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Subsolidus structure of the $Ni–Cr–O–Al_2O_3$ system and justification of advanced composites

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The thermodynamic basing of the use of heat-resistant nickel alloys in composite materials with a metal matrix requires a detailed consideration of the subsolidus structure of a multicomponent metal-oxide system containing nickel and chromium as the base metal components, and corundum fiber $Ni–Cr–O–Al_2O_3$ are presented. The introduction of corundum fiber into the metal chromium-nickel matrix as a complex modifier — a reinforcing component that also functions as an antioxidant significantly increases both the operating temperature and the corrosion resistance of the composite material.
Keywords: metal matrix, corundum fiber, heat-resistant alloys, metal-oxide system, subsolidus structure, spinel.

Представлены результаты термодинамического обоснования использования жаростойких никелевых сплавов в композиционных материалах с металлической матрицей на основании детального рассмотрения субсолидусного строения многокомпонентной металл — оксидной системы, содержащей в качестве металлического компонента основные металлы жаропрочных сплавов — никель и хром, а в качестве оксидного компонента — корундовое волокно — $Ni–Cr–O–Al_2O_3$. Установлено, что введение в состав металлической хром-никелевой матрицы корундового волокна в качестве комплексного модификатора — армирующего компонента, выполняющего и функцию антиоксиданта, рационально и позволит существенно повысить как температуру эксплуатации, так и коррозионную стойкость композиционного материала.

Субсолідусна будова системи $Ni–Cr–O–Al_2O_3$ та обгрунтування перспективних складів композитів. *С.М.Логвінков, Г.М.Шабанова, А.М.Корогодська, А.А.Івашура, М.М.Івашура.*

Наведено результати термодинамічного обгрунтування використання жаростійких нікелевих сплавів у композиційних матеріалах з металевою матрицею на основі детального розгляду субсолідусної будови багатокомпонентної метал-оксидної системи, яка містить як металевий компонент основні метали жароміцних сплавів – нікель та хром, а як оксидний компонент корундове волокно – $Ni–Cr–O–Al_2O_3$. Установлено, що введення до складу металевої хром-нікелевої матриці корундового волокна як комплексного модифікатора – армуючого компонента, який виконує також функцію антиоксиданту, раціонально та дозволить суттєво підвищити як температуру експлуатації, так і корозійну стійкість композиційного матеріалу.

1. Introduction

Nowadays, composites with a metal matrix reinforced with nanoparticles of refractory oxides, carbides, etc. are increasingly used instead of the metallic materials to work at high temperatures.

Metal composite materials have some advantages over the polymer ones. In addition to higher operating temperatures, they are characterized by better isotropy, stability of properties during operation and higher erosion resistance [1]. The ductility of metal matrices gives the composition the required viscosity. It contributes to the rapid alignment of local mechanical loads. An important advantage of metal composite materials is a higher workability of the manufacturing process, molding, heat treatment, the formation of compounds and coatings.

The advantages of metal-based composite materials are higher values of characteristics depending on the properties of the matrix. These are primarily temporary resistance and the modulus of tensile elasticity in the direction perpendicular to the axis of the reinforcing fibers, compressive and flexural strength, plasticity, and fracture toughness. In addition, composite materials with a metal matrix maintain their strength characteristics up to higher temperatures than materials with a non-metallic base. They are more moisture-resistant, non-combustible, and they have electrical conductivity. High electrical conductivity of metallic composite materials protects them well from electromagnetic radiation, lightning and reduces the risk of static electricity. The high thermal conductivity of metallic composite materials protects against local overheating, which is especially important for products such as rocket caps and leading edges of wings. Currently, the main applications of composite metallic materials are aerospace structures; in the future they can replace metal alloys in many ground-based applications, including automotive equipment [2].

The combination of substances in one material, that differ significantly in chemical composition and physical properties highlights the problem of thermodynamic compatibility of the components in developing, manufacturing and combining composite materials. Thermodynamic compatibility is understood as the ability of the matrix and reinforcing fillers to be in a state of thermodynamic equilibrium for an unlimited time at temperatures of production and operation [3].

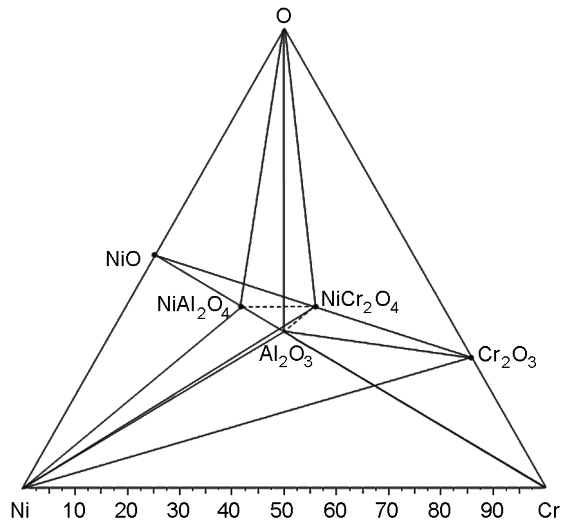

Fig. Subsolidus structure of the Ni–Cr–O–Al_2O_3 system.

The most promising materials for matrices of metal composite materials are metals with low density (Al, Mg, Ti), and alloys based on them [4], as well as nickel, which is currently widely used as the main component of heat-resistant alloys. The latter can significantly raise (up to 1200°C) the working temperature of heat-resistant materials. The most common heat-resistant nickel alloys are Inconel and Hastelloy. The main function of these alloys is an effective operation at high temperatures and pressures, as well as under conditions of contact with aggressive substances, when ordinary or cheaper alloys do not adequately meet the technological requirements, for example, in the equipment of nuclear reactors, various chemical units, pipes and valves in chemical industry.

Thus, thermodynamic basing of the use of heat-resistant nickel alloys in composite materials with a metal matrix requires a detailed consideration of the subsolidus structure of a multicomponent metal-oxide system containing nickel and chromium as base metal components of superalloys and corundum fiber Ni–Cr–O–Al_2O_3 as the metal component.

The aim of the work is tetrahedron description of the Ni–Cr–O–Al_2O_3 system, calculation of its subsolidus structure characteristics and finding of all two-, three- and four-phase thermodynamically stable combinations in order to predict the properties of the composites of the studied system in terms of physical chemistry.

2. Previous studies

Binary compositions of the considered four-component system are the following [5]. The Ni–Cr binary system has a melting point of eutectic which is studied in full. Thus, in the Ni–Cr system, the melting points of nickel and chromium at atmospheric pressure are 1455°C and 1907°C, respectively; at 1345°C, the eutectic composition contains 51 wt % of Cr [6]. During the eutectic reaction, two solid solutions are formed — a face-centered cubic (FCC) one based on nickel and a body-centered cubic (BCC) one based on chromium. The systems containing metal and corundum, Ni–Al_2O_3 and Cr–Al_2O_3, as well as O–Al_2O_3 do not have binary compounds and are not of significant interest.

In the Cr–O binary system, two particular and sharply different systems can be distinguished: a system with low oxygen concentrations: Cr–Cr_2O_3, and a system with high oxygen concentrations: Cr_2O_3–CrO_3. The first of them is a typical high-temperature system; its compounds are stable only at high temperatures [7]. On the contrary, the compounds in the Cr_2O_3–CrO_3 system are stable only at relatively low temperatures and, apparently, chemically represent chromate chromites (or chromic salts of other chromium acids). Thus, the most stable compound in this system at temperatures above 1000°C is Cr_2O_3; this fact is taken into account in further studies. Chrome spinel Cr_3O_4 has a small range of temperature stability and its role in mutual phase transformations can be neglected without a significant error. In the Ni–O binary system, the most thermodynamically stable in a wide temperature range is nickel oxide NiO; this is taken into account in further studies [8]. Among the ternary systems, the most studied is the Ni–Cr–Al_2O_3 system, since its compositions are formed by the action of aggressive factors on special Ni–Cr alloys.

The authors [9] studied the effect of the Al_2O_3 content on the mechanical and tribological properties of the Ni–Cr alloy from room temperature to 1000°C. The results showed that the composite of NiCr — 40 wt.% Al_2O_3 has good wear resistance, and its compressive strength remains equal to 540 MPa even at 1000°C. It was found that from 800°C to 1000°C, an adhesive and plastic oxide layer on the worn surface of the composite is responsible for the low coefficient of friction and the coefficient of wear. Binary and ternary compounds in this system are absent.

The state diagram of the Ni–Cr–O system is important from the point of view of studying the oxygen corrosion of special nickel alloys. It has been found out that a thermodynamically stable compound is formed in the system of $NiCr_2O_4$ nickel-chrome spinel, melting at 2030°C [10]. The coexistence of this spinel with Ni, NiO, Cr_2O_3 and oxygen unambiguously triangulates this system into 5 elementary triangles, which does not contradict the rule of L.S.Kurnakov [11].

In the Ni–Al_2O_3–O system, the metal is oxidized to a stable NiO oxide, which unambiguously determines the presence of a NiO–Al_2O_3 pseudobinary cross section, which has been studied and contains a binary compound, nickel-aluminum $NiAl_2O_4$ spinel, which breaks the system into 4 elementary triangles [12].

In the Cr–Al_2O_3–O system, there is also a pseudo-binary section of Cr_2O_3–Al_2O_3, however it does not contain binary compounds; the system is a continuous series of solid solutions, which leads to a division of the system into 2 elementary triangles [13].

The presented results of studying the literature data allow us to fully switch to tetrahedral description of the four-component Ni–Cr–O–Al_2O_3 system, taking into account all known thermodynamically stable compounds.

3. Thermodynamic modeling of a Ni–Cr–O–Al_2O_3 system subsolidus structure

It is advisable to start the tetrahedral processing of the system from the angle corresponding to metallic Ni, with the participation of which the tetrahedron is closed:

1) Ni–Cr–Cr_2O_3–Al_2O_3.

Further the tetrahedral processing is possible by closure, according to the principle of geometric necessity [14] of internal coupling of Al_2O_3–$NiCr_2O_4$ and $NiCr_2O_4$–$NiAl_2O_4$, which completely close the remaining tetrahedrons of the system:

2) Cr_2O_3–Al_2O_3–$NiCr_2O_4$–Ni;
3) Al_2O_3–Ni–$NiCr_2O_4$–$NiAl_2O_4$;
4) Ni–$NiCr_2O_4$–$NiAl_2O_4$–NiO;
5) Cr_2O_3–Al_2O_3–$NiCr_2O_4$–O;
6) $NiCr_2O_4$–Al_2O_3–$NiAl_2O_4$–O;
7) $NiCr_2O_4$–$NiAl_2O_4$–NiO–O.

Thus, the four-component Ni–Cr–O–Al_2O_3 system is divided by two internal tie lines (conodes) (Table 1) into 7 elementary tetrahedrons (Fig. 1); their geometrical-topological characteristics are presented in Table 2; and the characteristics of the phases of the system are in Table 3 (calculated according to the method [11]).

Table 1. Characteristics of the tie lines (conodes) of Ni–Cr–O–Al_2O_3 system

Phase	Coexisting phases and co-existing lengths of conodes, ‰
Ni	NiO (214.0); $NiAl_2O_4$ (629.8); $NiCr_2O_4$ (647.2); Al_2O_3 (1000.0); Cr_2O_3 (884.5); Cr (1000.0)
Cr	Cr_2O_3 (320.0); Al_2O_3 (1000.0); NiO (912.0); Ni (1000.0)
O	Cr_2O_3 (680.0); $NiCr_2O_4$ (631.5); Al_2O_3 (1000.0); $NiAl_2O_4$ (797.9); NiO (786.0)
Al_2O_3	Cr (1000.0); Cr_2O_3 (884.5); $NiCr_2O_4$ (823.9); $NiAl_2O_4$ (383.0); O (1000.0); Ni (1000.0)
Cr_2O_3	O (680.0); $NiCr_2O_4$ (242.5); Al_2O_3 (884.5); Ni (884.5); Cr (320.0)
NiO	O (786.0); $NiCr_2O_4$ (496.3); $NiAl_2O_4$ (529.0); Ni (214.0); Cr (912.0)
$NiCr_2O_4$	O (631.5); NiO (496.3); $NiAl_2O_4$ (542.7); Ni (647.2); Al_2O_3 (823.9); Cr_2O3 (242.5)
$NiAl_2O_4$	O (797.9); $NiCr_2O_4$ (542.7); NiO (529.0); Ni (629.8); Al_2O_3 (383.0)

Table 2. Elementary tetrahedra of the Ni–Cr–O–Al_2O_3 system

No.	Elementary tetrahedra	Volume, ‰	Degree of asymmetry L_{max}/L_{min}
1.	Ni–Cr–Cr_2O_3–Al_2O_3	315.7	3.13
2.	Cr_2O_3–Al_2O_3–$NiCr_2O_4$–Ni	48.3	4.13
3.	Al_2O_3–Ni–$NiCr_2O_4$–$NiAl_2O_4$	56.7	2.61
4.	Ni–$NiCr_2O_4$–$NiAl_2O_4$–NiO	41.5	3.02
5.	Cr_2O_3–Al_2O_3–$NiCr_2O_4$–O	177.2	4.12
6.	$NiCr_2O_4$–Al_2O_3–$NiAl_2O_4$–O	152.5	2.60
7.	$NiCr_2O_4$–$NiAl_2O_4$–NiO–O	208.1	1.61
	Total volume	1000.0	–

Table 3. Geometric-topological characteristics of the phases of the Ni–Cr–O–Al_2O_3 system

No.	Phase	Number of coexisting phases	Number of elementary tetrahedrons	Total volume of existence, %	Probability of existence, ω_i
1	Ni	6	4	462.2	0.1155
2	Cr	4	1	315.7	0.0789
3	O	5	3	537.8	0.1345
4	Al_2O_3	6	5	750.4	0.1876
5	Cr_2O_3	5	3	541.2	0.1353
6	NiO	5	2	249.6	0.0624
7	$NiCr_2O_4$	6	6	684.3	0.1711
8	$NiAl_2O_4$	5	4	458.8	0.1147
	Amount			4000.00	1.0000
	Maximum	6	6	750.4	0.1876
	Minimum	4	1	249.6	0.0624

4. Conclusions

Summarizing the results of the geometric-topological analysis of the four-component Ni–Cr–O–Al_2O_3 system, we can conclude the following:

— in the pseudo-triple Cr_2O_3–Al_2O_3–NiO section separating the region of combinations with a direct participation of oxygen from the region of metal-oxide combinations, the central part is represented by an elementary triangle with vertices at the points of the spinel ($NiCr_2O_4$ and $NiAl_2O_4$) and corundum (Al_2O_3) compositions;

— the presence of a pseudo-triple Cr_2O_3–Al_2O_3–NiO section in the studied system indicates the impossibility of the formation of free oxygen in the composition of nickel-chromium alloys when they are reinforced with dispersed Al_2O_3 particles;

— the complex reinforcement of the nickel-chromium alloys should be considered as more rational, since the combination of Cr_2O_3 and Al_2O_3 provides the most refractory combination of the Cr_2O_3–Al_2O_3–Ni–Cr phases;

— under the experimental conditions, local oxidation of nickel in the alloy can be blocked by the formation of nickel oxide capable to form thermodynamically stable spinels, alumina-nickel and chromium-nickel, with a complex modifier — reinforcing oxides (Cr_2O_3 + Al_2O_3); this ensures the formation of a more stable four-phase Ni–$NiCr_2O_4$–Al_2O_3–Cr_2O_3 combination;

— local oxidation of chromium in the composition of the alloy with the complex modifier will be blocked by the resulting chromium-nickel spinel in the composition of the thermodynamically stable four-phase Ni–Cr–Cr_2O_3–$NiCr_2O_4$ combination.

Thus, the introduction of corundum fiber into the metal chromium-nickel matrix as a complex modifier functioning both as a reinforcing component and an antioxidant is rational; this might significantly increase both the operating temperature and the corrosion resistance of the composite material.

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