FTD-TT-65-1875

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THE STRUCTURAL-KINETIC INVESTIGATION OF THE PROCESS OF OXIDATION OF NICKEL, CHROME, AND ALLOYS BASED UPON THEM

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FTD-TT- 65-1275/1+2

UNEDITED ROUGH DRAFT TRANSLATION

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English pages: 13

SOURCE: AN SSSR. Institut Metallurgii. Issledovaniya po
Zharoprochnym Splavam, No. 4, 1959, pp. 346-351.

S/2569-059-000-004

TT6000032

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WP-AFB, OHIO.

Date 2 March 19 66

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THE STRUCTURAL-KINETIC INVESTIGATION OF THE PROCESS OF OXIDATION OF NICKEL, CHROME, AND ALLOYS BASED UPON THEM

D. V. Ignatov and R. D. Shamgunova

The wide application of alloys of nickel with chrome in the presence of high temperatures in oxidizing atmospheres is dependent on their heat stable and heat resistant properties. However, articles on the study of heat stable properties and especially on the study of the mechansim of the oxidation of nickel-chrome alloys, have been published only to a small extent in both native and foreign literature. Up to the present time, no protective oxide film composition has ever been established, even with the simple two component alloy, containing 80% Ni and 20% Cr. From those works which have been published, it is not clear which composition of the oxide film establishes a satisfactory stability against the oxidation of nickel chrome alloys: Cr_2O_3 or $NiCr_2O_4$. According to certain authors, the protective film consists in Cr_2O_3 [1], and according to others, it consists in $NiCr_2O_4$ [2]. Even less data is found in literature concerning the oxidization of three component of multi-component nickel-chrome alloys. Meanwhile, data is necessary with respect to the composition and structure of oxide film forming on multi-component alloys as a function of the temperature and the time, in order to classify the mechnnism of the chemical reactions and the phase conversions on the surface of alloys, and of the development of heat stable alloys and of protective coverings against gas corrosion. Besides this, from the composition by which the alloy becomes weakened in the process or oxidization.

The work assigned is in the first stage of experimental research of the process of oxidization of alloys based on nickel and chrome. Its purpose is the establishment of a conformity with kinetic laws in the oxidization of nickel-chrome alloys, the determination of structure, composition, speeds of development, and the protective properties of oxide films coming into being on them as a function of the concentration of the alloying elements (Al and Ti) and the temperature and time of oxidization.

The chemical composition of the alloys investigated is seen in Table 1.

Methodical investigations are based on the weight method of establishing the rapidity of oxidization and on the electronographical determination of the structures of oxide films. Moreover, a metallographical

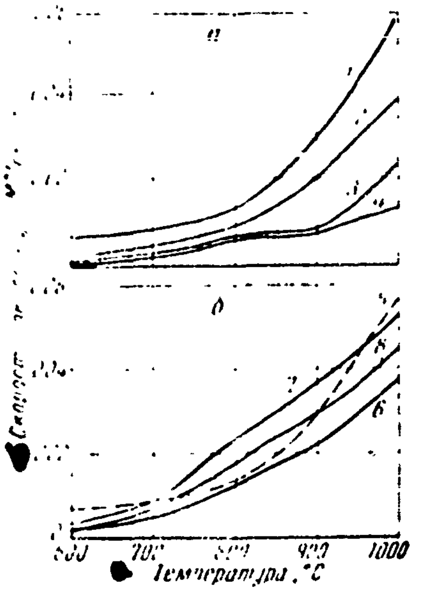

Fig. 1. Curve of the speed of oxidization of the alloys Ni-Cr-Al (a) and Ni-Cr-Ti (b) as a function of temperature.

1 - 0% Al; 2 - 1% Al; 3 - 4.18% Al; 4 - 7.22 Al; 5 - 0% Ti; 6 - 0.68% Ti; 7 - 3.44% Ti; 8 - 5.80% Ti.

KEY: a - temperature; b - rate of oxidation, mg/cm^2 per hour.

analysis is used for the study of the microstructure of transverse section of the oxidation formation. The results of kinetic tests of the oxidization of alloys are shown in Fig. 1 in the aspect of curves showing the speed of oxidization as a function of temperature.

For purposes of comparison, we conducted investigations of the oxidization of nickel and chrome. The speeds of oxidization of these metals (in mg/cm^2 per hour) for temperatures from 600 to 1000° are presented in Table 2.

From Table 2 it can be seen that the speed of oxidization of the binary alloy (80% Ni, 20% Cr) at temperatures of 800 - 1000° are the lower speeds of the oxidization of chrome, while with an increase of temperature, the difference in their speeds is increased. Alloy containing 80% nickel and 20% chrome is subject to internal oxidization.

Analysis of the oxidization curves of the alloys Ni-Cr-Al (Fig. 1a) shows that an addition of alumimum decreases the speed of oxidization of nickel-chrome alloy which is observed especially clearly at temperatures

Table 1

Chemical Composition and Micro-Structure of the Alloys Ni-Cr-Al

Cr	Al 1 синтез	Al анализ 2	Ni	Микроструктура 3
20	0		4 Остальное	γ-твердый раствор 5
20	1	.	»	»
20	5	4,18	»	$\gamma + Ni_3Al$ (начало выделения второй фазы) 6
20	7,5	7,22	»	$\gamma + Ni_3Al$
20	10,0		»	$\gamma + Ni_3Al$

KEY: 1 - synthesis; 2 - analysis; 3 - micro-structure; 4 - residual; 5 - γ - solid solution; 6 - γ + Ni_3Al (inception of precipitation of the second phase).

Chemical Composition and Micro-Structure of the Alloys Ni-Cr-Ti

Cr	Ti	Ni	Микроструктура 1
20	0,68	Остальное 2	γ — твердый раствор 3
20	3,44	»	$\gamma + Ni_3Ti$ по границам зерен 4
20	5,88	»	$\gamma + Ni_3Ti$ по границам зерен и по зерну 5
20	9,76	»	То же 6

KEY· 1 - micro-structure; 2 - residual; 3 - γ - solid solution; 4 - γ + Ni_3Ti along the border of the grain; 5 - γ + Ni_3Ti along the border of the grain and along the grain; 6 - the same.

above 700°; thus, the higher the aluminum content in the alloy, the lower the speed of its oxidization. Besides, additions of aluminum in a quantity higher than 4% prevent intercrystalline oxidization of nickel-chrome alloys.

Table 2

Температура, °C 1	600	700	800	900	1000
Ni	0,032	0,084	0,125	0,24	0,40
Cr	0,007	0,014	0,02	0,06	0,10
Ni – Cr	0,008	0,009	0,014	0,03	0,057

KEY: 1 - temperature.

From curves of the speed of the oxidization of alloys Ni-Cr-Ti (Fig. 1b), it can be seen that an addition of titanium in the nickel-chrome alloy in a quantity of 0.68%, at all temperatures, decreases the speed of its oxidization. Additions of titanium in a quantity of 3.44% and higher, slightly increases the speed of the oxidization of the alloy. In this case, the speed of oxidization of an alloy with 3.44% Ti (inception of the precipitation of the second Ni_3Ti phase) is higher than in the case of the alloy with 5.88% Ti. As is seen from these curves, titanium shows no greater effect on the speed of oxidization of the nickel-chrome alloy.

Alloys with additions of aluminum possess more heat stability at temperatures of 900 - 1000° than do alloys with additions of titanium. To explain this difference in speeds of oxidization, it is necessary to consider the data concerning the structures of oxide films, as shown in Table 3. From this table, it can be seen that on the Ni-Cr alloy, oxide films of the following composition originate: at 600 - 700°, α - Cr_2O_3 with every thickness of the cinder; at 800 - 1000°, double layer films;

Table 3

The Structure and Composition of the Cinder Forming on Samples of the Alloys Ni-Cr and Ni-Cr-Al in the Course of a 25 Hour Oxidization in Air

1 Темпера-тура, °C	2 Положение в окалине	Структура и состав окалины 3				
		Ni – Cr	Ni – Cr + 1% Al	Ni – Cr + 4,18% Al	Ni – Cr + 7,22% Al	Ni – Cr + 10% Al
600	4 гр. о/г*	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	
	Середина	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_2$	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	
	гр. м/о**	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	—	
700	4 гр. о/г	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	5 шп. a^{***}=8,29Å	5 шп. a=8,28Å	
	Середина	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	—	—	—
	гр. м/о	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	—	—	
800	4 гр. о/г	$NiCr_2O_4$	шп. a=8,30Å	5 шп. a=8,27Å	5 шп. a=8,25Å	5 шп. a=8,25Å
	Середина	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$		—	—
	гр. м/о	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	—	5 шп. a=7,9Å	—
900	4 гр. о/г	$NiCr_2O_4$	шп. a=8,30Å	5 шп. a=8,27Å	5 шп. a=8,22Å	5 шп. a=7,9Å
	Середина	$NiCr_2O_4$	шп. a=8,30Å	5 шп. a=8,20Å	5 —	—
	гр. м/о	$\alpha - Cr_2O_3$	$\alpha - Cr_2O_3$	5 шп. a=7,9Å	шп. a=7,9Å	—
1000	4 гр. о/г	$NiCr_2O_4$	шп. a=8,27Å	5 шп. a=8,21Å	5 шп. a=8,19Å	5 шп. a=7,9Å
	Середина	6 $NiCr_2O_4$	шп. a=8,27A			
	гр. м/о	Тонкий слой $\alpha - Cr_2O_3$	6 Тонкий слой $\alpha - Cr_2O_3$	5 шп. a=8,14Å шп. a=7,9Å 5	5 шп. a=8,03Å шп. a=7,9Å 5	5 — шп. a=7,9Å

KEY: 1 - temperature; 2 - position in the cinder; 3 - structure and composition of the cinder; 4 - limit, cinder/gas. center. limit, allcy/cinder; 5 - oxidizer with structure of the spinel type; 6 - thin layer.

in addition, the outer layer consists of $NiCr_2O_4$ and the interior one consists of $\alpha - Cr_2O_3$. With an increase in temperature of oxidization, the thickness of the layer of $NiCr_2O_4$ increases in relation to the thickness of the entire oxide film. Oxide films of the same composition originate on an alloy with 1% Al. On the remaining alloys, Ni-Cr-Al, after

25 hours of oxidization, oxide films of the following composition originate: at 600° - α - Cr_2O_3; at 700 - 1000°, we have oxides of the spinel type with a significant constancy, changing from 8.31 to 7.9 Å as a function of the aluminum content in the alloy as a function of the heat temperature and as a function of the position of the layers in the cinder. Taking into consideration the fact that oxides of the spinel type are solid solutions, the principal form of the spinel $NiCr_2O_4$ (α = 8.31 Å), $NiAl_2O_4$ (α = 8.05 Å) as well as of the spiral γ - Al_2O_3 (α = 7.9 Å), and that the parameter of the lattice of the spinel is smaller the higher the concentration of the oxide of aluminum, following can be considered as established:

1. The nearer the layer is situated to the alloy/cinder limit, the higher the concentration of oxide of aluminum.

2. The higher the control of aluminum in the alloy and the higher the heating temperature, the higher the concentration of oxide of aluminum in the cinder.

Oxide films on alloys Ni-Cr-Ti, in the principal formation, consist of TiO_2 with the rutile structure.

Analysis of the Results Obtained

The chemical composition of oxide films do not correspond to the chemcial composition of the alloys. It essentially changes as a function of the temperature and the heating time. This fact is an indication that the process of oxidization in a given case is accomplished by the diffusion of metallic particles (appearing as ions or atoms) from the alloy/

cinder limit to the cinder/gas limit. The diffusion of oxygen takes place on a parallel with the diffusion of metallic particles. This can be seen, particularly, from the composition of oxide films on the binary alloy. The thickening of the $NiCr_2O_4$ layer with an increase in temperature can be explained by the increase in the speed of the diffusion of the oxygen across the oxide film. However, the speed of the diffusion of the ions of metals significantly exceeds the speed of the diffusion of oxygen. In cases where continuous, timeless, and fissureless oxide layers are tightly adjoining the surface of the alloy, the diffusion of the ions of the etal is the regulating process.

The chemical composition of the oxide films also is changed by its thickness. This fact indicates that in the process of oxidization of alloys, secondary reactions of oxidization and deoxidization take place which occur between the components of the alloy and the earlier forming oxides such as:

$$3\,NiO + 2\,Cr = Cr_2O_3 + 3\,Ni$$

$$3\,NiO + 2\,Al = Al_2O_3 + 3\,Ni \text{ etc.}$$

As can be seen from the thermo-dynamic properties of the oxides shown in Table 4, the given reactions are possible.

Judging by the composition of the oxide layers on the alloy containing 80% Ni and 20% Cr, its oxidization takes place principally at the expense of the chrome. To a lesser extent, the speed of oxidization of this alloy in comparison with the chrome can be explained as having two causes.

Table 4

Thermodynamic Characteristics of Oxides

1	2	3	4
$1/3\ Al_2O_3$	126,0	133,4 ± 0,1	24,8
$1/2\ TiO_2$	106,2	112,8 ± 0,1	22,1
$1/3\ Cr_2O_3$	83,5	90,0 ± 0,3	21,8
NiO	51,3	58,0 ± 0,5	22,4

KEY: 1 - oxide; 2 - ΔF_{298} kcal; 3 - ΔH_{298} kcal; 4 - ΔS_{298} cal/dyne.

1. More energy of activation of the diffusion of the chrome across the oxide film of the $NiCr_2O_4$ composition than across $\alpha - Cr_2O_3$. The justification of this explanation is confirmed by tests on the diffusion of chrome across samples of $NiCr_2O_4$ and $\alpha - Cr_2O_3$ conducted by Belyanin and Belokurov. According to this test of the significance of the coefficients of the diffusion of chrome in $\alpha - Cr_2O_3$ is of higher significance than the coefficient of the diffusion in $NiCr_2O_4$ [3].

2. More energy of the transition of the ions of the chrome into cinder, from the alloy Ni-Cr in comparison to the energy of the transition from the chrome. In the case of ots oxidization of a pure chrome, the ions of the latter make a transition immediately from the surface of the metal into the cinder; in the case, therefore, of oxidization of the alloy after the lapse of a period of time beyond the inception of oxidization, the surface layer of the alloy is weakened by chrome. Ions of chrome make a transition into the cinder, diffusing to the alloy/cinder limit from deeper layers of the alloy.

To a lesser extent, the speed of oxidization of alloys of Ni-Cr-Al in comparison with the Ni-Cr alloy, can also be explained by the great energy of activation of the diffusion of the components of the alloy through the oxide film of the $NiAl_2O_4$ - composition and γ - Al_2O_3 in comparison with films of the α - Cr_2O_3 and $NiCr_2O_4$ composition, which is also shown in article [3]. Moreover, the solidity of the interatomic bond in the Ni-Cr-Al alloys is greater than in the Ni-Cr alloys, as is shown by the investigations of Kurdyumov and Gruzin [4]. As a consequence, the energy of the transition of the alloys Ni-Cr-Al into the cinder will be higher than for the alloy Ni-Cr.

In accordance with data of the same authors [4], additions of titanium also increase the solidity of the interatomic bond in nickel-chrome alloy. In a bond with this, the energy of transition of the ions of metals into a cinder, from the alloy Ni-Cr-Ti will be higher than from the alloy Ni-Cr. However, oxide films of the TiO_2 composition forming on the surface of Ni-Cr-Ti alloys are not protective films. A crystal rutile lattice will contain vacant anion nodes, as a consequence of which the diffusion of oxygen through it is as rapid as possible. Therefore, the effect of the titanium is a double one. A slight addition (0.68%) lowers the speed of oxidization of the nickel-chrome alloy. An addition of 3.44% and higher into the quanityt when the second phase Ni_3Ti forms (which occurs principally along the limit of the grain) and when the cinder, consisting of the rutile, forms on the alloy, does not increase the speed of oxidization of the nickel-chrome alloy evoking the intercrystal oxidization.

In the case of the oxidization of the Ni-Cr-Al alloys, a selection of the second phase of the Ni_3Al in the reverse manner, avoids the intercrystal oxidization of the alloy just as in the presence of oxidization of this phase, the oxide $\gamma - Al_2O_3$ comes into being; the lattice of which, as is the case with the usual spinel, presents its dense cubic packing of ions of oxygen, and thus, the diffusion of the latter through it is made difficult.

Conclusions

1. The speed of oxidization of a binary alloy containing 80% Ni and 20% Cr, is less than the speed of oxidization of chrome at temperatures of 800 - 1000°. The oxide films originating on this alloy consist, at 400° of oxide of nickel (NiO); at 500 - 700°, they consist of oxide of chrome ($\alpha - Cr_2O_3$); at 800 - 1000° - of two layers of various compositions. The surface layer of the oxide film consists of an oxide of the spinel type ($NiCr_2O_4$). That of the inside layer consists of oxide of chrome ($\alpha - Cr_2O_3$). The thickness of the layer of $NiCr_2O_4$ increases with increasing heating temperature, in comparison to the thickness of all oxide films. The thickness of the $\alpha - Cr_2O_3$ type layer decreases in a corresponding manner. The alloy is subject to intensive internal oxidization at the expense of the chrome. The course of the great heat stability of the alloy containing 80% Ni and 20% chrome, in comparison with that of chrome, is found to be in the formation on the surface of the alloy, of an oxide film, the outside layer of which consists of $NiCr_2O_4$, and the higher energy of transition of the chrome ions from the

alloy into the oxide film in comparison with that of pure chrome.

2. The speed of oxidization of the nickel-chrome alloy decreases with additions of aluminum. The effect of the latter is clearly indicated at temperatures higher than 700°. For a satisfactory protection of the alloy Ni-Cr, from oxidization up to a temperature of 900°, an aluminum content in a quantity of 4 - 5% suffices, and at 1000°, 7% suffices.

3. Oxide films forming on alloys with 1% of aluminum with 4.18% Al, 7.22% Al, and 10% Al at 400°, consist of oxide films of NiO; at 500 - 600°, they consist of oxide of chrome α - Cr_2O_4; at 700 - 1000°, they consist of solid solutions of oxides of the spinel type, $NiCr_2O_4$, $NiAl_2O_4$, and γ - Al_2O_3. Oxide of aluminum is concentrated in the inner layers of the oxide film. The usual concentration of oxide of aluminum in the cinder is increased with an increase of temperature and of the aluminum content in the alloy.

4. Slight additions of titanium (0.68%) decrease the speed of oxidization of the Ni-Cr alloy and large additions increase it. This is connected with the formation of the Ni_3Ti phase and also with the inception on these aloys of a large quantity of oxide of titanium which lowers their protective properties. Moreover, additions of titanium evoke inter-crystallite oxidization of the alloy.

5. The process of oxidization of the given alloys is principally caused by the diffusion of the ions of the metals. Chemical reactions of oxidization and deoxidization take place between the components of the alloy and the oxides.

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