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CONSIDERATIONS ON CORROSION AND CORROSION PROTECTION OF SURFACES WORKING UNDER HIGH TEMPERATURE CONDITIONS

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Abstract: Heat-resistant functional coatings have a substantial influence on the operating properties of materials at high temperatures. The stresses of the turbine components having different destinations are taken into account in the design phase but the technological requirements imposed on construction and materials used have currently limited their development. The temperature represents the essential limit in the construction of gas turbines. By eliminating the structural defects of the heat-resistant coating, the thermal conductivity of the deposited material is improved and also the temperature gradient is reduced. A component of a jet engine, coated with a low porosity heat-resisting layer, deposited by spraying a ceramic material in a plasma jet exhibits an increased durability under mechanical stress at high cyclical temperature.

Keywords: the rate of corrosion, the heat-resistant coating, ceramic material, plasma jet exhibits, gas turbines, blades, high resistance to thermal cyclic loads, the functional coatings.

1. THE CORROSION IN GASES

1.1. Metal corrosion in gaseous environment at high temperature

In this case, the corrosion rate depends on the chemical composition, velocity and environment temperature. The influence of the environmental gas composition on the corrosion depends on the nature of the two phases and it is manifested in the emergence of the aggressive component into the gaseous environment, varying very little with its composition. When replacing a habitual atmosphere by an oxygen one, the corrosion rate of a sample of iron (Fe) at 800-1000 ° C, or a sample of copper (Cu) to 700 ° C increased approximately twice and not five times as it would increase if direct

proportionality between the change in corrosion rate and the partial pressure of oxygen. The corrosion of metal increases in air at high temperature in the presence of impurities given by aggressive gases as water vapors, carbon monoxide (CO) or gaseous hydrochloric acid (HCl). The gas velocity affects the metal corrosion only during the first moments of the phases contact. After the film formation the rate of corrosion is determined by the rate of particles diffusion through the film. Therefore the corrosion rate does not depend on the contribution of the gas convection. At very high flow rates of gas the corrosion enhances due to the erosive destruction of the film.

1.2. Influence of the corrosive environment temperature on the rate of corrosion in gases.

The practice shows that by increasing temperature, the corrosion rate increases according to Arrhenius differential equation:

$$\frac{dy}{dt} = K = A' \cdot e^{\frac{Q}{RT}} \quad (1)$$

where: K = constant of the chemical corrosion rate, Q = constants that can be calculated based on experimental determination of the rate of corrosion K of at least two different temperatures T1 and T2. The chemical corrosion rate varies with the inverse of the temperature, a fact verified by practice.

2. THE FUNCTIONAL COATINGS

2.1. Heat-resistant functional coatings

In order to meet their basic use, which is to reduce requirements for cooling, the heat-resistant functional coatings must have a low thermal conductivity, a low density, and a reflective capacity to resist cyclic loading. These are requirements for the two and three-layer coatings of 0.3 mm thickness whose outer layer consists of zirconium oxide, ZrO2 stabilized with different compositions, 12% Y2O3 + 3% MgO, ThO2, CaO. As a metal joining substrate the systems Ni - Cr - Al - Y, Ni - Cr - Fe - B - Si, Co - Cr - Al - Y are utilized. It stands out that Zr, Y, Th, Co oxysulphids consisting of oxides of these metals are barriers to diffusion of sulfur. As an interlayer Cr is applied. In plasma-jet spraying method is mainly used for the heat-resistant coatings.

2.2. Specific of the state of stress under strain and deteriorating conditions of the covered functional components

To be efficient in operation it is essential for coated metals to have a high resistance to thermal cyclic loads. Depending on the ratio of the basic metal characteristics to coating (coefficient of linear extent - α , longitudinal modulus - E, flow thresholds) and also the thickness of layer h, the conditions of developing plastic deformations can be substantially different. To illustrate the above we will analyze the conditions of adaptability and cyclical forming on the basic metal and coating. The notation utilized will be the following: **m** for the ratio of the coating surface to the basic metal surface in the model (component) section, **α_1** and **E1** for α and E values of the coating and **α_2** and **E2** for the basic metal values. We apply the linear law of change of the fluid threshold with temperature: $\sigma T = \sigma_0 - qt$. We consider the temperature of both the basic metal and coating to be the same. In this case, the plastic deformations of the cycles are formed in the coating, when t_{max} cycle maximum temperature reaches the value t_P .

$$t_p = \frac{2\sigma_{OP}(1/E_1 + m/E_2)}{\alpha_1 m(E_1/E_2) + \alpha_2 + q_P(1/E_1 + m/E_2)} \quad (2)$$

and in the basic metal when $t_{max} > t_M$,

$$t_M = \frac{2\sigma_M(1 + mE_1/E_2)}{m\alpha_1 + (E_2/E_1)\alpha_2 + q_P(E_2/E_1)(1/E_1 + m/E_2)} \quad (3)$$

The ratio of 2 to 3 is true if the following conditions are met:

$$m > \frac{\sigma_{OP} - q_P t_P k_2}{\sigma_{oM} - q_M t_P k_2}; \quad m \leq \frac{\sigma_{OP} - q_P t_M k_1}{\sigma_{oM} - q_M t_M k_1},$$

where: $k_1 = t/t_M > 1$; $k_2 = t/t_P > 1$

In a more general situation we must use the actual values of the thresholds of fluidity and elastic modulus depending on temperature. Using the ratio of 2, 3 and Kofin's equation: $\Delta \epsilon_{p1}^{k_0} N_0 = C_1$ (3.1), where: k_0 and C_1 = constants, $\Delta \epsilon_{p1}$ = plastic deformation and N_0 = number of cycles to failure, we'll analyze



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the conditions of cracks formation in models with coatings, under temperatures which do not lead to extensive creep.

If $t_p > t_M$, then for the given value t_{max} with an equal plasticity of the basic metal and coating, the thermal fatigue cracks will be formed in case of the amplitude of temperature during the thermal cycle Δt which is sufficient for the emergence of $\Delta \epsilon_{PL} > 0$ in basic metal.

Already formed cracks will propagate from the basic metal to the thermal protection layer. If the speed of cracks propagation is small enough when Δt is increased up to sufficient values to form the metal plastic deformation $\Delta \epsilon_{PL} = \Delta \epsilon_{PL1}$, during the thermal cyclic deformation process, the cracks occur at first in the basic metal at $\Delta \epsilon_{PL1}$ (after N_1 cycles) and only afterwards in the in thermal protection layer (after N_2 cycles). During this process the condition $(dl/dN < h / (N_2 - N_1))$ must be met.

If $t_p < t_M$ the cracking will first occur in the thermal protection layer. If $t_M < t_p$ the forming capacity of the thermal protection layer is also substantially lower than in case of the basic metal. When $\Delta t > t_p$ the damage of the thermal protection layer will occur first and only afterwards the basic metal will crack.

When using the ratio of 2 to 3 we must consider the anisotropy of the elasticity modulus. From formula (3.1)

$\Delta \epsilon > \alpha_1 t_p$ if $\Delta \epsilon > \alpha_2 t_M$ we get:

$$\frac{N_1}{N_2} = \left(\frac{\Delta \epsilon - \alpha_2 t_M}{\Delta \epsilon - \alpha_1 t_P} \right)^{k_0} \frac{C_P}{C_M} \quad (4)$$

where: $\Delta \epsilon = \alpha_2 \Delta t$ - full deflection amplitude; C_P / C_M - ratio of the thermal protection layer plasticity to the basic metal at the temperature t_{min} to the k_0 .

For the cycle Δt leading to emergence of tensions smaller than the elasticity limit,

instead of (3.1) is it recommended to use equations based on the criteria $\sum_{i=1}^{n_0} (\Delta P_i)^{n_0} = C_2(N_0)$ (1.2.2).

The models load in terms of physical and mechanical properties of their thermal protection layer changes depending on thickness and more, when their distribution changes during operation, it can be performed only by numerical methods.

Regarding the theoretical method of calculating the rate of spread for thermal fatigue cracks with coating models, one can say that this problem is not theoretically resolved.

Based on consideration of the difference between the linear expansion coefficients, the modulus of elasticity of the thermal protection layer (α_1, E_1) and the basic metal (α_2, E_2) at t_{min} of the cycle, work [S3] gives a model to calculate the crack growth rate dl / dN to the basic metal after its occurrence in the fragile coating thickness h . The following dependence relation is proposed:

$$dl / dN = A \exp(\Delta K_g) \quad (5)$$

and the relation for calculating the intensity scale of the deformation coefficients according to $E_1 / E_2, h, l, \Delta \epsilon T_y$ and $\Delta \epsilon \alpha$ ($\Delta \epsilon \alpha$ - scale of deformation at t_{min} given by the difference between α_1 and $\alpha_2, \Delta \epsilon T_y$ - scale of basic metal deformation during the cyclic heating).

The authors of paper [S1] have obtained a qualitative coincidence between the results of the tested blades with fragile heat-resistant layers and the results calculated by formula 1.5. The composition of the thermal protection layer has a substantial influence on the coefficient of linear expansion. Thus, for NiAl, $\alpha = 15 \times 10^{-6} [\text{deg}^{-1}]$, for Ni₃Al, $\alpha = 8.5 \times 10^{-6} [\text{deg}^{-1}]$, and for the condensed coating of the system Ni - Cr - Al when Al content increases from 3 to 30%, α decreases to $13 - 14 \times 10^{-6} [\text{deg}^{-1}]$.

2.3. Mechanical properties of refractory alloys coated with thermal protection functional coatings

Regarding the heat resistance quality of nickel-based metals we can say that they are less sensitive to notches as the coatings has a little influence over the average level of tension. Studies on coatings influence on the limit of time resistance, which were conducted in standard models under temperature conditions when the corrosion process does not play a significant role, have revealed that usually, differences between coated models and those without coating are not noticeable. Thus, in works [Z1, T1] are given data on the positive influence of the aluminide coatings on the JS6K alloys time resistance at 1000⁰ C. However, in outdoor experiments performed on models of 4 mm diameter, made from CrNi70VMoTiYFe alloy at 900⁰ C and described in [N2] a substantial time resistance decrease was found for those models having a calorized surface at low temperatures. According to the authors, such behavior is caused by the increased development of cracks under the plastic coating at 900⁰ C while for the uncoated models the cracks are impeded to spread after oxidation of their edges.

A number of authors have made attempts to check the time resistance a hostile environment [N2]. In situations where the coating is protective (does not crack during creep) a significant increase in time resistance has been found. In this connection the temperature of the brittle - viscous transition is decisive. We can expect that with the deformation, the strain rate (the test time increasing), and the brittle - viscous temperature fall. If the temperature brittle - viscous is lower than the test temperature, then the coating can have a positive influence on the creep resistance.

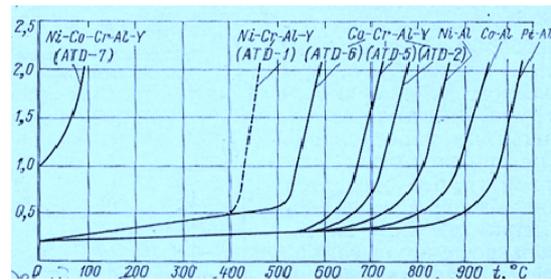


Fig. 1 [N3]. Temperature of a brittle -viscous transition (threshold of breaks) of some coatings from condensed aluminide and obtained by thermal diffusion.

In paper [N3] the plasticity-temperature relationship was studied for coatings made from Co - Cr - Al - Y with different contents of chromium and aluminum, Ni - Cr - Al - Y. The highest fragile - viscous temperature is found to Co - Cr - Al - Y alloys with 15% Cr and 10% Al and to coatings from SIB (Figure 4.16) [N3]. A comparison between the plasticity and the heat resistance of condensed coatings and of those obtained by heat diffusion demonstrates the superiority of the first ones. Similar results were obtained during the models testing of the IMAS - 5S installation : cracking of aluminide and silicon coating was observed when the of $\epsilon=0,75\%$ at 20⁰ C value was reached ,while for the condensed coatings of Ni - Al - Cr - Y no cracks were found until the damage of the mold from EP220alloy.

A number of researchers have studied various phases that determine the structure of aluminide coatings: Ni - Al in which Cr, Mo, Ni Al are dissolved. It was established that NiAl is brittle only up to 650⁰C, much higher temperatures (above 800-900 C⁰) containing NiAl coatings are plastic. Molybdenum enhances the plasticity and resilience over time of the nickel aluminide.

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mechanical and thermal fatigue resistance features of refractory alloys with aluminide coatings prove to be superior [T1]. The increase in fatigue resistance of alloys at normal temperatures is noticeable. Paper [N1] describes the thermal fatigue strength of models from different steels with protective coatings: from aluminide with Ni - Cr - Al - Y, with two layers of aluminide and chromium, from aluminide and silicon. The tests were made in liquid bath extending the cycle by 6 minutes. It was established that the number of cycles until the crack formation during the tests under $1088 \leftrightarrow 315^{\circ} \text{C}$ for all tested materials and types of coatings is 1.5 - 3 times higher than that of unprotected models. The higher increase of the thermal resistance during the heating cycle was found in coatings made from Ni - Cr - Al - Y on TAZ8A alloys, 4500-6500 cycles respectively instead of 600-800 cycles for the models without protection. The differences regarding the durability are determined by the influence exerted by the oxidation processes on the thermal fatigue during the cyclic heating of the unprotected models at $t_{\text{max}} = 1088^{\circ} \text{C}$. One of the factors that determine the sustainability of the coated models is the difference in the thermal dependence of the expansion coefficient of the basic metal and coating. A positive influence of aluminized coatings (Al and Al + Ti) on the thermal fatigue resistance was also obtained in testing the models of EP220 alloy at $t_{\text{max}} = 900^{\circ} \text{C}$ and the blades of CrNi60VTi alloy at $t_{\text{max}} = 1050^{\circ} \text{C}$. On the other hand, the coatings from azotize / chromium nitride visibly reduce the thermal fatigue durability of the alloy from Cr18Ni9 [G1] austenite in order to increase the wear resistance. Paper[D1] shows that the thermal durability of 6.5 mm diameter models, from JS6K and VJL12U alloy without coating is approximately 30% higher compared with

models with Al, NiCr35Al15Y, NiCr10Al16Y coating. The influence of the models surface chromium plating by diffusion on the thermal resistance of the JS6K alloy under the testing conditions at $t_{\text{max}} = 850^{\circ} \text{C}$. was studied in IMAS -5S facilities. It was established that damage (formation of thermal fatigue cracks) of superficial layer with a hardness of 8500 MPa, which exceeds the basic metal hardness, in some cases occurs after several cycles, which represent 15% of the overall sustainability of the model. The characteristics of this protective coating at high temperatures are effective during the operation time, which is noticeably shorter than the durability of the alloy JS6K. The micro-cracks, which are formed in the surface layer, include the brittle phase and are stopped in the plastic area of the metal.

3. CONCLUSIONS.

During the assessment of the functioning capacity of heat-resistant coatings, the correlation between the electrochemical potential of the coating and the electrochemical potential of the basic metal in a corrosive environment appropriate to the operating temperature is of high importance. If the electrochemical potential of the coating is greater than the electrochemical potential of the basic material then the coating protection particularities will manifest as long as it is compact; after the coating has been damaged in some places, the basic metal corrosion will occur more quickly than if it had been used without coating. The ratio of the two potentials may change depending on the changing of the corrosion products composition, when temperature and time will change. Regarding the usefulness of the practical application of coatings we can say that one should not take into account only data from researches on the

protection peculiarities of these coatings in a proper corrosive environment. The final decision is made, usually based on the results of research on the working capacity of coatings that are performed by testing composites (which consist of core and shell) under static, vibration and thermal cycling loads.

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