

*Materials Science*

## Heat-Resistant and Refractory Alloys for Special Application

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**ABSTRACT.** Progress of modern technologies in aeronautics, space exploration, nuclear power, etc. requires creation of new structural materials operating in extreme conditions: high temperatures, aggressive media, high mechanical loads, etc. However, practice shows that combining all the required properties in a single material is rather a hard task. In such cases special relevance is drawn towards creation of particular resistant coating technique for protection of refractory matrix from corrosion, wear or radiation. At present, as a coating material to protect refractory matrix from high-temperature degradation high-chromium alloys Fe–45%Cr–4%Al doped with rare earth metals La or Y are used. Reliable protection of matrix is ensured by the formation  $Al_2O_3$  layer along the coating-matrix interface. Stability of the interface layer is promoted by rare-earth metals. In present paper the authors offer an iron-chromium alloy (up to 16% Cr) doped with Zr and Ce (Fe–16.0%Cr–5.0%Al–0.5%Zr–0.3%Ce). Addition of Ce changes the mechanism of formation of the protective oxide ( $Al_2O_3$ ) layer at the coating – matrix interface, resulting in the improved properties (adhesion, abrasion resistance, strength characteristics, etc.). Positive influence of Ce on the formation of protective oxide ( $Al_2O_3$ ) layer is enhanced by its co-doping with Zr. From this point especially important is the economic aspect of the specified technology, which appears to be significantly cheaper. The reduced chromium content (to 16%) makes it possible to provide air melting under flux and fabricate the product easy to forge, roll and process by cutting. © 2017 Bull. Georg. Natl. Acad. Sci.

**Key words:** alloy, coating, corrosion

The problem of creating new materials capable of operating in extreme conditions such as high temperatures, aggressive media, high mechanical loads, etc., is highly relevant. Practice shows that to combine all the necessary properties for special purpose in one material is extremely difficult. In such cases particular importance is acquired by protective coat-

ings applied to the refractory matrix, protecting it from damage, and increasing the service life of the node.

In present paper, the possibility of using the alloy Fe–16.0%Cr–5.0%Al doped with Zr 0.5% and Ce 0.3% as a material for the protective coating is being considered. Protective effect of the alloy is due to the formation of stable oxide layer  $Al_2O_3$  +

**Table. Parameters of heat and corrosion resistance of the alloys**

№	Composition	W, mg/cm <sup>2</sup> 1200°C, 100 h. air	W, mg/cm <sup>2</sup> 1300°C, 100 h. air	W, mg/cm <sup>2</sup> 1300±50°C, 500 h.
1	Fe-16% Cr-5%Al-0.5% Zr	1.67		through oxidation
2	Fe-16% Cr-5%Al-0.3%Ce	1.15		
3	Fe-16%Cr-5%Al-0.5%Zr-0.3%Ce	0.71	2.4	1.31

Cr<sub>2</sub>O<sub>3</sub> at the protective coating-metal base interface.

Initial stage of oxidation is a purely chemical process of interaction of oxygen and metal atoms. Further oxidation process depends on the rate of the atoms diffusion through the formed multiphase oxide layer. The scales of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are characterized by extremely low volume diffusion parameters and, therefore, growing oxide grain boundaries are main arteries of mass transport. For this reason, one of the main principles of development of high chemical resistance alloys is blocking grain boundary diffusion.

According to [1] the presence of cerium (Ce) contributes to inhibition of the grain boundary diffusion of chromium (Cr) and aluminum (Al), thus changing the mechanism of formation of the metal based protective oxide layer: external diffusion of chromium (Cr) and aluminum (Al) is replaced by diffusion of oxygen (O<sub>2</sub>). At this case, the scale is formed at the metal base protective coating interface. As a result, a number of properties of the coating are improved: adhesion, strength characteristics, high-temperature chemical resistance, etc. Positive effect of cerium (Ce) on the formation of a protective oxide layer Al<sub>2</sub>O<sub>3</sub> + Cr<sub>2</sub>O<sub>3</sub> is enhanced by its co-doping with zirconium.

The technology for producing such alloy is significantly less expensive, than the technology for producing high-chromium alloy (Fe45.0% Cr4.0% Al + 0.25% La or Y) [2], used for similar purposes; Ce and Zr are much cheaper and technologically acceptable than lanthanum (La) and yttrium (Y). The reduction of chromium (Cr) to 16% makes it possible to provide submerged melt in the air and get completely tech ingots, which are well forged, rolled and processed by cutting.

## Experimental

**Influence of Zr and Ce on Heat and Corrosion Resistance of Alloy** Steel bars for tests (Fe-16%Cr-5%Al-Zr,Ce) were obtained in magnesite crucible by induction melting under flux. Cylindrical samples (d=10mm and h=20mm) were cut from the ingots rolled at T≈1000°C. The samples were tested on heat resistance at 1200°C and 1300°C in the air and corrosion resistance at 1300±50°C in the atmosphere of combustion products of gaseous fuels.

The initial stages of oxidation were studied by the method of continuous weighing on the installation "SETARAM"; long stages – by the method of periodic weighing. The samples of refractory matrix were coated by using the method of electron beam evaporation followed by condensation (4). Morphology of the metal-coating interface layer was studied on the SEM, DSM-960, Zeiss, Germany. Chemical composition and the concentration distribution of the elements in the scale were determined by X-ray micro-analysis, COMIBAX, CAMECA.

Influence of zirconium (Zr) and (Ce) on heat resistance of the matrix is rather positive; however, the effect is much more favorable in the case when the matrix is jointly doped with these elements. Thus, the weight gain W, mg/cm<sup>2</sup> of the samples doped with zirconium and cerium for 500h is 1.31 mg/cm<sup>2</sup>, while in the samples without cerium the through oxidation is observed under similar conditions.

Basing on the above mentioned, steel Fe–16.0%Cr–5.0%Al doped with 0.5% Zr and 0.3% Ce was selected for protective coating. Stability of the oxide layer Al<sub>2</sub>O<sub>3</sub> + Cr<sub>2</sub>O<sub>3</sub>, formed on the coating-metal matrix interface provides reliable protection of the matrix (Fig.1).

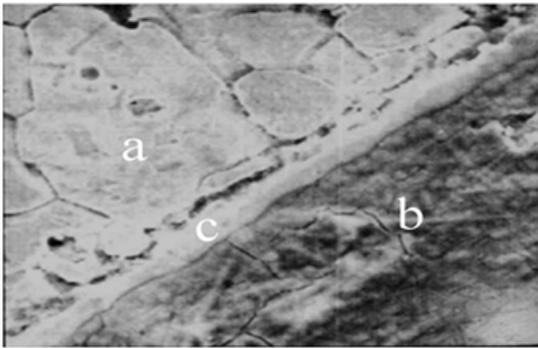


Fig. 1. Microstructure of cross-section of the coating condensed on the matrix: matrix (a) - coating (b) - transition layer (c).

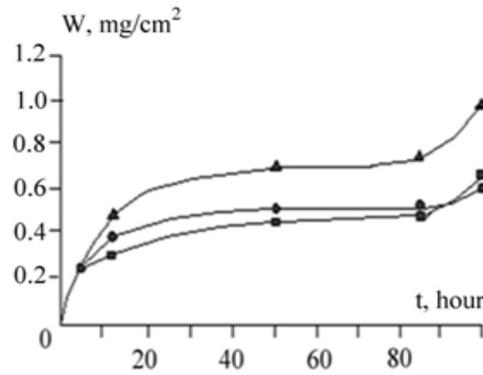


Fig. 2. Kinetics of steel oxidation in air,  $T = 1200\text{ }^{\circ}\text{C}$ .

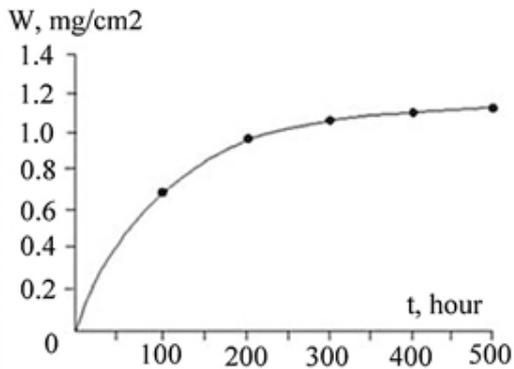


Fig. 3. Kinetics of steel oxidation in the atmosphere of the combustion products of gaseous fuel  $T = 1300 \pm 50\text{ }^{\circ}\text{C}$ .

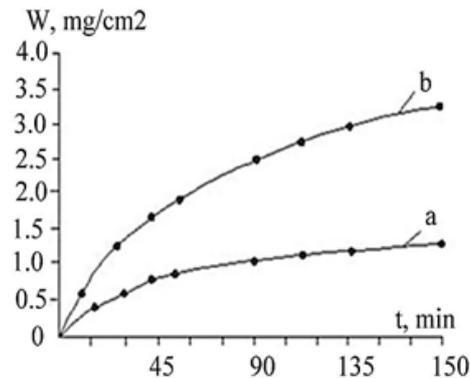


Fig. 4. The initial stages of oxidation of steel in air: a)  $T = 1200\text{ }^{\circ}\text{C}$ ; b)  $T = 1300\text{ }^{\circ}\text{C}$ .

The procedure of coating process was realized by using the electron-beam evaporation and condensation technique [3].

The oxidation kinetics of the selected steel was studied in open air at  $t = 1200\text{ }^{\circ}\text{C}$  under isothermal mode (Fig 2). It can be seen that the value of specific weight gain of three identical samples is extremely low:  $W \approx 0.7\text{--}0.9\text{ mg/cm}^2$  for 100 h.

Similar studies were conducted in the atmosphere of the combustion products of gaseous fuel at  $t = 1300 \pm 50\text{ }^{\circ}\text{C}$  in cyclic mode (Fig. 3). Here, the influence of micro-additives of cerium are particularly well-manifested. Specific weight gain does not exceed  $WH \approx 1.31\text{ mg/cm}^2$  for 500 h of testing, with high thermal resistance to thermocycling. This fact also indicates good adherence of protective oxide layer with the metal base. It should be noted that the scale formed on the steel (not containing cerium) during

the process of cooling starting from  $1200\text{ }^{\circ}\text{C}$  is detaching from the matrix.

Studies of the initial stages of isothermal oxidation in air of the similar steel showed that the formation of the surface protective film of aluminum oxide requires 30-50 min (Fig 4); then the film was thickened due to the oppositely directed diffusion of the interacting atoms of oxygen and metals. In this case, it is important to note that the slowly increasing protective layer has higher adhesion to the metal matrix thus providing stable and long work of the assembly as a whole.

Thus, high chemical stability of the alloys is mainly achieved due to the following two factors: a) reduction of the rate of formation of the protective oxide film (scale) and b) improvement of its adherence. For the alloys working under varied temperature field, long duration of protective scale ensures operative duration of the material.

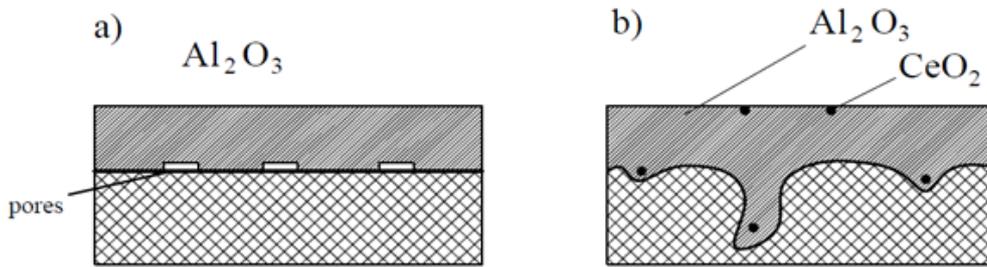


Fig. 5. Schematic exposure of the growth of  $\text{Al}_2\text{O}_3$ -scale. a) on the steel not alloyed with Ce; b) on the steel alloyed with Ce.

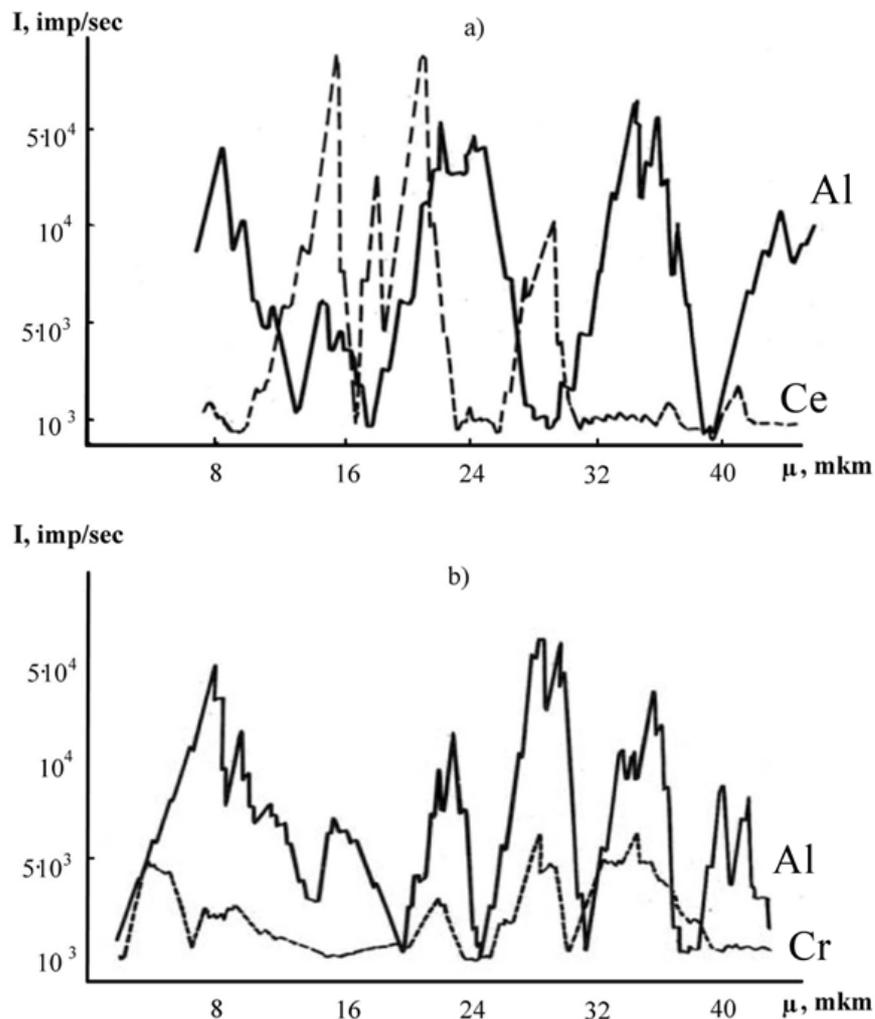


Fig. 6. Curves of the distribution of elements in the scale: a) Al and Ce; b) Al and Cr.

Influence of Ce on high-temperature corrosion and on the resistance of the protective oxide layer to thermal cycling is well explained in the work of Yasutoshi Saito [4]. It is well known that the standard free energy of formation of  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  per oxy-

gen mole makes (- 801) and (-787) kJ, respectively. These values are so close to each other, that it can be assumed that Al and Ce are simultaneously oxidized on the alloy surface. Then, according to Yasutoshi Saito, growth of  $\text{CeO}_2$  becomes preferable

due to high diffusion permeability of oxygen ions through that oxide. Therefore, along the grain boundaries, the so-called, "Oxide fastening pins" of  $\text{CeO}_2$ , appear fixing the growing slag of  $\text{Al}_2\text{O}_3$  (Fig. 5).

With the specificity of the cerium effect on high-temperature corrosion of the alloys and with the version of "pin" fixing of  $\text{Al}_2\text{O}_3$ -scale with cerium oxide  $\text{CeO}_2$ , offered by Yasutoshi Saito, the results of our micro-X-ray analysis of the protective oxide film, are in good agreement: as seen from the picture of distribution of elements in the scale, the concentration maxima as well as minima of aluminum (Al) and chromium (Cr) coincide well (Fig. 6b). It is in these locations that the maxima of concentrated peaks of cerium are observed (Fig. 6a). Therefore, we can assume that the diffusion of iron (Fe) in the absence of cerium (Ce) occurs in these sites of the surface. At high temperatures iron (Fe) is oxidized with the formation of iron oxide which is not known to have any

protective properties at such high temperatures. Apparently, these circumstances provide the through oxidation of the materials not containing rare earth metals.

## Conclusions

1. Special alloy was developed for protective coating of heat-resistant matrix (Fe – 16.0%Cr – 5.0%Al – 0.5%Zr – 0.3%Ce).
2. Doping the steel with zirconium (Zr) and cerium (Ce) helps to improve the protective properties of the coating.
3. The mechanism of the effect of alloying elements on the morphology and properties of the protective coating material has been identified.
4. Application of the developed alloy is recommended for protecting the operating units of power plants from the high-temperature degradation of their properties.

## მასალათმცოდნეობა

# სპეციალური დანიშნულების მხურვალმედვეი და მხურვალმტკიცე შენადნობები

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დღეისათვის, თანამედროვე მანქანათმშენებლობის მოთხოვნებიდან გამომდინარე, მწვავედ დგას ისეთი კონსტრუქციული მასალების შემუშავების აუცილებლობის საკითხი, რომლებიც შეძლებენ მუშაობას ექსტრემალურ პირობებში (მაღალი ტემპერატურები, აგრესიული გარემო, მაღალი მექანიკური დატვირთვები და ა.შ.). ამჟამად, ყველა საჭირო თვისების შეთავსება ერთ მასალაში, პრაქტიკულად, შეუძლებელია. ამიტომ, აღნიშნული პრობლემის გადასაჭრელად აქტიურად განიხილება დამცავი დანაფარების გამოყენება, რაც შესაძლებელს ხდის ლითონური ფუძე-შრის ფიზიკურ-ქიმიური თვისებების დაცვას მაღალტემპერატურული დეგრადაციისაგან.

ამჟამად, დანაფარის მასალად, ძირითადად, გამოიყენება სხვადასხვა შედგენილობის მაღალქრომიანი მხურვალმედვეი შენადნობები, მაგალითად Fe-45,0% Cr-4,0% Al, ლეგირებული 0,25% (La ან Y).

ჩვენ შემთხვევაში, ანალოგიური მიზნებისათვის, შემოთავაზებულია ახალი შენადნობი (Fe-16,0%Cr-5,0%Al), რომელიც ლეგირებულია ცირკონიუმით (0,5%Zr) და ცერიუმით (0,3%Ce). ნაჩვენებია, რომ Ce დადებითად მოქმედებს ლითონურ ფუძესა და დანაფარს შორის გამყოფ ზედაპირზე დამცავი შრის ( $Al_2O_3+Cr_2O_3$ ) ფორმირების პროცესზე. რის შედეგადაც უმჯობესდება მთლიანი კვანძის რიგი თვისებები (ადგენია, ცვეთამედეგობა, სიმტკიცის მახასიათებლები). Ce-ს დადებითი გავლენა ძლიერდება შენადნობის Zr-ით ერთდროული ლეგირებისას. აქვე უნდა აღინიშნოს, რომ შემოთავაზებული შენადნობის მიღების ტექნოლოგია გაცილებით მარტივია და იაფი.

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