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Effect of Directional Solidification on the Structure and Properties of Ni_3Al-Based Alloy Single Crystals Alloyed with Cr, Mo, W, Ti, Co, Re, and REM

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Abstract—The effect of the solidification rate ($R = 2$, 5, 10, 20 mm/min) at the same solidification gradient ($G = 150$°C/cm) on the structural parameters of single-crystal blade workpieces made of an alloy based on the γ'(Ni_3Al) intermetallic compound and alloyed with cobalt and rhenium apart from chromium, molybdenum, titanium, and rare-earth metal microadditions is studied. The single crystals have a dendritic–cellular structure. Primary γ'-phase precipitates are observed in the interdendritic space of heterophase γ' + γ dendrites. An increase in the solidification rate from 2 to 20 mm/min at a solidification gradient of 150°C/min leads to refinement of all structural constituents by a factor of 1.5–2, with the morphology and the mutual position of the structural constituents being independent of the solidification rate. In experiments with moderate additional alloying with cobalt and rhenium, the yield strength increases by 10–20% and the long-term strength increases by at least 20–25% at a temperature of 900 and 1100°C upon holding for 100 and 500 h. The VKNA-25 alloy single crystals have moderate plasticity (δ = 6–20%) over the entire temperature range (20–1200°C) and have no sharp increase in the plasticity characteristic of a VKNA-1V alloy without cobalt and rhenium. During long-term tests, local raft structure regions misoriented with respect to the tension direction form in γ' + γ dendrites. γ'-Phase nanoparticles precipitate in the γ layers. During tests, refractory-metal-rich nanoparticles of a predominantly acicular–lamellar shape precipitate in dendrite arms.

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INTRODUCTION, FORMULATION OF THE PROBLEM

The works on improving the physicomechanical properties and the service characteristics of cast heterophase γ' + γ alloys, which are based on the γ'(Ni_3Al) intermetallic compound and are intended for long-term operation at temperatures up to 1200–1250°C and short-term operation up to 1300°C, are being developed in the following two main directions: the optimization of alloy compositions and the optimization of the processes of production and heat treatment [1–3].

The strengthening of γ' and γ solid solutions at low and moderate temperatures increases with the difference between the atomic sizes and the electronic structures and alloying elements (AEs) and the metal to be replaced (Ni and/or Al). For example, for the AEs substituting for aluminum, the strengthening increases in the row Cr, V, Ti, Mo, Si, W, Nb, Ta, Zr, and Hf. These elements and Fe and Co also strengthen γ solid solutions. At temperatures $\geq 0.6T_m$, the strength, the fatigue life, and the creep resistance are improved due to the retardation of diffusion processes caused by alloying of Ni_3Al-based alloys with "slow" refractory metals, such as W, Re, Ta, Mo, Nb, Ru, and Hf. The contents of these metals are limited by the alloying-induced increase in the density, their solubility in the γ' and γ solid solutions, and the danger of formation of coarse topologically close-packed (TCP) phase precipitates [4]. Interest in studying the effect of alloying with reaction- and surface-active rare-earth metals (REMs), especially lanthanides, on the structure and properties of heterophase γ' + γ alloys based on the γ'(Ni_3Al) phase has recently been quickened [5–9]. Since the atomic radii of REMs are significantly larger than those of aluminum and, of course, nickel, REMs do not dissolve in the solid solutions based on nickel aluminides γ'(Ni_3Al), NiAl, and γ-Ni. They should be localized in defect structure regions, i.e., interfaces of various kinds, interphase boundaries, and interdendritic space, and form excess phases with nickel, aluminum, and impurity elements. Due to a high surface activity, REMs can decrease the surface tension of a liquid metal and the energy of formation of grain nuclei, increasing their number. REMs should affect the nucleation and growth of crystals during solidification and, hence, the mechanical properties of the solidified alloy. These processes depend substantially on the technological parameters of melting alloys, in particular, the method of introducing the components that differ in the melting temperature, the evaporation temperature, the density, the reactivity, and the solidification conditions, into a charge or a melt [10–12].

The influence of a crystallographic orientation (CO) and the solidification parameters (solidification gradient and rate) on the structure and properties of alloys was studied earlier on an intermetallic Ni_3Al-based VKNA-1V alloy with low contents of refractory metals (Cr, Mo, W), which was made according to the process that ensures a uniform distribution of the alloy components in microvolumes in single-crystal samples [13].

The purpose of this work is to study the changes in the structure and properties of a cast single-crystal VKNA-type alloy based on the $\gamma'(Ni_3Al)$ intermetallic compound that are caused by additional (apart from Cr, Mo, W, Ti) alloying with cobalt, rhenium (to strengthen the γ solid solution), and REM (La and Sc microadditions modify a structure).

EXPERIMENTAL

The chemical composition of the base VKNA-25 alloy is as follows (wt %): Ni base, 8.37 Al, 5.7 or 5.14 Cr, 3.03 W, 5.14 Mo, 0.52 Ti, 3.5–4.5 Co, 1.6 Re, 0.8 Si, 0.03 C, and 0.015 La. The impurity contents are as follows (wt %): 0.005 S, 0.005 P, 0.001 Pb, 0.0005 Bi, 0.003 Sn, and 0.003 Sb. We additionally introduced 0.2–0.3 wt % REM in the alloy charge. The base composition was chosen so that a natural eutectic composite structure, which consists of 85–90 vol % γ' and 15–10 vol % γ and is thermally stable up to the near-melting temperatures, formed in it.

Based on the studies of a $\gamma'(Ni_3Al)$-based VKNA-1V alloy [13], we decided to investigate only [001] and [111] single crystals, since [011] single crystals have lower strength and hot strength characteristics. To grow single crystals by high-gradient directional solidification (HGDS), we chose a temperature gradient $G = 150°C/cm$ during solidification, which allowed us to form a more homogeneous structure than the structure that forms during HGDS at $G = 60–80°C/cm$.

In this work, we studied single crystals grown at a solidification rate $R = 2$, 5, 10, and 20 mm/min.

Alloy charge workpieces were melted upon vacuum induction melting (VIM) in a furnace with a basic lining. After controlling the chemical composition, the cast workpieces were remelted by VIM for subsequent HGDS. The rods after HGDS had a diameter of 16 mm and a length of 170–180 mm, had no structural macroboundaries, and met the following conditions: the deviation of a given CO is ≤10°, and the grain misorientation is ≤6°. The microstructure of the rods was analyzed on an Olympus GX51 optical microscope and an LEO 1420 scanning electron microscope (SEM). The mechanical properties of the rods were determined by standard techniques. We performed long-term high-temperature tests to determine the fatigue life on a computer-assisted ZST2/3-VIET bench according to the requirements of State Standard GOST 10145 “Metals. Long-term strength test technique,” GOST 3248 “Metals. Creep test technique,” and ASTME139 “Generally accepted technique for creep, creep to failure, and long-term strength tests of metallic materials” using solid cylindrical specimens with a gage portion diameter and length of 5 and 25 mm, respectively. To remove mechanical stresses, the specimens were annealed at 1150°C for 1 h. The experimental points achieved upon short-term tests were averaged over at least three specimens. When the long-term strength was determined at a temperature of 900, 1000, 1100, and 1200°C for 100, 500, and 1000 h, each experimental point was obtained by averaging over at least ten specimens.

RESULTS AND DISCUSSION

Figures 1–3 show the characteristic structures of [001] and [111] VKNA-25 alloy single crystals grown at various temperature gradients and solidification rates.

In a longitudinal section of the [001] single crystals, primary dendrite arms correspond to the [001] direction and are extended along a heat flow throughout almost the entire ingot (sample) length. Secondary dendrite arms are located across a heat flow and, hence, are less developed: their rows form along (100) and (010) planes, and it is seen in a cross section that they are perpendicular to each other (Figs. 1a, 1b, 1d, 1e). The [111] single crystals have no dendrite arms predominantly developed in a certain direction. When such a crystal grows in the same [001] direction, primary dendrite arms alternate with secondary dendrite arms or they transform into each other. As a result, the dendritic structure acquires the shape of a three-dimensional network with a cell size corresponding to the dendrite arm spacing. The ordered arrangement of dendrite arms in (001) planes manifest themselves in a cross polished section of a [111] single crystal in the form of three systems of [011] lines intersecting at an angle of 60° and forming equilateral triangles (Fig. 1g). Three systems of lines are also visible in a longitudinal (110) polished section; however, two of them are parallel to each other and the third system is perpendicular to them. The same dependence of the morphology of dendrite arms on the orientation of a single crystal is observed for an Ni_3Al-based VKNA-1V alloy [13] and fcc nickel superalloys [14].

The dendrites that form in the VKNA-25 alloy single crystals grown upon solidification at a gradient of 150°C/cm have the following two-phase structure: γ-phase precipitates are uniformly distributed in a

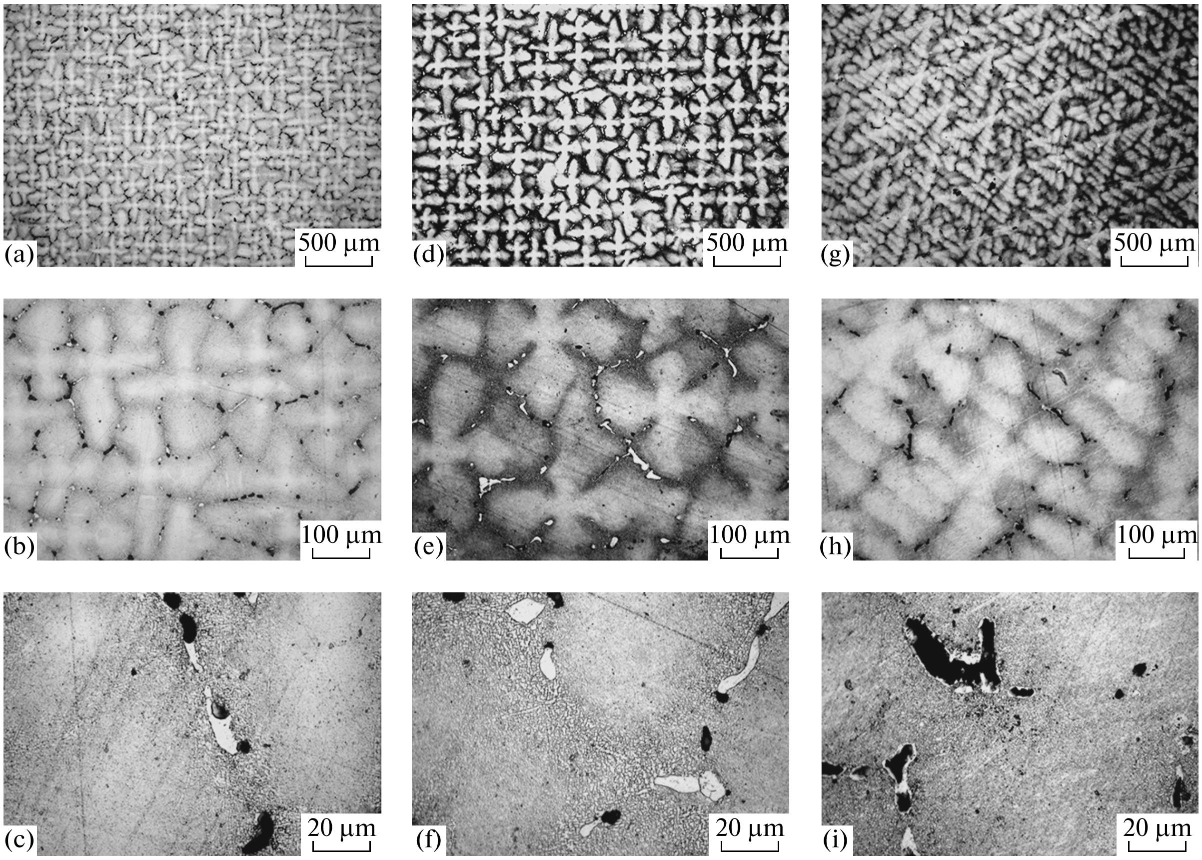

Fig. 1. (a–c) Microstructures in the cross section of [001] VKNA-25 alloy single crystals, R = 10 mm/min; (d–f) [001], R = 5 mm/min; and (g–i) [111], R = 5 mm/min. Optical microscopy.

γ' matrix and form a network of discontinuous layers, and coarse γ'(Ni_3Al)-phase precipitates (primary precipitates having formed upon solidification) free of γ layers are uniformly distributed over the cross section in the interdendritic space (Figs. 1c, 1f, 1i, 2a, 2d, 2e, 3a, 3b, 3d, 3e). Some γ'(Ni_3Al)-phase regions (primary precipitates) have a higher etching ability as compared to the base material volume (Figs. 1c, 1f, 1i, 2a, 2d, 3a, 3b, 3d, 3e), which is likely to be related to the formation of nonequilibrium inclusions (probably, β(NiAl) phase) with a high aluminum content in them during solidification. The volume fraction of primary γ'(Ni_3Al)-phase precipitates in the samples cut from different sections along the single crystal length oscillates in the range 3–4 vol % and does not depend on the solidification rate. The main differences in the structures of the samples grown at different solidification rates concern the structural constituent sizes (Table 1). Note that the sizes of the γ' regions between γ layers are significantly larger than those in dendrite arms (Figs. 2b, 2c, 2e, 2f, 3b, 3c, 3e, 3f; Table 1).

Table 1. Sizes of the structural constituents in [001] and [111] VKNA-25 alloy single crystals grown at a gradient G = 150°C/min and various solidification rates R (mm/min)

Structural constituent	R = 2, CO [111]	R = 5, CO [001]	R =10, CO [001]	R = 20, CO [111]
Primary dendrite arm spacing λ, μm	250–260	220–230	165–175	160
Primary γ'_{prim} precipitate size, μm	14–16	9–11	7.5–8.2	6.0–7.4
Size of γ' regions between γ layers in the interdendritic space, μm	1.3–1.5	~1	~0.7	0.5–0.6
The same in dendrite arms, μm	0.6–0.7	0.35–0.5	~0.35	~0.25

The scatter of the values reflects the difference between the structural constituent sizes in samples cut from different sections along the length of single crystals grown at various solidification rates R.

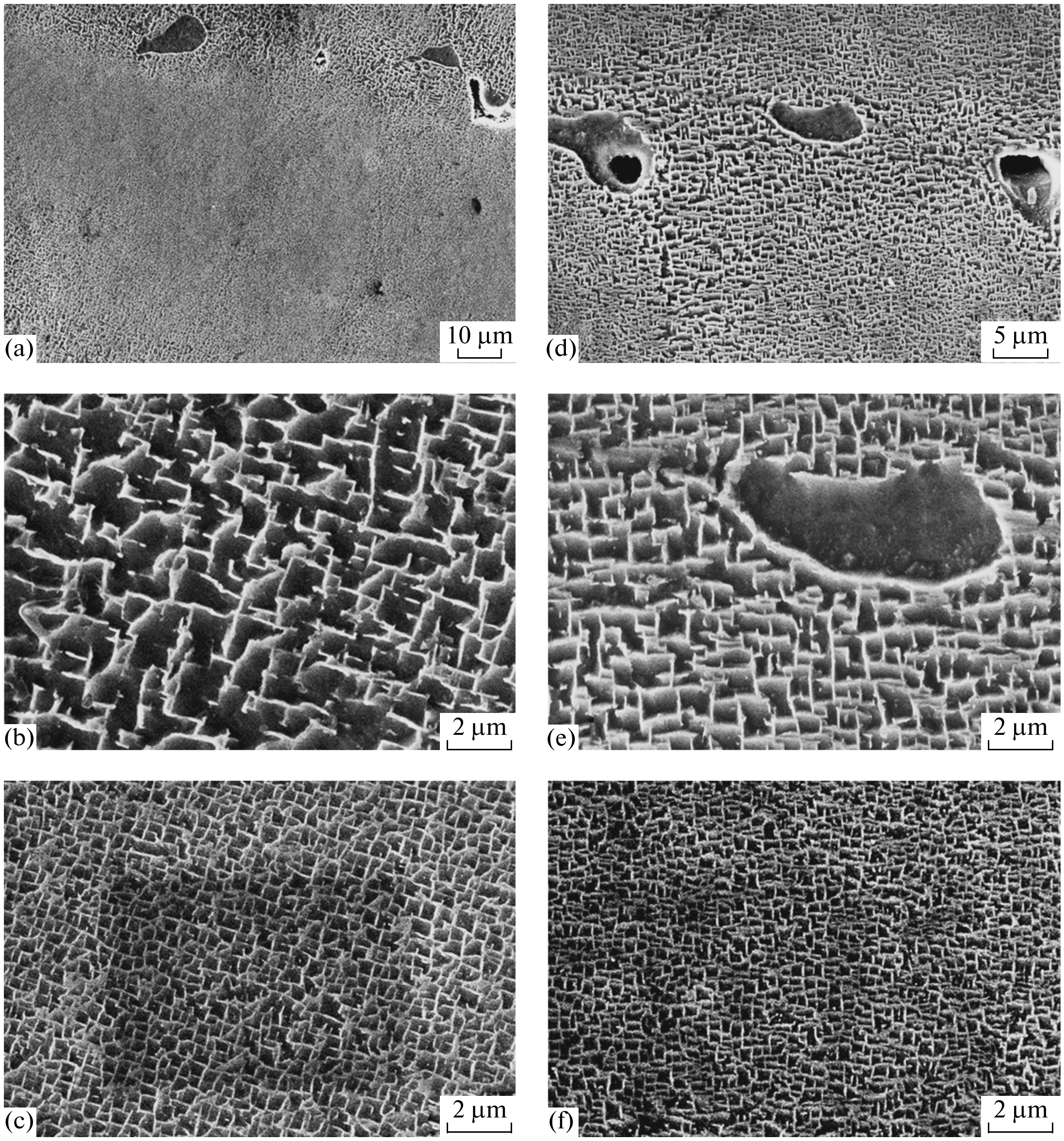

Fig. 2. SEM images of the microstructures of [001] VKNA-25 alloy single crystals at R = (a–c) 5 and (d–f) 10 mm/min in the interdendritic space of γ' + γ dendrites; (a, b, d, e) primary γ'-phase precipitates; and (c, f) γ' + γ dendrite arms.

According to the data in Table 1 and Figs. 1–3, an increase in the solidification rate from 2 to 20 mm/min (by an order of magnitude) at a constant solidification gradient leads to refinement of all structural constituents by 1.5–2 times, and the morphology and the relative position of the structural constituents are independent of the solidification rate.

When studying the strength and the high-temperature strength of other Ni_3Al-based alloys, we found that they were maximal for [111] single crystals [7, 8, 11, 13]. Therefore, in this work we focused on an analysis of single crystals with this CO. In [13], we showed that the [111] single crystals grown by HGDS at a solidification gradient G = 150°C/min and a solidification rate R = 10 mm/min had the following important properties: a high high-temperature strength over the entire temperature range under study, a high low-temperature plasticity, a moderate high-temperature plasticity, and no plasticity drop at 800°C (which is characteristic of single crystals with other COs). As a result, we were able to reduce the experiment volume and to test the strength properties of an alloy with rhenium and cobalt using its [111] single crystals.

A comparison of the mechanical properties of the VKNA-25 alloy [111] single crystals additionally alloyed with rhenium and cobalt with the properties of a VKNA-1V alloy with refractory metal additions showed that alloying with rhenium and cobalt

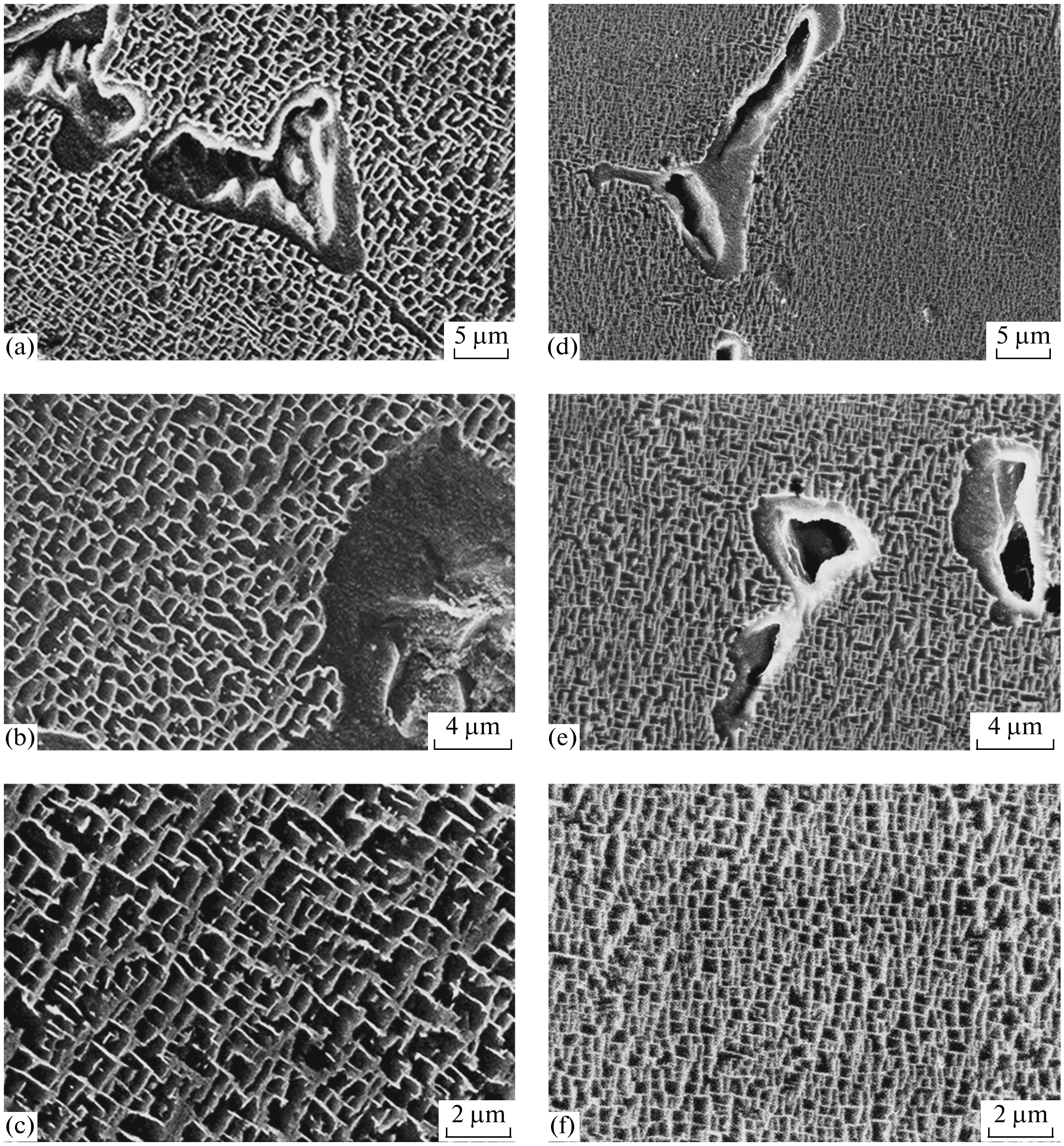

Fig. 3. SEM images of the microstructures of [111] VKNA-25 alloy single crystals at R = (a–c) 2 and (d–f) 20 mm/min in the interdendritic space of $\gamma' + \gamma$ dendrites; (a, b, d, e) primary γ'-phase precipitates; and (c, f) $\gamma' + \gamma$ dendrite arms.

increases the yield strength by 10–20% [13] (Table 2). As the temperature increases, the relative elongation grows; however, the single crystals have a moderate plasticity (δ = 6–20%), which is retained over the temperature range 20–1200°C, and the sharp increase in the plasticity that is characteristic of the low alloy, especially of single crystals with other COs, is absent. This change of the properties upon alloying should increase the shape stability of products and the creep resistance at these temperatures.

When studying a low-alloyed Ni_3Al-based alloy without rhenium and cobalt, we showed that a change in the solidification gradient in the range G = 60–150°C/cm weakly influenced the long-term strength at 100 and 500 h [13]. Therefore, in this work we performed long-term tests of the single crystals grown at a gradient G = 150°C/cm. The solidification rate (R = 10 mm/min) was chosen to ensure the economic efficiency of the process and the formation of stable structures during solidification.

The following changes occur in the structure of the material in the course of long-term strength tests performed at high temperatures under stressed conditions during long-term holding (Fig. 4).

During long-term tests, local raft structure regions misoriented with respect to the tension direction form in $\gamma' + \gamma$ dendrites (Figs. 4a, 4b). γ'-Phase nanoparticles (20–400 nm) precipitate in γ layers (Figs. 4c, 4d).

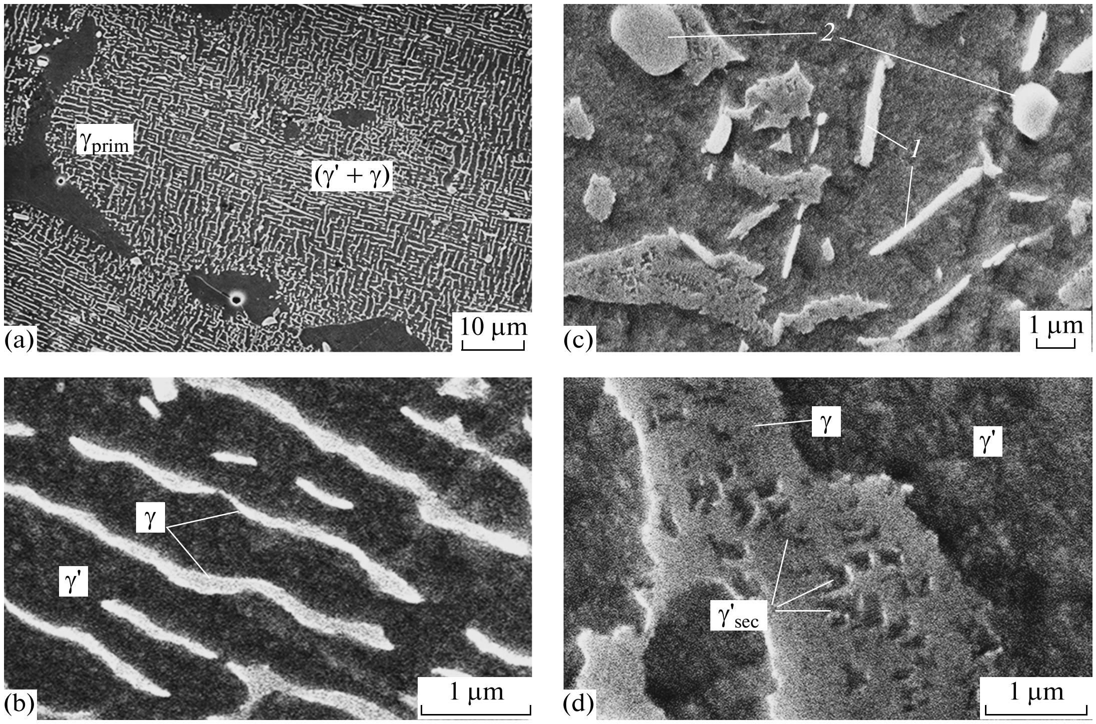

Fig. 4. Microstructure of a [111] VKNA-25 alloy single crystal with 0.015 wt % La after tests at a temperature of 1100°C and a load of 50 MPa for 1400 h (sample did not fail): (a) dendrite, (b) local raft structure region, (c) region with (*1*) acicular and (*2*) rounded TCP phase precipitates, and (d) secondary γ'-phase precipitates in γ layers.

During tests, disperse particles of an acicular–lamellar shape of a variable composition enriched in refractory metals (in at %, up to 15 Cr, up to 20 Mo, up to 15 W, and up to 30 Re) and having a high nickel content (up to 45 at %) and 8 at % Co precipitate in dendrite arms (Figs. 4a, 4c). Rounded particles containing up to 18 at % Cr, ≤35 at % Mo, ≤7 at % W, and ≤14 at % Re; a high nickel content (up to 50 at %); and 8 at % Co are also detected (Fig. 4c). Additional investigations are necessary to identify these phases completely.

Table 2. Mechanical properties of [111] VKNA-25 alloy single crystals

T_{test}, °C	σ_u	$\sigma_{0.2}$	δ	φ
	MPa		%	
20	1070–1120	830–880	6–10	6–19
800	910–950	900–910	9–11	9–11
900	680–730	610–660	5–17	7–20
1000	520–550	420–510	7–21	7–22
1100	360–390	340–370	6.5–9.5	16–19
1200	150–170	170–180	11–20	20–39

The long-term strengths of VKNA-25 alloy single crystals with 0.015 wt % La are given in Table 3, and the data on the effect of the introduction of REMs in a charge on the fatigue life of the alloy (τ_{fail}) are presented in Table 4.

A comparison of the long-term strengths of the low-alloyed VKNA-1V alloy [13] and the alloy with cobalt and rhenium additions shows that moderate alloying with cobalt and rhenium increases the long-term strength by at least 20–25% at a temperature of 900 and 1100°C for 100 and 500 h.

Figure 5 illustrates the effect of the temperature and the REM content on the long-term strength and the fatigue life of VKNA-25 alloy single crystals.

According to the data in Table 4 and Fig. 5, an increase in the REM content during VIM increases

Table 3. Long-term strength of [111] VKNA-25 alloy single crystals with 0.015 wt % La

T_{test}, °C	σ_{100}	σ_{500}	σ_{1000}
	MPa		
900	440	360	330
1100	125	95	85
1200	60	40	–

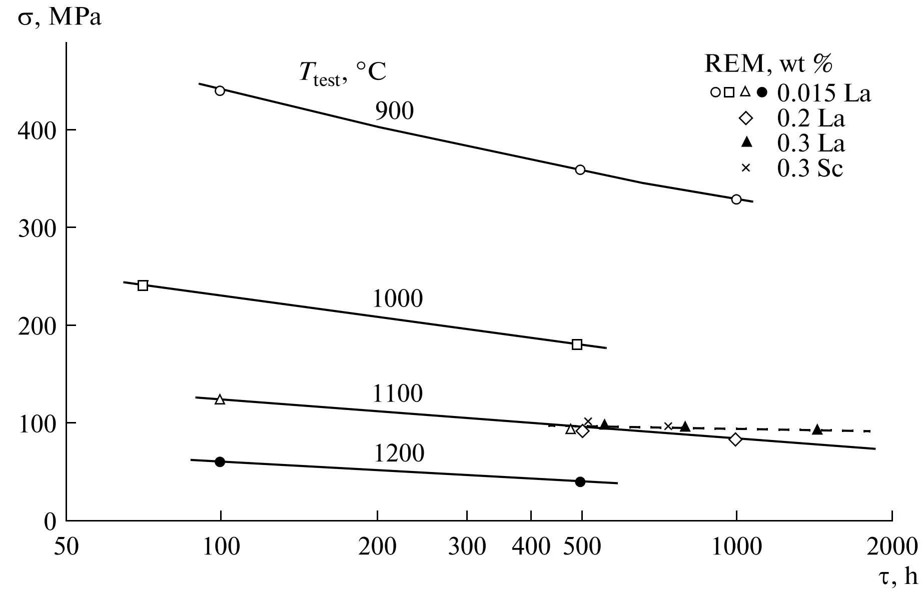

Fig. 5. Effect of the test temperature (numerals at the curves) on the long-term strength of [111] VKNA-25 alloy single crystals with various REM contents (G = 150°C/cm, R = 10 mm/min).

the fatigue life and the long-term strength of the alloy at 1100°C. An increase in the lanthanum content from 0.015 to 0.2 wt % increases the fatigue life by three times at a temperature of 1100°C and the same stress level (95 MPa; see Table 4). The introduction of 0.3 wt % La or Sc is less effective: the fatigue life increased by a factor of 1.7 in the case of lanthanum.

These data demonstrate that the [111] VKNA-25 alloy single crystals alloyed with REM microadditions and grown at a gradient G = 150°C/cm and R = 10 mm/min have the set of properties (high-temperature strength over the entire temperature range under study, moderate high-temperature plasticity) that makes them promising for the working and nozzle blades in a gas turbine engine (GTE).

Table 4. Fatigue life of [111] VKNA-25 alloy single crystals with various REM contents

REM, wt %	T_{test}, °C	σ, MPa	t_{fail}, h
0.015 La	1000	240	71.2
0.015 La	1000	180	491
0.015 La	1100	95	480
0.2 La	1100	95	1430
0.3 La	1100	95	800
0.3 La	1100	100	563
0.3 Sc	1100	100	519
0.3 Sc	1100	95	737

CONCLUSIONS

(1) We studied the effect of the solidification rate (R = 2, 5, 10, 20 mm/min) at the same solidification gradient (G = 150°C/cm) on the structural parameters of single-crystal blade workpieces made of an alloy based on the γ'(Ni_3Al) intermetallic compound and alloyed with cobalt and rhenium apart from Cr, Mo, W, Ti, and REM microadditions.

(2) It was found that an increase in the solidification rate from 2 to 20 mm/min at a solidification gradient of 150°C/min leads to refinement of all structural constituents by a factor of 1.5–2, with the morphology and the mutual position of the structural constituents being independent of the solidification rate.

(3) The influence of temperature and alloying on the long-term strength and the fatigue life of the alloy was studied. It was shown that moderate additional alloying with cobalt and rhenium increased the yield strength by 10–20% and the long-term strength by at least 20–25% at a temperature of 900 and 1100°C upon holding for 100 and 500 h.

(4) The VKNA-25 alloy single crystals that have moderate plasticity (δ = 6–20%) over the entire test temperature range (20–1200°C) exhibit no sharp increase in the plasticity characteristic of the alloy without cobalt and rhenium.

(5) The set of strength properties of the [111] VKNA-25 alloy single crystals grown at a solidification gradient G = 150°C/cm and a solidification rate R = 10 mm/min makes them promising for the working and nozzle blades in GTE.

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REFERENCES

1. O. A. Bazyleva, E. G. Arginbaeva, and E. Yu. Turenko, "High-temperature intermetallic alloys for GTE parts," Aviatsionnye Materialy i Tekhnologii, No. 3, 26–31 (2013).
2. K. B. Povarova, N. K. Kazanskaya, V. P. Buntushkin, V. G. Kostogryz, V. G. Bakharev, V. I. Mironov, O. A. Bazyleva, A. A. Drozdov, and I. O. Bannykh, "Thermal structural stability of an Ni_3Al-based alloy and its application for blades in small gas-turbine engines," Russian Metallurgy (Metally), No. 3, 269–274 (2003).
3. O. A. Bazyleva, E. G. Arginbaeva, and E. Yu. Turenko, "Ni_3Al-based intermetallic alloys," in *All Materials. Encyclopedic Handbook* (Nauka i Tekhnologii, Moscow, 2012), Vol. 5, pp. 27–29.
4. K. B. Povarova, "Physicochemical principles of developing thermally stable alloys based on transition metal aluminides," Materialovedenie, No. 12, 20–27 (2007); No. 1, 60–67 (2008).
5. K. B. Povarova, N. K. Kazanskaya, A. A. Drozdov, and A. E. Morozov, "Rare-earth metals (REMs) in nickel aluminide–based alloys: I. Physicochemical laws of interaction in the Ni–Al–REM and Ni_xAl_y–REM–AE (alloying element) systems," Russian Metallurgy (Metally), No. 1, 46–51 (2008).
6. K. B. Povarova, A. A. Drozdov, N. K. Kazanskaya, A. E. Morozov, Yu. R. Kolobov, T. N. Vershinina, and E. V. Kozlov, "Rare-earth metals (REMs) in nickel aluminide–based alloys: II. Effect of a REM on the phase composition of a multicomponent Ni_3Al-based alloy," Russian Metallurgy (Metally), No. 5, 410–418 (2008).
7. K. B. Povarova, O. A. Bazyleva, N. K. Kazanskaya, and A. A. Drozdov, "Rare-earth metals in nickel aluminide–based alloys: III. Structure and properties of multicomponent Ni_3Al-based alloys," Russian Metallurgy (Metally), No. 2, 154–159 (2009).
8. K. B. Povarova, A. A. Drozdov, N. K. Kazanskaya, O. A. Bazyleva, M. V. Kostina, A. V. Antonova, and A. E. Morozov, "Influence of rare-earth metals on the high-temperature strength of Ni_3Al-based alloys," Russian Metallurgy (Metally), No. 1, 48–56 (2011).
9. V. V. Sidorov, V. E. Rigin, D. V. Zaitsev, and A. V. Goryunov, "Formation of a nanostructured state in a cast high-temperature alloy upon its microalloying with lanthanum," VIAM Transactions, No. 1 (2013). http://viam-works.ru/ru/articles?year=2013&num=1. Cited November 4, 2014.
10. K. B. Povarova, O. A. Bazyleva, N. K. Kazanskaya, and A. A. Drozdov, "Ni_3Al-based cast alloys and a method of their smelting," Zagotovit. Proizv., No. 1, 29–35 (2010).
11. O. A. Bazyleva, A. A. Drozdov, K. B. Povarova, N. K. Kazanskaya, A. E. Morozov, and M. A. Samsonova, "Structural high-temperature Ni_3Al-based alloys: manufacture, structure, and properties," Materialovedenie, No. 4, 39–48 (2011).
12. K. B. Povarova A. A. Drozdov, O. A. Bazyleva, Yu. A. Bondaremko, M. A. Bulakhtina, E. G. Arginbaeva, A. V. Antonova, A. E. Morozov, and D. G. Nefedov, "Effect of the method of producing Ni_3Al-based alloy single crystals on the macro- and microhomogeneity of component distribution, structure, and properties," Russian Metallurgy (Metally), No. 5, 380–391 (2014).
13. K. B. Povarova, A. A. Drozdov, Yu. A. Bondarenko, O. A. Bazyleva, M. A. Bulakhtina, A. E. Morozov, and A. V. Antonova, "Effect of directional solidification on the structure and properties of Ni_3Al-based alloy single crystals alloyed with W, Mo, Cr, and REM," Russian Metallurgy (Metally), No. 1, 545–550 (2014).
14. R. E. Shalin, I. L. Svetlov, E. B. Kachanov, V. N. Toloraiya, and O. S. Gavrilin, *Single Crystals of Nickel Superalloys* (Mashinostroenie, Moscow, 1997).

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