CELLULAR STRUCTURED ALLOYS

STABILITY OF COMPOSITE MATERIALS NiAl – REFRACTORY METAL WITH CELLULAR STRUCTURE

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The structure and mechanical properties of NiAl – W and NiAl – W – Mo composite materials (CM) obtained by sintering from powders are studied. Comparative analysis of the effect of hot compressive deformation of a compact material at 1000 – 1300°C on the integrity of the microspecimens and of the tungsten shells on NiAl granules in CM with cellular structure is performed. The thermokinetic stability of the grain structure of unalloyed nickel aluminide NiAl and of a NiAl – W composite material with cellular structure is investigated. The temperature of the beginning of recrystallization of the NiAl intermetallic is determined. A map of structural states is plotted in the "temperature - operating time" coordinates for CM with cellular structure. The local chemical composition of the "NiAl – refractory metal" phase boundary is studied in CM with cellular structure and without it. The effect of the structural state of CM on the yield strength in compressive tests at 1000°C is determined. The oxidation resistance at 1000 – 1300°C is studied and a treatment approaching the oxidation resistance of CM with cellular structure at 1000 – 1300°C to the level of high-temperature strength of unalloyed NiAl and of its alloy with 4 wt.% Hf is suggested.

INTRODUCTION

Composite materials with specified combination of properties can be fabricated by methods of powder metallurgy. Deposition of additional layers with different chemical composition on the powder particles and subsequent compaction gives composite materials with cellular structure. After pressing, the cladding coating of the particles forms a cohesive skeleton of a cellular structure and the cells are filled with the material of the powder particles. A refractory composite material obtained in this way on the base of NiAl intermetallic (a tungsten skeleton structure with NiAl filler in the cells) has a higher high-temperature strength than pure NiAl and than refractory $\gamma – \gamma'$ nickel alloys (at 1300°C) and possesses a higher low-temperature ductility than NiAl. At about 13 at.% tungsten such a CM has a contraction of up to 13% (in compressive tests), a yield strength of 50 – 80 MPa at 1300°C (pure NiAl has $\sigma_{0.2} = 8 – 10$ MPa), a specific (per unit mass) creep strength $\sigma_{\%/h}^{1210} = 0.52$ km (against 0.31 km in NiAl), and an oxidation rate (rate of scale growth) of about

20 μm/h at 1200°C [1, 2]. A composite with such properties is a promising structural material for aircrafts and spacecrafts.

The aim of present work consisted in studying the stability of the structure and mechanical properties of composite materials based on NiAl under the action of process (deformation, temperature) and operational (temperature, time, medium) factors.

METHODS OF STUDY

In the studied composite materials tungsten was present either in the form of a three-dimensional continuous skeleton enveloping the grains (powder particles) of NiAl (we call such materials CM with cellular structure) or in the form of isolated grains with a size of 10 – 22 μm.

NiAl powder with stoichiometric composition and particle size of 14 – 16 μm was covered with a layer of tungsten with a thickness of 0.5, 1.0, and 2.0 μm or successively with tungsten (with a thickness of 1 – 1.5 μm) and molybdenum (partially molybdenum carbide) (with a thickness of 1 – 1.5 μm) layers. Then the powder was subjected to hot pressing by different methods, namely, (*A*) in air with heating di-

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TABLE 1. Properties of Materials Based on NiAl

Material	State	Characteristic of the structure	Method of fabrication of compacts	$\sigma_{0.2}^{1000}$, MPa	v_{ox}, μm/h
NiAl	Initial	Equiaxial grains	A	125	2.4
			B	103	2.0
			C	95	2.1
	Annealing at 1200°C, 1 h	No change	A	98	–
	Annealing at 1450°C, 1 h	Grain growth by a factor of 2.5	A	113	–
NiAl – 4% Hf	Initial	Equiaxial grains	A	162	2.2
			B	169	–
NiAl – 9%Nb		Equiaxial grains	A	370	25
NiA – 9%Nb – W		Cellular structure	A	167	57
NiAl – W	Initial	Cellular structure h_c = 0.5 μm (13 at.% W)	C	164	17
		h_c = 1.0 μm (25 at.% W)	A	230	59
		h_c = 2.0 (43 at.% W)	A	240	115
			B	275	–
			C	197	100
	Annealing at 1300°C, 50 h	Cellular structure with h_c = 2.0 μm	A	225	–
	Annealing at 1500°C, 6 min	Decomposition of the cellular structure	A	141	–
	Annealing at 1500°C, 15 min	Decomposition of the cellular structure	A	70	120
	Annealing at 1500°C, 1 h	Decomposition of the cellular structure	A	70	–
	Compressive deformation by 60% at 1200°C	Extended cells in cellular structure with frequent discontinuities in the shell (50 at.% W)	A	–	170
	Initial	Mixture of grains of NiAl and W of the same size:			
		26 at.% W	A	105	–
		45 at.% W	A	153	130
NiAl – W – Mo	Initial	Cellular structure	A	340	200
			B	356	–

Notations: *A*) rapid pressing; *B*) method of fabrication of synthetic diamonds; *C*) gas isostatic pressing (GIP); $\sigma_{0.2}^{1000}$) yield strength in compression (t_{def} = 1000°C); v_{ox}) rate of oxidation at 1200°C; h_c) wall thickness of the cells.

Notation. In all cases of annealing it was performed in vacuum.

rectly by electric current [3], (*B*) in an installation using a method of fabrication of synthetic diamonds [4], and (*C*) by gas isostatic pressing (GIP). The first two methods were fast and powder-saving but inferior to method *C* with respect to the porosity and the content of uncontrolled gas admixtures in the obtained compacts. However, this did not affect significantly the mechanical properties (see Table 1).

A part of the experiments was made for NiAl alloys with 4 wt.% Hf or 9 wt.% Nb. In order to obtain CM with cellular structure a tungsten layer 0.4 μm thick was deposited on the powder particles of alloy NiAl – 9 wt.% Nb. The grain size in all the materials was determined by the method of secants. In the CM with cellular structure the middle of the tungsten (or molybdenum for CM with double-layer coating) layer was assume to be a boundary separating two grains.

Cylindrical specimens 4 – 5 mm in diameter and up to 7 mm high were tested for compression in a 1958U-10-1 uni-

versal testing machine in air at a speed of 1 – 2 mm/min (at a temperature of 20 – 1300°C) with recording the stress-strain diagram. The heating was ensured by direct passage of electric current [5].

Local chemical analysis of the material was made using a Stereoscan-500 scanning electron microscope at an accelerating voltage of 20 kV with the use of a "Link" system for microscopic x-ray spectrum analysis.[2]

Vacuum annealing of compact specimens was performed in a laboratory vacuum furnace with a molybdenum pipe heater 25 mm in diameter and 150 mm long. Vacuum (about 1.3×10^{-2} Pa) was created with the help of a diffusion pump. The temperature in the working zone of the heater was measured using a VR5/20 thermocouple. Maximum devia-

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[2] The phase microscopic x-ray spectrum analysis was performed by V. I. Chizhov.
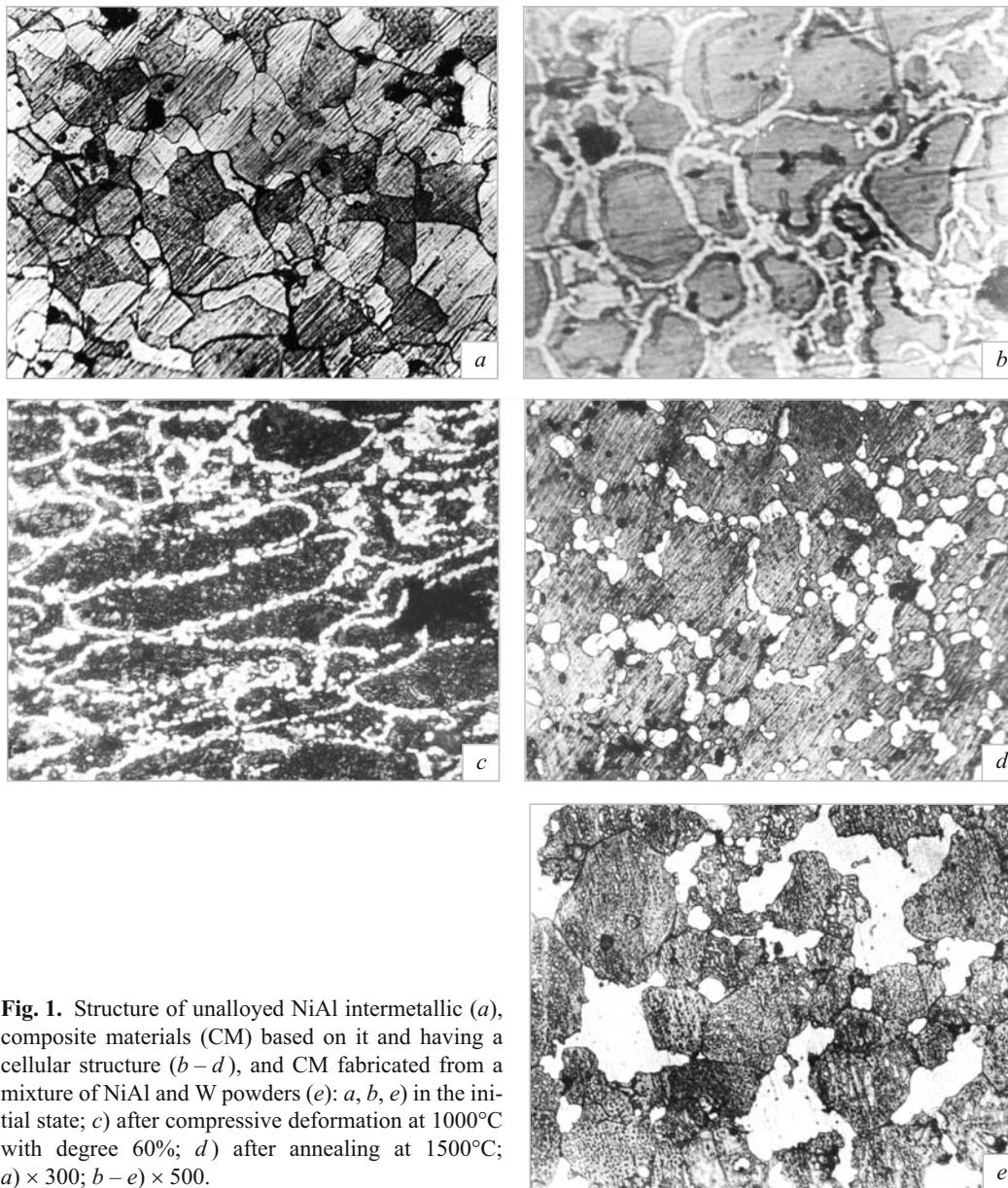
Fig. 1. Structure of unalloyed NiAl intermetallic (*a*), composite materials (CM) based on it and having a cellular structure (*b – d*), and CM fabricated from a mixture of NiAl and W powders (*e*): *a*, *b*, *e*) in the initial state; *c*) after compressive deformation at 1000°C with degree 60%; *d*) after annealing at 1500°C; *a*) × 300; *b – e*) × 500.

tions of the temperature from the specified value in a test did not exceed ± 15°C.

The resistance of the materials to high-temperature oxidation was studied in the process of annealing in air at a temperature of 1000 – 1300°C with a hold of up to 20 h. We analyzed the effects of the method (*A*, *B*, or *C*) of fabrication of the compact specimens, of the special features of the contact between the specimen and the air medium (annealing in an open alundum crucible in a SNOL-type resistance furnace or in an incompletely closed alundum crucible with heating in the furnace of the derivatograph), and of the time and temperature regime in the tests for oxidation resistance. We tested cylindrical specimens with a diameter of 5 – 10 mm and a height of 6 – 3 mm (the area of the surface was 1.5 – 2.5 cm^2). The accuracy of the measurement of their mass was about 10^{-2} g. The kinetics of the oxidation process

was studied using the results of the measurement of the mass of the specimens after annealing. When the annealing was finished and the external layer of the oxides was removed, we determined the loss in the mass of the specimen due to its transition to scale and due to the evaporation of the volatile W and Mo oxides. The data obtained were used for computing the rate of oxidation of the material v_{ox}, i.e., the thickness of the layer "burnt" in 1 h. We also used the data on the density of the material and on the initial surface area of the specimens in the computation.

RESULTS AND DISCUSSION

The structure of the studied materials is presented in Fig. 1. The sizes of the observed grains in the specimens of NiAl and its alloys after compaction corresponded to the di-
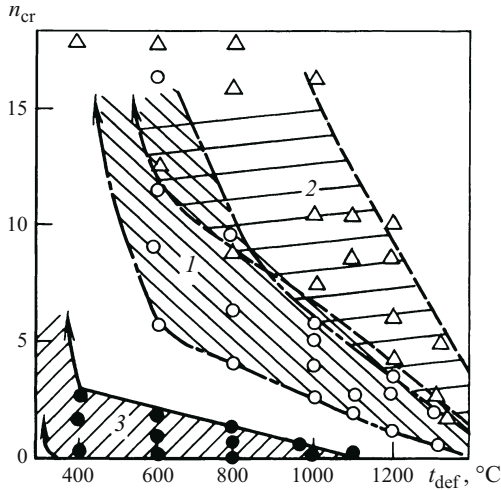
Fig. 2. Dependence of the number of cracks n_{cr} on the side surface of specimens of pure NiAl (regions *1* and *2*) and of a NiAl – W composite ($h_w = 2$ μm) (region *3*) on the temperature of compressive deformation with degree 50 – 60%: *1, 3*) for materials obtained by method *A*; *2*) for materials obtained by method *B*.
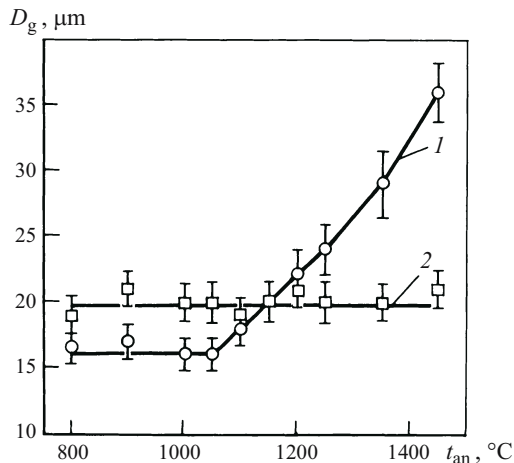
Fig. 3. Dependence of the grain size of unalloyed NiAl (*1*) and of a composite NiAl – W material ($h_W = 2$ μm) with cellular structure (*2*) on the annealing temperature ($\tau = 1$ h).

ameter of the initial powder particles (Fig. 1*a*, *b*, and *e*). In composite materials with cellular structure the body of a cell consisted of one grain (NiAl or its alloy with Nb). The structure of the refractory material on it (with a thickness of 0.4 – 3 μm) was undetectable either by light metallography or by scanning electron microscopy (on polished sections and on fractures).

Hot compressive plastic deformation of specimens at 1000 – 1300°C changes the microstructure and causes the appearance of cracks on the side surface of the specimens. In the structure of pure NiAl and of the CM with cellular structure the thickness of the tungsten layer is 2 μm; after compression with degree about 70% the initially equiaxial shape

of the grains changes for an extended shape. For both alloys the coefficient of grain shape anisotropy increases to 6 – 9 in the center of the specimen, where these changes are the highest, decreases to 2 toward the side surfaces, and remains virtually unchanged at the side surfaces. The coatings on the powder particles crush upon growth in the degree of the deformation (Fig. 1*c*); the number of breaks in the tungsten shell increases to 15 – 20 on the perimeter of the cross section of a grain in the zone of maximum strain (in the initial material this number does not exceed 0.5 – 1.5); compressive deformation with degree 30 – 35% causes the appearance of 6 – 7 breaks in the shells of the grains located in the central part of the specimen.

We chose the total number of visually observable cracks forming on the side surface of the specimen over the perimeter where the broadening is the highest as a microscopic characteristic that describes the capacity of the material to withstand hot plastic deformation without failure at compression. The advantage of the specimens of CM over the pure (without additives) NiAl intermetallic is especially obvious for deformation with degree 50 – 60% ($t_{def} = 1100 – 1300$°C); a specimen of a composite material with cellular structure withstands such deformation without failure (Fig. 2).

The effect of the temperature and the time of annealing on the structure of pure NiAl aluminide and of the CM based on it can manifests itself through changes in the grain size (including recrystallization) and decomposition of the cellular structure. In the pure intermetallic the first features of grain growth in the strained matrix appear after a 1-h hold at 1100°C and the processes of recrystallization develop fully upon heating to 1350°C. The cellular structure of the CM is stable even at 1400°C at a hold of no less that 50 h (Fig. 3). After heating to $t \geq 1450$°C it begins to deteriorate. This requires a hold of no less than 40 h at 1450°C or 6 min at 1500°C. At 1550°C the process begins immediately. During the deterioration of the cellular structure the continuous shell of refractory metal over the boundaries of NiAl grains (which has the form of a continuous net on the surface of the polished section) transforms into a dashed line of fine "drops" (Fig. 1*d*). With growth in the temperature and time of annealing the ordered pattern of the "drops" over grain boundaries of NiAl disappears, and the material melts as a whole upon heating to over 1600°C. We generalize these data in the form of a map of structural states in Fig. 4. The relation between the time τ (in seconds) before the beginning of the deterioration of the cellular structure and the temperature T (in Kelvin degrees) in the "time logarithm – inverse temperature" coordinates can be described by the equation

$$\ln (\tau) = -184.6 + 3.386 \times 10^5 \times 1/T.$$

Extrapolation of this dependence to a temperature of 1400°C and lower temperatures gives a "lifetime" of the cellular structure of about 15,000 h or longer.

High temperatures in the process of compaction cause changes in the chemical composition of the material in the
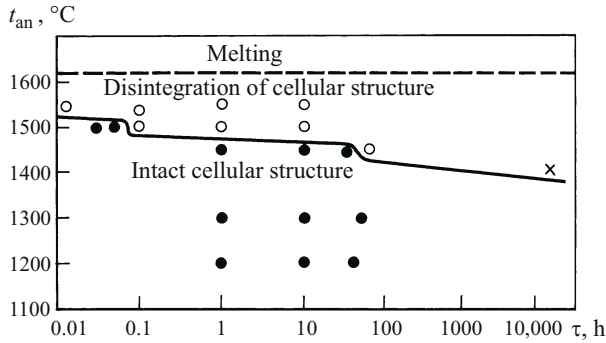
Fig. 4. Map of structural states of a NiAl – W composite material ($h_W = 2$ μm): (●, ○) experimental data; (×) results of extrapolation.

Fig. 5. Distribution of alloying elements (AE) over a cross section of a composite material (h is the distance from the middle of the layer of the refractory metal) with cellular structure before (*a, b*) and after (*c*) its disintegration: *a*) NiAl – W ($h_w = 2$ μm); *b, c*) NiAl – W – Mo.

region of contact of powder particles; Ni (from 10 to 33 at.%) and aluminum (from 15 to 30 at.%) dissolve in the tungsten coat. Dissolution of W in NiAl or interpenetration of W and Mo in materials with many-layer coats on powder particles do not occur (Fig. 5). The formed solid solution of Ni and Al in tungsten (and in the W – Mo alloy in the case of a four-component Ni – Al – W – Mo system) is saturated; a similar qualitative and quantitative distribution of chemical elements is observed in the structural components formed as a result of disintegration of the cellular structure or melting of the entire material (in Fig. 1*c* and *d* the dark regions correspond to NiAl and the light regions correspond a tungsten alloy with Ni and Al). Our data show that chemical compounds or intermetallics do not form as a result of such a unidirectional flow of atoms in the solid body in the region of the NiAl – W interface; an x-ray phase analysis has shown only the presence of NiAl and W lines (plus Mo lines in the CM with a double-layer coat on powder particles). The interface does not bear significant porosity either. The results obtained do not depend on the method of fabrication of the specimens (*A, B,* or *C*).

The results of compressive tests of compact specimens at 1000°C (see Table 1) show that the yield strength of pure NiAl does not change significantly with growth in the annealing temperature (and thus with growth in the grain size), i.e., $\sigma_{0.2}^{1000} = 95 - 125$ MPa. In specimens with cellular structure with powder particles coated with a tungsten layer about 2 μm thick the yield strength decreases inconsiderably in the annealing process (from 240 to 225 MPa) until the cellular structure itself is preserved. When the cellular structure breaks, the yield strength decreases by a factor of $1.7 - 3.4$ to $\sigma_{0.2}^{1000} = 70 - 140$ MPa; these values do not exceed $\sigma_{0.2}^{1000}$ of the CM produced from a simple mixture of NiAl and W powders (Fig. 1*e*).

Tests for oxidation resistance have shown the following. The oxidation kinetics of the studied materials in the specified range of temperatures and holds is almost linear in the initial period of time ($1 - 2$ h). This allowed us to deal with averaged (with respect to the time) values of the oxidation rate v_{ox} (see Table 1).
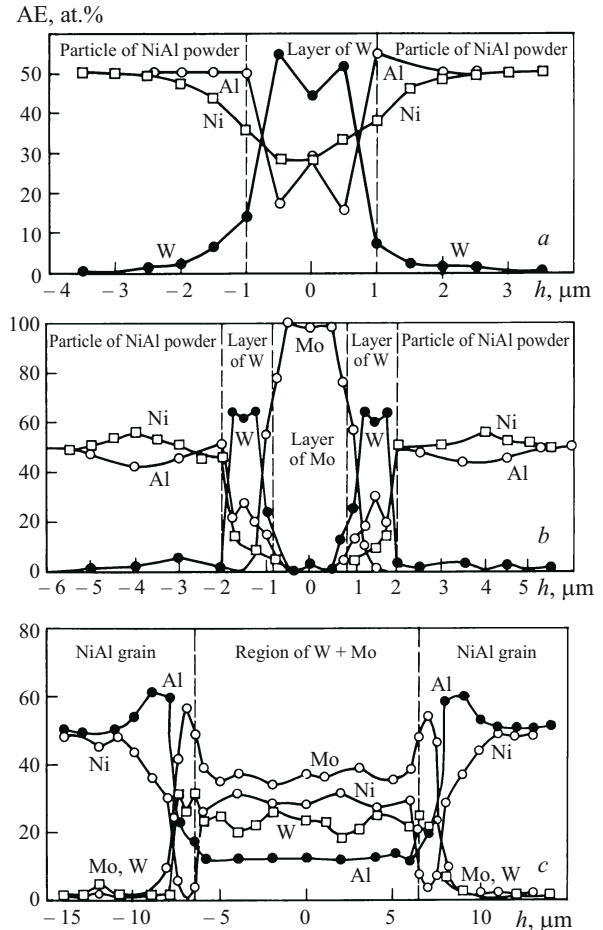
Unalloyed NiAl and its alloy with hafnium have the lowest oxidation rate, i.e., $v_{ox} = 2.1 - 2.4$ μm/h at 1200°C. The scale on the specimens is bound to the metal strongly enough and consists of the Al_2O_3 oxide and $NiAl_2O_4$ spinel. In the alloys with hafnium the scale also bears the HfO_2 oxide. The addition of niobium to the NiAl intermetallic raises the oxidation rate to $v_{ox} = 25$ μm/h. This can be associated with the change in the initial phase composition of the alloy; the compacts fabricated from the powder obtained by mechanical alloying and pressed by the rapid method contain a Ni_3Al intermetallic that has a lower oxidation resistance than NiAl [6, 7].

The introduction of tungsten into the NiAl intermetallic in the form of individual grains or in the form of a continuous net over the boundaries of granules (cellular structure) decreases the oxidation resistance of the material in all cases. At 1200°C the oxidation resistance decreases with growth in the thickness of the tungsten coat h_W on the granules; at $h_W = 0.5$ μm the oxidation rate $v_{ox} = 17$ μm/h and at

$h_W = 2$ μm $v_{ox} = 100 - 115$ μm/h. The scale layer appearing of the CM specimens has poor cohesion with the surface of the metal and consists of Al_2O_3, $NiAl_2O_4$, $AlWO_4$, and $NiWO_4$ compounds. The amount of the $AlWO_4$ and $NiWO_4$ spinels increases with growth in the tungsten content in the alloy. In the CM with composition NiAl – 9 wt.% Nb – W the rate of oxidation at 1200°C is $40 - 76$ μm/h, which is $2 - 3$ times higher than that of the same alloy without tungsten. This high oxidation susceptibility of the composition is accompanied by the appearance of a high amount of WNb_4O_{13} spinel in the scale in addition to $NiWO_4$ and a small amount of $NiAl_2O_4$. The introduction of molybdenum into the CM (in the form of a second layer in the cellular skeleton) increases considerably the oxidation rate to v_{ox} about 200 μm/h, which can be associated with the higher volatility of the molybdenum oxides as compared to tungsten oxides [8]. The scale bears $NiAl_2O_4$, $NiWO_4$, and $NiMoO_4$. Below we present the results of an evaluation of the thickness of the oxide layer hox by the method of metallographic analysis of cross sections of compacts fabricated by rapid pressing and subjected to oxidation at 1300°C for 3 h in a closed crucible.

Material	h_{ox}, μm
NiAl	180
NiAl – W ($h_W = 1$ μm)	220
NiAl – W ($h_W = 2$ μm)	300
NiAl – Nb – W ($h_W = 0.3$ μm)	450
NiAl – W – Mo ($h_W = 1$ μm)	$\gg 500$

Decrease in the porosity of the studied materials promotes growth in their oxidation resistance. GIP reduces the porosity of monolithic specimens by no less than a factor of 3. This decreases the thickness of the scale layer under the same conditions by several times, i.e., to 16 μm for NiAl and to 90 μm for the NiAl – W composite ($h_W = 2$ μm). The oxidation rate decreases simultaneously (from 0.32 to 0.1 μm/h and from 30 to 19 μm/h, respectively).

A fuller contact with an oxygen-bearing medium (annealing in an open crucible) produces a reverse effect, i.e., the oxidation rates of all the materials increase by several times. For example, in a test of the NiAl – W composite ($h_W = 2$ μm) at 1200°C in a closed crucible $v_{ox} = 14$ μm/h, whereas in an open crucible v_{ox} is about 100 μm/h.

"Stage oxidation" is an effective method for raising the oxidation resistance of CM with cellular structure at operating temperatures below 1200°C. A NiAl – W composite with cellular structure ($h_W = 0.5$ μm) preliminarily oxidized at $t \geq 1200$°C has $v_{ox} = 0.4 - 1.5$ μm/h in the process of subsequent operation at 1000 and 1100°C, which is close to the oxidation rate of unalloyed NiAl intermetallic ($v_{ox} = 0.1 - 0.6$ μm/h). We detected primarily a $NiWO_4$ compound on the surface of the specimen and in the scale. On the specimens initially oxidized at 1000 – 1100°C we detected compounds that necessarily contained aluminum (Al_2O_3, $AlWO_4$, $NiAl_2O_4$).

CONCLUSIONS

1. Composite materials (CM) with cellular structure based on NiAl possess higher strength and ductility at 1000 – 1300°C than unalloyed nickel aluminide.

2. The cellular structure of the CM, the bearing component of which is a three-dimensional tungsten skeleton enveloping NiAl grains, is stable in a hold of no less than 15,000 h at a temperature of up to 1400°C. Grain growth in unalloyed nickel aluminide begins after heating to 1400°C.

3. Disintegration of the cellular structure lowers the mechanical properties of the CM to values typical for unalloyed nickel aluminide.

4. The oxidation resistance of the composite materials is lower than that of unalloyed nickel aluminide and of alloy NiAl – 4% Hf. Preliminary oxidation of CM with cellular structure at 1200°C raises their oxidation resistance at 1000 and 1100°C to values typical for unalloyed nickel aluminide.

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