferrite and σ-phase. After oxidation at 700°C iron oxides of spinel type are observed in the scale – magnetite Fe_3O_4 (a = 8.39 Å) and chromite $FeCr_2O_4$.

The data from the microhardness measurements of the high nitrogen alloy 0Cr18N1.2 are shown in Fig. 2. The microhardness increases with rising the oxidation temperature. In this way the maximum microhardness (1113 HV) is observed at oxidation temperature of 1000°C, the scale layer being 70-80 µm.

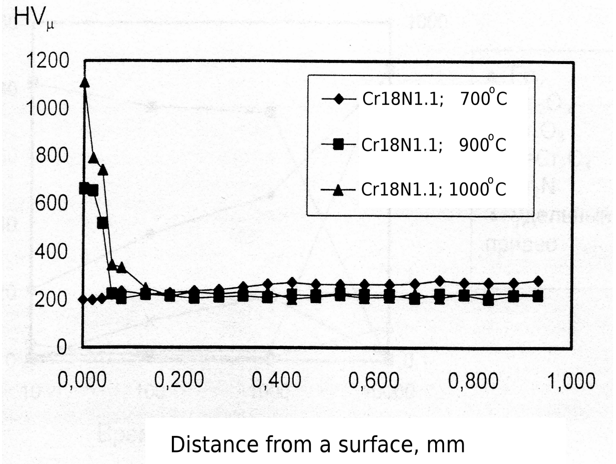


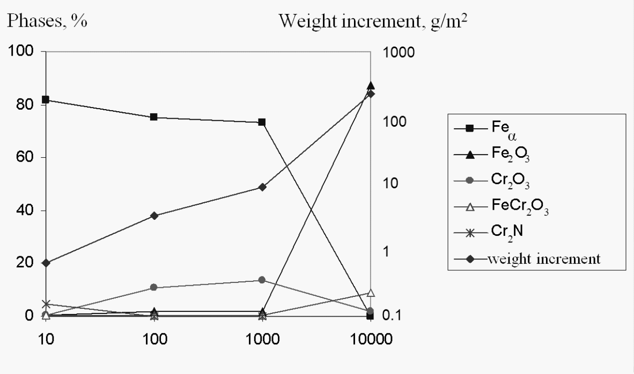
Fig. 2. Effect of oxidation temperature on the microhardness (ÍV) of the surface layer of the high nitrogen alloy 0Cr18N1.2 for duration of oxidation 1.10^4 min.

The X-ray structural analysis of the oxidized surface (by means of the method of micro section photos) shows the diffraction maximums of several phases. The phase changes in the scale of high nitrogen alloy 0Cr18N1.2 at oxidation temperature of 1000°C are shown in Fig. 3a. The intensity of the Fe_α reflections decreases with increasing duration of oxidation at the expense of the oxide film growth. The low oxidation rate of the alloy for duration up to 1.10^3 min is related with the protective action of chromium oxide Cr_2O_3. The increase of the oxidation rate for duration of 1.10^4 min is related with the formation of phases of spinel type ($FeCr_2O_4$, Fe_3O_4) in the scale.

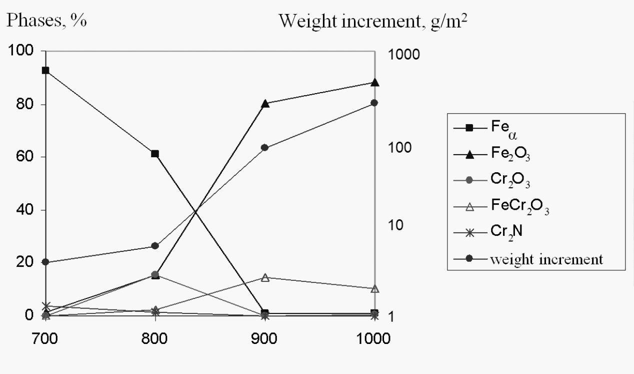
The rising of oxidation temperature from 700 to 1000°C (duration of oxidation of 1.10^4 min) (Fig. 3b) leads to further growth of the amount of hematite Fe_2O_3 and chromite $FeCr_2O_4$ and, respectively, to reduction in the share of chromiun oxide Cr_2O_3, which also leads to an increase of the oxidation rate.

The results of the X-ray phase analysis of the scale on 0Cr18N1.2 alloy after 1.10^4 min of oxidation at 700 and 1000°C show (Table 2) gradual diminution of the share of phase scale components and rising of the matrix alloy phase components (ferrite and chromium nitrides Cr_2N).

The analysis of the results of the research carried out provides a ground to conclude that the oxidation process of the alloys studied is determined mainly by the diffusion of chromium and iron ions in the surface



a) Duration of oxidation, min



б) Oxidation temperature, °C

Fig. 3. (a) effect of the duration of oxidation at 1000°C, (b) effect of the oxidation temperature for duration 1.10^4 min on the phase composition of the scale and the specific weight increment of 0Cr18N1.2 alloy.

layers. The diffusion of these elements is hampered due to the protective effect of chromium oxide Cr_2O_3, which is especially strongly expressed at oxidation temperatures lower than 900°C and duration oxidation up to 1.10^3 min.

The ferrite sub-scale layer (beneath the surface scale), formed during the oxidation process of high nitrogen chromium alloys plays the role of a natural protective coating [5-7]. In the course of the ferrite layer formation under the scale, its gradual saturation with chromium proceeds, which contributes to increase of heat resistance of the alloys.

The alloys containing 18-21% Cr and more than 1 % N may be regarded as heat resistant materials, working at temperatures up to 800°C under conditions of relatively short-term heat impacts. In this case they are not inferior with respect to oxidation resistance to the well known heat resitant steels of Cr23Ni18 type.

The patent issued for these steels [7] contains some facts about their good technological properties for hot and cold processing.

CONCLUSIONS

On the basis of the results obtained in the present study the following conclusions could be made;

In all cases of oxidation regimes of the new chromium-nitrogen alloys studied the scale was not fractured and delaminated and it was dense, non-porous with good adhesion to the alloy matrix.

Table 2. Results of the layer X-ray phase analysis of specimen scale of the 0Cr18N1.2 alloy.

Alloy	Oxidation temperature, °C	Time of oxidation, min	Distance from specimen surface, µm	Phase quantity, %						
				$Fe_α$	Fe_2O_3	Cr_2N	Cr_2O_3	CrN	Fe_3O_4	$FeCr_2O_4$
0Cr18N1.2	700	1.10^4	0	92	2	4	2	–	–	–
			20	89	–	8	–	3	–	–
	1000	1.10^4	0	–	88	–	~1	–	~1	10
			30	7	81	–	~1	–	–	11
			60	92	~1	5	~1	–	~1	–

It was confirmed that the sub-scale ferrite layer, formed in the process of oxidation iof the high nitrogen alloys plays a role of natural protective coating.

The alloys containing 18–21% Cr and more than 1 % N may be considered as heat resistant materials, working at temperatures lower than 800°C under conditions of relatively short-term heat impacts. In this case they are not inferior to the well known heat resistant high-nickel steel of Cr23 Ni18 type.

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