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# Structural Transformations in heat resistant coatings containing rare earth elements

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# Structural Transformations in heat resistant coatings containing rare earth elements

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**Abstract.** Degradation of two-layered coatings and ZhS6U alloy microstructure were studied during long-term processes of high temperature annealing and creeping. It was shown that yttrium and zirconium oxides are promising as protective coatings for heat resistant nickel based alloy.

## 1. Introduction

One of the main targets of material science today is providing adequate environmental protection of heat resistant alloys. This target can be solved by application of protective coatings. Under influence of high temperature chemical composition and structure of coating and alloy may significantly change due to diffusion transfer processes. Component diffusion of protection system into alloy decreases its strength and creep resistance; diffusion of alloy components into coating leads to decreasing its heat resistance. Moreover, diffusion of impurities fluxes in interfacial area has an impact on recrystallization, creeping and freeness in grain boundaries, and pore formation [1].

Study of mechanism of coating structure degradation is very important for developing of optimal protection systems and techniques that can be used to coat alloy surfaces. Also, it is valuable to study the influence of coatings on mechanical properties of heat resistant alloys.

Ni(Co)-Cr-Al-Y–based heat resistant coatings [2] are used to protect alloy-treated heat resistant nickel based composites. Studies have shown [3] that these coatings do not prevent from full penetration of oxygen to alloy surface which may lead to internal oxidation of alloy under coating and deteriorating its protective properties.

## 2. Experimental section

In this work, double-layer coatings were used to prevent internal oxidation of alloys. On treated surface of ZhS6U (C-0.18, Cr-9.0, Co-4.8, W-10.3, Mo-1.5, Al-5.4, Ti-2.6, Ni-base, Nb-1.0, Zr-0.04, B-0.02) alloy the first (internal) layer consisting of Ni-20%Cr-13%Al-0.5%Y (weight %) was coated. Composition of the second (external) layer is 40%Y2O3-40%ZrO2-10% Cr2O3-10% Al2O3 ceramics. The thickness of internal coating was 100 microns and external coating was 50 microns. Coatings were studied using high energy vacuum plasma spraying techniques [4]. The method of vacuum plasma technology for high-energy (MVPT) developed VIAM. Use a vacuum arc ion energy 30-150ev. The cathode is made of an alloy coating. Method of vacuum-plasma technology of high energies (VPTHE) developed in VIAM. Used vacuum arc ions with energy of 30-150ev. The cathode is made of alloy coating.

Mechanical tests on stretching and creeping were conducted at temperature of 1273 K and vacuum pressure of $10^{-3}$ kPa in air atmosphere. Flat samples were used with size of working heads $2*3*20$ mm$^3$. Structural and chemical transformations at surface layers of alloy and in the coatings were studied during annealing and creeping processes by X-ray structure analysis, X-ray spectrum analysis, optical and electron microscopies.

## 3. Results and discussion

Figure 1a,b presents general view of two-layered coating and surface layer of ZhS6U alloy at different time of annealing with air at temperature of 1273 K. Long-term annealing leads to the structural degradation of ceramic coating. It was observed that after 50 hours of annealing, coating is becoming crumbled; pores and microfractures are formed, deteriorating and layer destruction take place.

On surface of ZhS6U alloy and less on Ni-20%Cr-13%Al-0.5%Y alloy coating formation of oxide scale was observed which is crumbled and exfoliated with increase of annealing time. After 100 hours of annealing with air nickel-based coating became thin in 10-15%, but still remained indiscrete and preserved its protective properties. Both between coatings and internal layers of alloy diffusion zones were formed (figure 1). Dependence of diffusional zone from annealing time complied with parabolic law. Growth rate of diffusional zone in the process of creeping is 3-4 times less than at annealing without loading. This is probably connected with compressed tensions that appeared in cross-section of sample during the process of creeping.

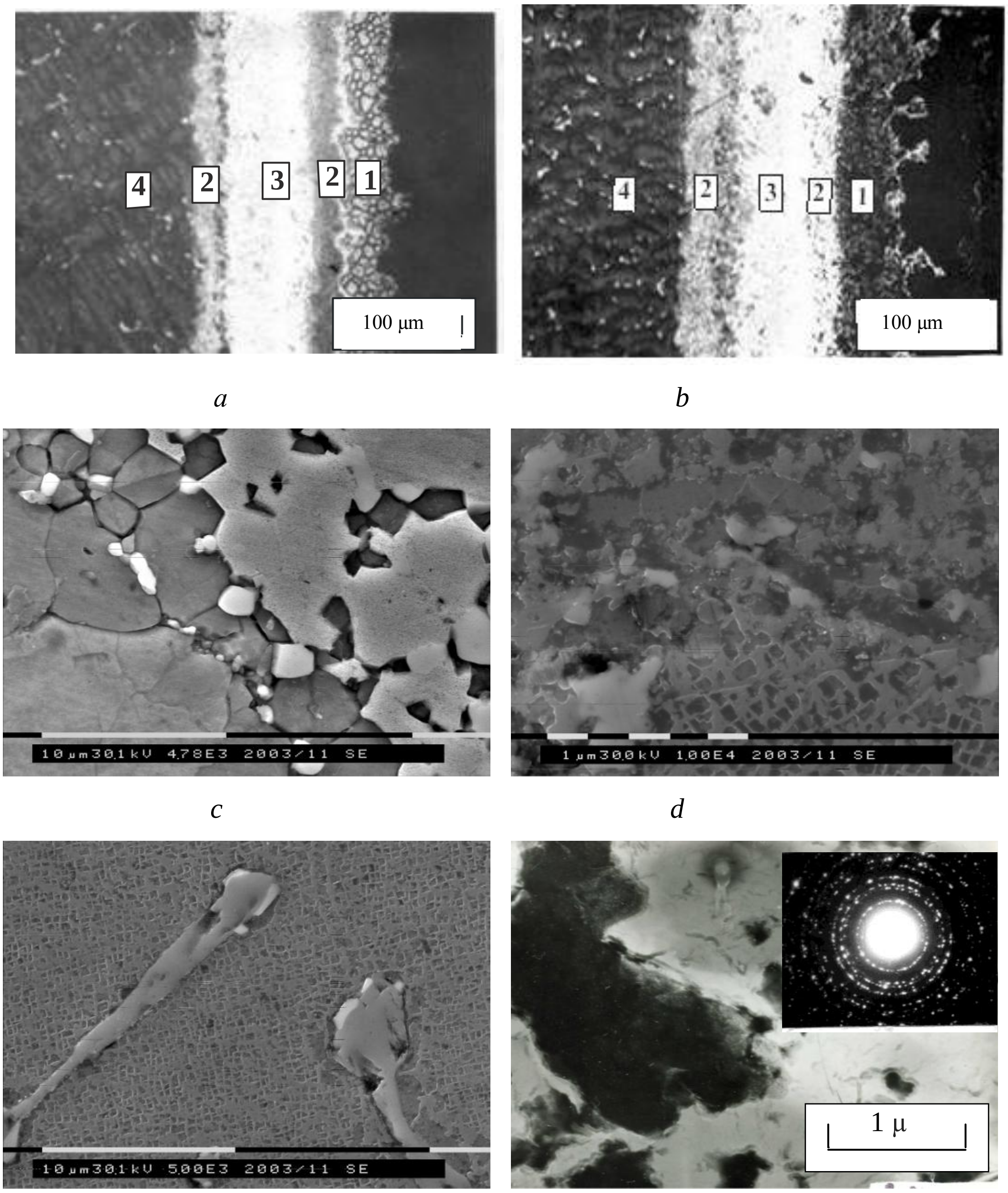
ZhS6U alloy has dendritic structure (figure 1a). Predominant strengthening phases are $\gamma'$ ($Ni_3Al$) and carbides $Cr_7C_3$ (figure 1e). Volume fraction of $\gamma'$-phase consists of 55%. Particles with size of 0.1-0.3 microns have cubic shape (figure 1e). Large particles of $\gamma'$-phase and $\gamma'/\gamma$ –eutectic are observed with size of up to 10 microns. At all modes of thermal treating topological close-packed phases in alloys were not observed. After 4 hours of annealing at temperature of 1273 K size of grains in alloy is 30-40 microns. Carbide particles have shape of plates and bars with length of 15 microns and thickness up to 5 microns (Fig.1e). Coalescence of grains and phases in alloy is observed during annealing and creeping at 1273 K. After 50 hours of annealing size of grains increases twice as much, and size of particles $\gamma'$-phase reaches 0.8-1 microns.

After treating, both coatings have ultrafine-grained structure with size of grains and phases of 0.2-0.3 microns. Grained structure in alloy Ni-20%Cr-13%Al-0.5%Y has high thermal stability. Annealing during four hours at temperature of 1273K leads to increasing of average size of grains in this layer up to one micron (figure 1*d*), and after 50 hours up to 2.2 μm. In 40%$Y_2O_3$-40%$ZrO_2$-10% $Cr_2O_3$-10% $Al_2O_3$ ceramic coating average size of grains consists of 5 (figure 1*c*) and 15 microns after corresponding thermal treating.

NiAl, $Ni_3Al$ phases and free chrome in the first coating were observed by X-ray structure analyses. Set of detected phases is typical for all studied modes; however, distribution of relative intensity depending on thermal treating is changed. Relative intensity of X-ray lines of Ni Al phase decreases, and $Ni_3Al$-phase increases. Decreasing of amount of NiAl phase is connected with aluminum consumption for $Al_2O_3$ oxides and aluminum diffusion into alloy. In $Y_2O_3$ - $ZrO_2$ ceramic based coating phases $Y_2O_3$, $Cr_2O_3$, $ZrO_2$, $\alpha$ - $Al_2O_3$ were found.

Figure 2 shows distribution of alloying elements in coatings and at surface layer of alloy. It is observed higher content of aluminum and titanium between alloy and coating. This is connected with aluminum, diffusion from coating into alloy which lead to increasing of volume fracture of $\gamma'$-phase and oxygen penetration into alloy surface with formation of titanium oxides (figure 1*f*).

In alloys with one layered coating oxidation of alloy surface under coating starts after 5-10 hours of annealing and creeping in air at temperature of 1273K. In alloy with two layered coating formation of oxides takes longer time (40-50 hours). During this period of time formation of open-ended pores is occurred in ceramic coating, and oxygen is penetrating to the surface of first coating and diffuses through it. On the surface of ZhS6U alloy under Ni-20%Cr-13%Al-0.5%Y alloy formation of titanium and nickel oxides take place. Structure of oxides is presented in figure 1*d*.



*a* *b*

*c* *d*

*e* *f*

**Figure 1**. *a*, *b* – two-layered structure of coating after 4 and 50 hours of annealing at temperature of 1273K, 1 – ceramic coating, 2 – diffusion zones, 3 – Ni-20%Cr-13%Al-0.5%Y alloy coating, 4 – alloy, *c* – grained structure of ceramic coating after 4 hours annealing, *d* – carbides and γ′-phase in ZhS6U alloy after 4 hours of annealing, *f* – oxides of Ti and Ni in alloy after coating with microelectronogram.

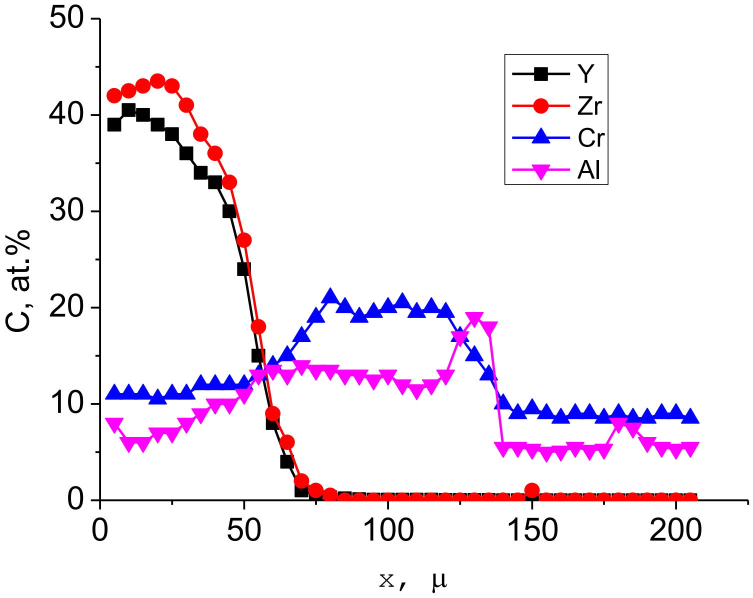


**Figure 2.** Dependence of element concentration in coatings and in surface layer of ZhS6U alloy from the depth

Ultimate strength of ZhS6U alloy without coating and with one layered and two layered coatings at temperature of 1273 K in vacuum on temporary base of 100 hours without taking into account cross section of covering consists of 170 MPa. Coatings at 1273 K have low ultimate strength at high loading (3-5 MPa), therefore, if take into account cross-section of coating, the strength of samples is decreased [5]. Tests with air at the same conditions lead to decrease of time when samples without coating start destructing up to 50 hours and with one-layered coating from Ni-20%Cr-13%Al-0.5%Y alloy up to 80 hours. Difference in time, when samples start destructing both in air and in vacuum, decreases when size of sample is increasing. It is connected with abnormal demonstration of scale factor at long term tests in corrosion conditions. Additional coating on the base of $Y_2O_3$ – $ZrO_2$ ceramics allow increasing the time till destruction of samples up to 90 hours.

$Y_2O_3$ – $ZrO_2$ - ceramic based coatings have lower heat resistance in comparison with coating from Ni-20%Cr-13%Al-0.5%Y alloy. Coating with thickness 50 microns is completely destructed for 80 hours of annealing in air atmosphere at temperature of 1273 K. During annealing it is observed intensive growth of grains in ceramic coating on internal and external interfacial areas with pore formation. After 50 hours of annealing at 1273 K on boundaries of grains formation of open-ended pores is occurred and oxygen easily penetrates to the first coating. Ni-20%Cr-13%Al-0.5%Y coating remains indiscrete and preserves its protective properties after 100 hours of annealing in air with no load. Additional ceramic coating increases time when ZhS6U alloy sample starts destructing on 10% in the process of high temperature creeping in air.

## 4. Conclusions

Putting additional ceramic coating with composition of 40% $Y_2O_3$-40% $ZrO_2$-10% $Cr_2O_3$-10% $Al_2O_3$ on Ni-20% Cr-13Al-0,5% Y coating leads to delay of oxygen penetration to the ZhS6U heat resistant surface for 80 hours. Destruction time of ZhS6U samples with two-layered coating at ultimate strength of 170MPa and 1273K temperature increases from 100 to 150 hours in comparison with destruction time of one-layered Ni-20% Cr-13% Al-0.5% Y samples. During annealing it is observed intensive growth of grains in ceramic coating on internal and external interfacial areas with pore formation. It is not recommended to use ceramics with 40% $Y_2O_3$-40% $ZrO_2$-10% $Cr_2O_3$-10% $Al_2O_3$ composition as one- layered coating for heat resistant nickel-based alloys. Prior to putting coating on alloy it is necessary to use interface heat resistant coating which contains nickel or cobalt as a base.

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