ISSN 2075-1133, Inorganic Materials: Applied Research, 2019, Vol. 10, No. 1, pp. 220–225. © Pleiades Publishing, Ltd., 2019.
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The Influence of Sulfur, Phosphorus, and Silicon Impurities on Structure and Properties of Single Crystals of Nickel Heat-Resistant Alloys

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Received February 27, 2018

Abstract—Structural modifications in single crystals of nickel heat-resistant alloys with increased content of sulfur, phosphorous, and silicon are described. A negative influence of these impurities on long-term and fatigue strength at operating temperatures has been demonstrated using large test bases.

Keywords: heatresistant alloy, single crystal, structure, properties, impurities, sulfur, phosphorus, silicon

DOI: 10.1134/S2075113319010234

INTRODUCTION

An important task of aviation engine manufacturing is increasing the operating temperature of gas and the engine lifetime. At present, an efficient solution of this problem is application of blades with single-crystal structure in gas turbine engines [1].

However, as demonstrated by domestic and foreign experience, high quality blades with faultless single crystal structure can be produced only on the basis of alloys with ultralow content of harmful impurities, gases, and nonmetallic inclusions. On one hand, this is attributed to the fact that impurities are a nucleation source of parasitic grains, that is, they prevent growth of single crystal of predetermined crystallographic orientation, and on the other hand, they are concentration centers of strains which initiate crack nucleation upon operation of blades.

Analysis of publications demonstrates that the most harmful impurities negatively affecting the structure and properties of polycrystalline alloys are sulfur, phosphorus, and silicon [2–4]. Sulfur combines with alloy components into sulfides which concentrate stresses and decrease long-term and fatigue strength as well as plasticity of alloys [5]. Phosphorus is concentrated in interdendritic regions and forms a phosphorus-containing phase which is the dominant site of formation and propagation of cracks, which accelerates destruction of the alloy at high temperatures [6, 7]. Silicon increases the amount of eutectic γ' phase and promotes formation of lamellar carbides, which negatively affects long-term strength of alloys at higher temperatures and leads to formation of TCP phases during operation [8].

Meanwhile, upon smelting of alloys, these impurities are inevitably captured from blend materials and phosphorus is uncontrollably transferred into the melt from the lining of the smelting crucible containing up to 4% P_2O_5.

In contrast to equiaxial melting, during oriented solidification of monocrystalline alloys owing to prolonged contact of alloy with the ceramic mold and rod paste containing free (unbound) SiO_2, the melt is saturated with silicon, especially carbon alloys [9].

It should be mentioned that all previous studies of the influence of aforementioned impurities on structure and properties were carried out only on alloys with equiaxial structure where the impurities segregate onto the grain boundaries and defects of crystalline structure. Behavior of the impurities in single crystals of nickel heat-resistant alloys (NHRA), that is, without high angle boundaries, has not been studied up to now.

This work is aimed at study of the influence of sulfur, phosphorus, and silicon on the structure and properties of single crystals (NHRA).

EXPERIMENTAL

Russian carbon-free monocrystalline nickel heat-resistant alloys (MNHA) were studied: ZhS36-VI, VZhM4-VI, and VZhM5-VI. Their compositions are summarized in Table 1.

The alloys were smelted in an UVNS-4 vacuum induction furnace (VIAM-2002). Some batches were smelted with addition of S, P, and Si.

Table 1. Nominal chemical composition of the considered MNHA

Alloy	Ni	C	Cr	Co	Mo	W	Re	Ru	Nb	Al	Ti	Ta
ZhS36-VI*	Base	≤0.015	4.0	7.0	1.6	11.75	2.05	–	1.1	5.85	1.1	–
VZhM4-VI**	Base	≤0.008	2.7	6.0	4.0	4.0	6.0	4.0	–	6.0	–	4.5
VZhM5-VI***	Base	≤0.015	4.5	9.0	1.9	6.0	3.75	–	–	5.95	0.8	6.0

*RF Patent no. 1513934, dated April 10, 1995.
**RF Patent no. 2293782, dated February 20, 2007.
***RF Patent no. 2318030, dated February 27, 2008.

The obtained blend pieces were used for casting of single crystals with crystallographic orientation [001] by the LMC (liquid metal cooling) method using a UVNK-9A commercial facility.

The sulfur content was measured by the IR method using a Leco CS-600 gas analyzer; the contents of silicon and phosphorus were measured by mass spectrometry using an ICAPQ inductively coupled plasma spectrometer equipped with a NWR 266 laser sampling device.

The microstructure and local chemical composition were analyzed using a Hitachi SU 8010 scanning electron microscope equipped with an EDS X-Max80 X-ray microanalyzer.[1]

The distribution of alloying elements and impurities in the structure of single crystals was studied using a Tecnai F20 S-TWIN transmission electron microscope equipped with an EDS X-Max80 energy dispersion analyzer.[2]

The long-term strength was tested in accordance with Russian State Standard GOST 10145 using a ZST2 machine (Schenck 3-VIET) on samples produced of thermally treated monocrystalline pieces. The low-cycle fatigue was tested in accordance with GOST 25.502 at the coefficient of asymmetry $R = 0.1$ and loading frequency of 1 Hz using a PSB-10 machine (Schenck).

RESULTS AND DISCUSSION

The studies of the microstructure of single crystals (NHRA) with varying content of sulfur, phosphorus, and silicon alloyed with lanthanum demonstrated the following:

(1) In single crystals of ZhS36-VI alloy with increased sulfur content, compounds on the basis of titanium sulfide are formed located in the vicinity of the eutectic γ' phase (Fig. 1a), while, upon alloying with lanthanum, sulfides on the basis of lanthanum are formed (Fig. 1b), which are retained after total heat treatment (THT) (Fig. 1c).

(2) In single crystals of VZhM5-VI alloy with increased phosphorus content (0.025 wt %), a white phase on the basis of hard melting metals (W and Re) is detected, around which during heat treatment (HT) there occurs fusing (Fig. 2). In samples with phosphorus content of 0.014 wt %, there are no traces of fusing around similar phases of HT, and at phosphorus content up to 0.010 wt %, no white phases are observed in the structure.

(3) in single crystals of VZhM4-VI alloy with increased silicon content (0.27 wt %), an increased amount of eutectic γ' phase is observed with formation of silicon enriched regions around it (Fig. 3a). After total heat treatment, the microporosity in such alloy increases, the structure is roughened, and a nonuniform distribution of the γ' phase in interdendritic segments is observed (Figs. 3b, 3c).

Tests of the mechanical properties demonstrated the following:

(1) Upon tensile testing of single crystals of ZhS36-VI alloy for long-term strength for 40 h, no negative influence of sulfur and phosphorus was detected; however, in the case of testing for 500 h, the lifetime of single crystals with increased content of impurities decreases by 1.3 and 1.15 times, respectively (Table 2).

(2) Upon tests of low-cycle fatigue (LCF) at $T = 900°C$, $\sigma = 980$ MPa, a dependence between the sulfur content and the average number of cycles to failure is observed: the lower the content of impurities, the higher the number of cycles (see Table 2).

(3) The tests of mechanical properties of single crystals of VZhM4-VI alloy demonstrated that silicon similar to sulfur and phosphorus negatively affects the long-term strength. It is established that, at a silicon content from 0.04 to 0.19, the long-term strength is within the range of specifications; the minimum value is at 0.19 wt %; and at 0.27 wt % of silicon in the alloy, the long-term strength was not within the specified range (Fig. 4).

Analysis of the microstructure of destroyed samples demonstrated the following:

(1) In VZhM4-VI alloy with increased phosphorus content (0.019 wt %), upon tests for long-term strength at $T = 1100°C$, $\sigma = 137$ MPa, the coagulation of the strengthening γ phase is more intense (Figs. 5a, 5b).

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[1] The studies were performed in cooperation with E.B. Chabina and E.V. Filonova.

[2] The studies were performed in cooperation with D.V. Zaitsev.

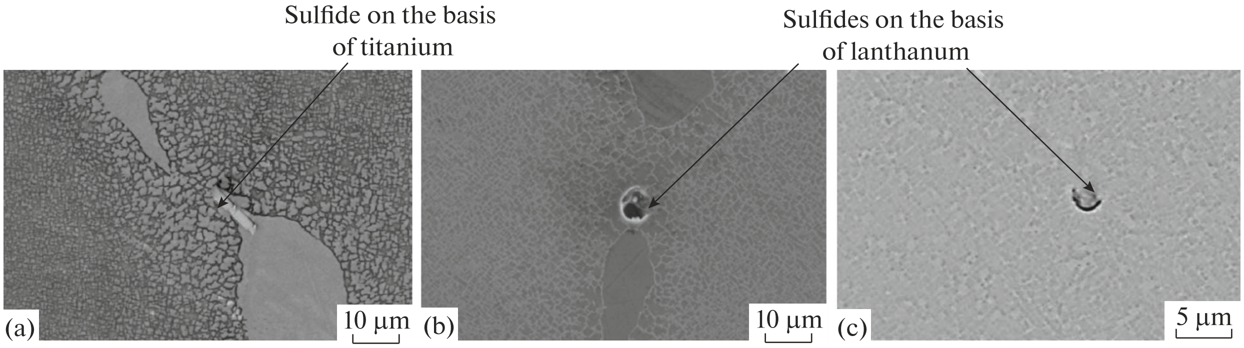

Fig. 1. Microstructure of single crystal of ZhS36-VI alloy: (a) 0.0072% S, as cast; (b) 0.0007% S, as cast; (c) 0.0007% S, after THT.

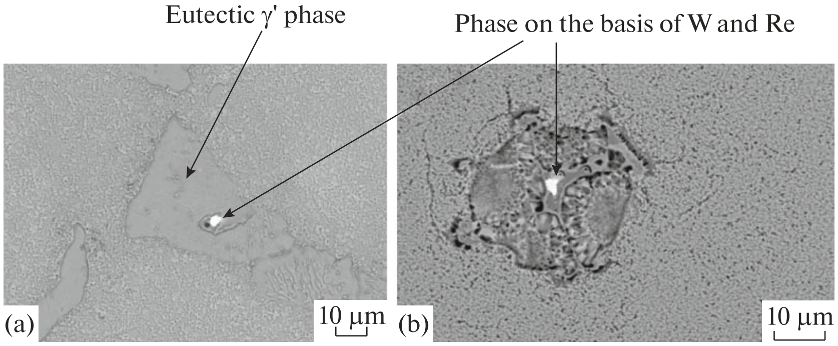

Fig. 2. Microstructure of single crystal of VZhM5-VI alloy with 0.025% P: (a) as cast; (b) after THT.

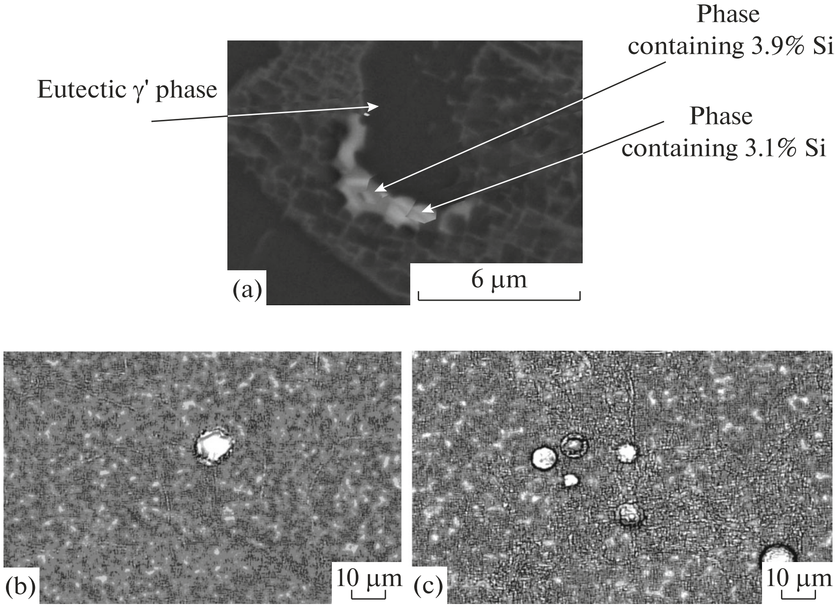

Fig. 3. Microstructure of single crystal of VZhM4-VI alloy: (a) 0.27% Si, as cast; (b) 0.085% Si, after THT; (c) 0.27% Si, after THT.

(2) In VZhM4-VI alloy with increased silicon content (0.27 wt %), upon tests for long-term strength using this mode, a similar regularity is observed (Figs. 5c, 5d).

In order to determine the reasons for the negative effect of the impurities on long-term strength of single crystals, the local distribution of sulfur and phospho-

Table 2. Mechanical properties of monocrystalline of ZhS36-VI alloy with varying content of impurities

Content of impurities and La	Operating lifetime at $T = 1000°C$, $\sigma = 185$ MPa reference value 500 h	Number of cycles to failure upon LCF tests at $T = 900°C$	
		$\sigma = 950$ MPa	$\sigma = 980$ MPa
0.0002% S 0.0013% P	363	2573	–
0.0007% S	–	–	1737
0.0014% S	–	–	755
0.0072% S	274	–	463
0.017% P	319	1903	–
0.017% P + La	375	3069	–

rus between the γ and γ' phases of single crystals of ZhS36-VI alloy was analyzed by high-resolution electron microscopy and X-ray spectral microanalysis.

The following has been established:

(1) After total heat treatment, sulfur and phosphorus are concentrated mainly in interlayers of the γ solid solution, which is confirmed by formation of peaks of increased content of both sulfur (Fig. 6a) and phosphorus (Fig. 6c) upon passing of the scanning probe across the interlayers of the γ solid solution.

(2) After tests of long-term strength at $T = 1000°C$ and $\gamma = 185$ MPa, a similar distribution of phosphorus and sulfur impurities in the interlayers of the γ solid solution is retained; in this case, the heterogeneity of the sulfur distribution between the γ/γ' phases after the tests is retained and manifested to a higher extent than before the tests, especially on the metal with increased sulfur content (0.0072 wt %) (Fig. 6b).

One can assume that, during tests of single crystals with increased sulfur content, it is redistributed owing to diffusion: its content decreases in the γ' phase and increases in the γ solid solution.

As a consequence of increased content of sulfur and phosphorus in local segments of the γ solid solution because of their nonuniform distribution in the metal, the structure and thermodynamic stability of single crystals are violated. We suppose that these impurities at interfaces destroy coherent bonds between the γ and γ' phases and increase the diffusion permeability of phase boundaries [10], which leads to a decrease in creep resistance and lifetime.

Since the increased content of sulfur, phosphorus, and silicon significantly impairs the operating properties of MNHA, it is required to develop methods of melt refining from these impurities. The Institute of Aviation Materials performs active developments in this field, and certain positive results are achieved. The developed method of melt refining from sulfur makes it possible to remove up to 90% of this impurity by means of addition of rare earth elements which are combined into hard meting compounds and removed from the melt by adsorption on surface of the ceramic crucible and melt filtration upon tapping [11, 12]. This method also provides removal of silicon from the melt [13], though the efficiency of its removal is significantly lower in comparison with sulfur. The investiga-

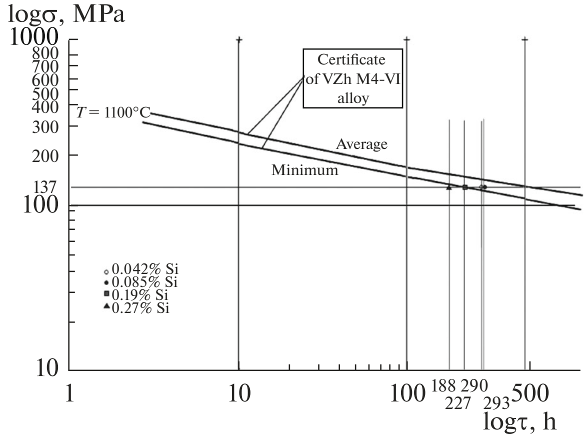

Fig. 4. Influence of silicon on long-term strength of monocrystalline VZhM4-VI alloy with ⟨001⟩ crystallographic orientation.

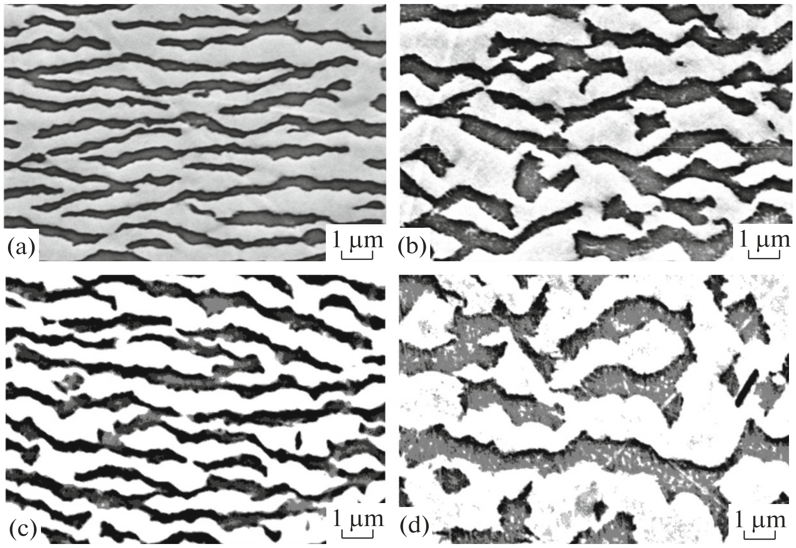

Fig. 5. Microstructure of VZhM4-VI alloy after long-term strength tests ($T = 1100°\text{C}$, $\sigma = 137$ MPa): (a) 0.010% P, $\tau = 798$ h; (b) 0.019% P, $\tau = 360$ h; (c) 0.085% Si, $\tau = 295$ h; (d) 0.27% Si, $\tau = 170$ h.

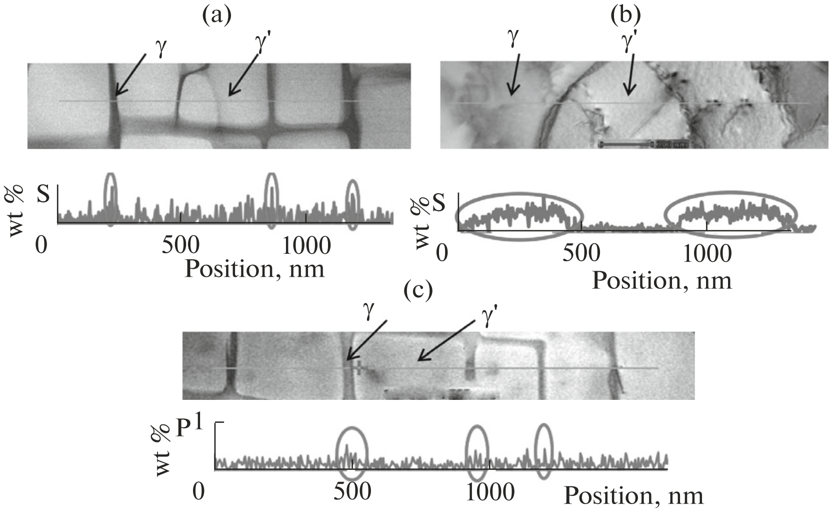

Fig. 6. Local distribution of impurities contents between γ and γ' phases of monocrystalline ZhS36-VI alloy: (a) 0.0072% S, after THT; (b) 0.0072% S, after long-term strength tests at $T = 1000°\text{C}$ and $\sigma = 185$ MPa; (c) 0.017% P after THT.

tions demonstrated that hard melting compounds with phosphorus formed upon alloying with rare earth elements are not removed from the melt [14]. However, addition of lanthanum to ZhS36 alloys increased the lifetime at operating temperature and LCF of single crystals with increased phosphorus content (see Table 2) [15].

In particular, the tests for long-term strength of single crystals of ZhS36-VI alloy with increased phosphorus content (0.017%) with and without lanthanum at 1000°C for 100, 500, and 1000 h with predictions up to 5000 h [16] (Fig. 7) demonstrated that the ultimate long-term strength increases owing to neutralization of the harmful impact of phosphorous by addition of lanthanum: for 100 h, by 5 MPa; for 500 and 1000 h, by 10 MPa; for 5000 h, by 20 MPa; that is, with

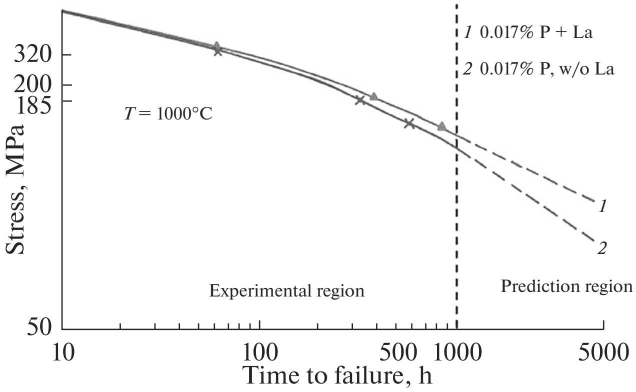

Fig. 7. Long-term strength of monocrystalline ZhS36-VI alloy with phosphorus content of 0.017 wt % and addition of lanthanum.

increased test duration, the long-term strength of the alloy with microdoping with lanthanum increases.

CONCLUSIONS

(1) Sulfur, phosphorus, and silicon promote generation of unwanted phases, roughening of the structure, increase in microporosity, or local fusing during thermal treatment, which violates the structure of monocrystalline heat-resistant nickel alloys and impairs their properties.

(2) The negative impact of these impurities is observed during tests for long-term and fatigue strength on numerous samples at operating temperatures; hence, they decrease the operating lifetime of components of gas turbine engines.

(3) Coagulation of the strengthening γ' phase occurs more rapidly in single crystals of VZhM4-VI with increased contents of phosphorus and silicon.

(4) Impairment of mechanical properties of single crystals with increased content of sulfur and phosphorus can be attributed to heterogeneity of the distribution between the γ and γ' phases, namely, generation of increased concentration of the γ solid solution in local segments, which decreases the structural and thermodynamic stability of single crystals.

ACKNOWLEDGMENTS

This work was carried out within the framework of R&D field 10.1: Resource Saving Smelting Technologies of Advanced Cast and Wrought Highly Heat-Resistant Alloys Including Reprocessing of All Wastes. (Strategic Trends of Development of Materials and Their Processing for the Period up to the Year 2030.) This work was partially supported by targeted fundamental scientific research project no. 13-08-12055_ofi_m.

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Translated by I. Moshkin