High temperature synthesis of nickel aluminide alloys with tungsten carbide

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Nickel aluminides of a composite structure, hardened by the inclusions of refractory transition metal compounds, have great potential in terms of creating new materials with the increased strength and heat resistance. The variety of compositions of alloying systems allows obtaining composite materials of different types with a complex of the improved operational characteristics. This work presents the research results of studying the synthesis conditions for metal matrix alloys from pure metal oxides. The microhardness, phase and element compositions of the resulting alloys have been investigated. It is found that composite alloys are formed in the result of thermally conjugated exothermic reactions in NiO – Al and WO_3 – C – Al systems. Thermodynamic analysis shows that the probability of obtaining cast products in the result of such reactions is very high. The dominant reaction corresponds to the parameters: G = –944 kJ/mol, adiabatic temperature (AT = 3150 K. The influence of the synthesis conditions on the composition of the intermetallic phase of the composite has also been studied. The possibility of the formation of Ni2Al3 and NiAl intermetallic compounds is proved. It is established that in order to create optimal conditions for the formation of intermetallic compounds an excess amount of aluminum (~ 30 wt.%) in the total initial charge mixture is required. An increase of carbon in the composition of the initial charge mixture to ~ 20 wt.% raises the content of tungsten carbide in the synthesized alloy. In this case, a decrease in the temperature causes the formation of Ni_2Al_3 intermetallic phase. Composite materials are represented by NiAl and Ni_2Al_3 phases with WC tungsten carbide inclusions according to the results of elemental, X-ray phase analysis and scanning electron microscopy. The volumetric content of tungsten carbide in alloys is ~20%. The resulting alloys have the increased microhardness due to the inclusion of the refractory interstitial WC phase (8.5–9.8 GPa) in their structure. Composite materials based on NiAl are promising for application as heat-resistant coatings.

Key words: nickel aluminide, tungsten carbide, aluminothermy microstructure, microhardness, metal matrix alloy.

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Introduction

The creation of new materials based on intermetallic compounds is one of the priority tasks for modern materials science. The intermetallic alloys of Ni – Al system having unique properties can be used as the basis for the creation of new high-temperature materials to be used in power engineering, aircraft and automotive industries. The process of hardening of intermetallic alloys due to the formation of a composite structure by the inclusions of refractory compounds (carbides, borides) plays the most important role in improving the physicomechanical properties of the intermetallides. These materials have the increased strength and thermal stability due to the inclusion of refractory interstitial phases in their structure. For example, nickel aluminides NiAl were obtained, hardened by inclusions of carbides or borides of transition metals NiAl – NbC, NiAl – TiC, NiAl – TiB_2, NiAl – MoB, etc. [1–7]. The variety of compositions of alloying systems promotes obtaining composite materials of different types with a complex of the improved operational characteristics. The problem of synthesis of nickel aluminides and composites on their basis is solved now by using conventional foundry technologies and powder metallurgy, which are characterized by multi-stage technological cycles, high

costs and not always provide the required quality of the target product [7–13].

The use of self-propagating high-temperature synthesis (SHS), metallurgy SHS in particular, presents certain prospects for the production of composite materials. High temperature degree, which is difficult to achieve by conventional heating, accompanies the termite processes and makes it possible to obtain cast composite materials according to a short scheme [14–20]. The effect of synthesis conditions on composition and structure of the target products is of particular interest in this research; to obtain alloys of nickel aluminide with tungsten carbide under deferent synthesis conditions being the goal of this work.

Methodology and materials

The following reagents were used as initial components for the reaction mixtures and which purity in wt.% was: nickel oxide NiO – 98.9, tungsten oxide WO_3 – 98.5, carbon source – technical soot, aluminum powder – 99.5 (average particle size – 50 μm), calcium fluoride CaF_2 of brand "Ch". The phase composition was determined on a diffractometer DRON-7 (Cu K – radiation). Microhardness was investigated on a microhardness tester PMT-3M. The microstructure and element composition were studied using a Hitachi SU-70 electron microscope with an EMF attachment. Metallothermic smelting was carried out in metal crucibles lined with refractory material. Two options were used for preparing the original mixture for synthesis. The first involved uniform mixing of all reagents for the composites synthesis. In the second, the charge mixture consisted of two layers: the lower layer contained reagents for the synthesis of tungsten carbide, the upper one had the charge mixture for the formation of nickel aluminide. The mixture was ignited in bulk, after vibration compaction at 100 Hz for 20 minutes. This vibrational compaction was carried out in order to obtain the maximum bulk density f the mixture. The optimum compaction frequency (100 Hz) was established in separate experiments.The reaction was initiated by electric fuse on top, and then it proceeded without external heating. The resulting nickel aluminide melt ignited the lower mixture of reagents and the synthesis of tungsten carbide proceeded together with the intermetallic melt. In that way the melts of matrix and reinforcing phases of the target material were mixed. As a result of melting, two types of products were formed: the metal phase in the form of a compact ingot and the oxide phase, distinctly divided into two layers. The oxide phase contains mainly Al_2O_3, CaO.

Results and discussion

The process of obtaining a composite material with a certain degree of approximation can be represented as the sum of the partial synthesis reaction of individual composite component (Table 1). At the first stage nickel oxide is reduced and nickel aluminides are formed. It is known that in the Ni – Al system, the formation of five intermetallic compounds of different compositions is possible:

Table 1

Thermodynamic characteristics of SHS systems

No.	Reaction system	Taget product	G_{1000K}, kJ/mol	AT, K	Melting point, K
1.	NiO + Al	Ni	–944	3150	1726
2.	Ni + Al	NiAl	–105	1912	1911
3.	Ni + Al	Ni_2Al_3	–254	1410	1406
4.	WO_3 + C + Al	WC	–1024	3860	3058

Al_3Ni, Al_3Ni_2, NiAl, $AlNi_3$, Al_3Ni_5. An intermetallic compound of one or another composition may predominate depending on the synthesis conditions, the process temperature, and the ratio of the components in Ni – Al system. In our case, the formation of NiAl intermetallic compound is preferable.

$$3NiO + 2Al = 3Ni + Al_2O_3 \quad (1)$$

$$Ni + Al = NiAl \quad (2)$$

The synthesis of tungsten carbide proceeds through the stage of tungsten oxide reduction and thus can be described by the chemical reaction equation:

$$WO_3 + 2Al + C = WC + Al_2O_3 \quad (3)$$

In the first synthesis variant the dispersed carbon is taken in a stoichiometric ratio of the Reaction 3 and with an excess of ~20 wt.% relative to the estimated. Carbon uniformly distributed in the charge mixture is involved in the endothermic reduction reaction.

$$WO_3 + 4C = WC + 3CO \quad (4)$$

This creates competition to aluminum and lowers the temperature of the reaction system. As a result, an intermetallic compound with a lower melting point of Ni_2Al_3 (1133 ^oC) is formed in the composition with WC. An increase of carbon concentration in the composition of the initial charge mixture increases the content of tungsten carbide in the synthesized alloy.

The second synthesis variant involves the use of a two-layer charge mixture, so a strong exothermic reaction (1) proceeds in the upper part of the crucible in the absence of carbon, and the temperature develops much higher than the melting point of the intermetallic compound NiAl (1638 ^oC). Whereas in the lower part of the crucible, the tungsten carbide synthesis reaction takes place (3). Given that the reactions are thermally coupled, the temperature developing in the system is sufficient for the propagation of the combustion front and the process of melting the products of the reaction. As a result, the final product of the reactions is a multicomponent high-temperature melt, where the metal and oxide phases are separated due to the densities difference. The metal phase is a composite alloy NiAl – WC, oxide phase – Al_2O_3. In this case the presence of the Ni_2Al_3 phase alongside with the NiAl phase in the obtained alloy is possible [21].

The composition of the initial charge mixture for the synthesis of the composite material has been established

Table 2
Composition and microhardness of composite materials

No.	Phase composition	The elements content in the alloys, wt.%				Micro-hardness, GPa
		Ni	Al	W	C	
1.	Ni_2Al_3 – WC	62.2	28.5	8.0	1.2	8.5
2.	NiAl – WC	61.5	24.7	11.5	1.6	9.8

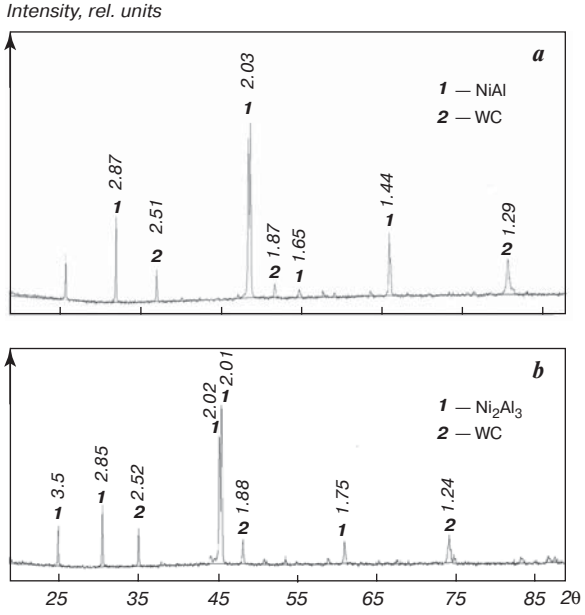

Fig. 1. *X*-ray diffraction patterns of composite materials: *a* — NiAl – WC; *b* — Ni_2Al_3 – WC

taking into account the stoichiometric ratio of the reactants in the equations of the main reactions (1–3). Obviously, for the successful formation of nickel aluminide, it is necessary to provide an excess of aluminum in the composition of the charge mixture. The experiments show that as the excess of aluminum increases to ~25 wt.%, a significant amount of it passes into the alloy without participating in the reduction reaction. This creates favorable conditions for the synthesis of nickel aluminides. For comparison, nickel aluminide doped with tungsten of NiAl – W composition was synthesized according to the previously described procedure [22].

The results of analysis of elements and microhardness values of the obtained alloys are presented in Table 2. The yield of metals in the alloys is 82–85% by mass. The results of the *X*-ray phase analysis are shown in Fig. 1. The analysis of the diffraction patterns indicates the formation of the aluminide matrix Ni_2Al_3 with tungsten carbide inclusion in alloy No.1, however the main phase in alloy No. 2 is NiAl with tungsten carbide inclusions. The structure analysis shows that the composites are represented by the intermetallic matrix with individual WC inclusions. The volume fraction of tungsten carbide in the alloys is 20–22%. (Fig. 2).

Composite materials based on NiAl intermetallic are promising for the use as functional coatings that provide

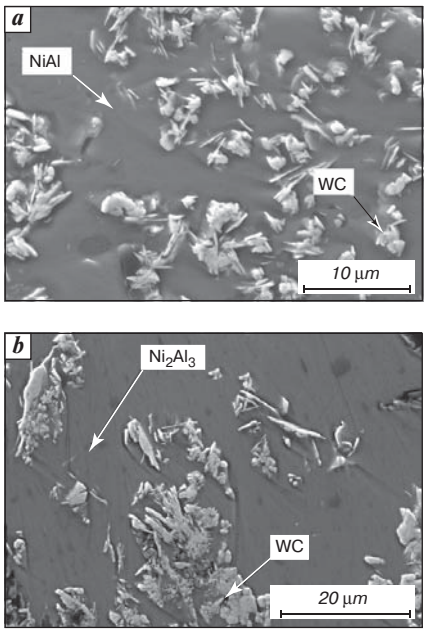

Fig. 2. Microstructure of composite materials: *a* — NiAl – WC; *b* — Ni_2Al_3 – WC

high heat resistance [23]. Positive results have been obtained when forming homogeneous coatings from the synthesized alloys, for example, NiAl – MoB, by magnetron sputtering [24].

Conclusion

It has been established that exothermic conjugate reactions in NiO – Al and WO_3 – C – Al systems rusult in the formation of nickel aluminide alloys with tungsten carbide inclusions. The possibility of the formation of intermetallic compounds of Ni_2Al_3 and NiAl composition depending on the synthesis conditions is evident. It is experimentally proved that the alloys have a composite structure i.e. tungsten carbide inclusions are distributed in the intermetallic matrix. The resulting composite materials have an increased microhardness (9.8 GPa).

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