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Influence of high temperature oxidation on surface layer and structure of Co-Ni-Cr-Mo alloys*

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The paper presents the results of structure analysis and chemical composition of the surface layer and matrix of Co-Ni-Cr-Mo alloys. The materials were subjected to oxidation in an air atmosphere at a temperature of 1100°C for 48 hours. Scanning microscope with an EDX microprobe was used to analyse the chemical composition. Analysis of structural changes, mainly from the aspect of stereological grain parameters, was also carried out using an optical microscope and computer image analysis. Scale formation was observed on the material surface after annealing. It was found that recovery and recrystallization of previously rolled materials takes place.

1. INTRODUCTION

Cobalt-based superalloys belong to the group of heat-resisting materials. They are produced for the needs of aviation industry, conventional power engineering and nuclear power engineering, aeronautics, armaments industry and medicine. The basic use of superalloys includes elements of gas turbines working as stationary (in power engineering) and aircraft engine. They are used as materials to manufacture blades and disks of turbine engines [1]. The required heat resistance for these elements amounts up to approximately 1300°C. The formation of protective oxide layers characterized by compact, homogenous structure on materials surface is a necessary condition which ensures intercrystalline and transcrystalline corrosion resistance.

In order to use superalloys to work in higher temperatures they are covered with heat resistant coating. While designing composites of this type it is necessary to take into account several factors related to work environment. The most frequently used materials for heat resistant diffusion coatings are: aluminium, Al-Si, Al-Cr, Al-Pt and MeCrAlY. The second group of materials is made up by thermal barrier-type, ceramic coatings (e.g. Al₂O₃, ZrO₂-Y₂O₃) or metal-ceramic coatings (e.g. Al₂O₃+5% Ni) [2].

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The aim of this investigation was to determine the chemical composition of annealing scale and the structural changes taking place during long time annealing.

2. MATERIALS AND METHODS

The materials were characterized by strain hardening as a result of rolling with the following values of the degree of cold work: $\varphi = 0.4$ and 0.3 for M1 and M2, respectively. The changes in the stereological parameters were examined as changes in grain shape and surface [3-5]. Structure analysis was carried out using Material Pro module of Image-Pro Plus 4.5 computer programme. The chemical composition of experimental cobalt-based alloys M1 and M2 is in Table 1.

Table 1. Chemical composition of M1 and M2 alloys

Alloy	Composition (%)								
	C	Cr	Ni	Mo	Ti	Nb	Mn	Si	Co
M1 (ISO 5832/6-80)	0.02	20.14	33.67	9.7	0.85	-	0.01	0.20	bal.
M2 (patent 150 030)	0.01	19.78	18.6	3.3	0.02	0.52	0.03	0.20	bal.
Others : 0.004 % S, 0.003 % P, N ₂ < 200 ppm, O ₂ < 100 ppm									

The tests were performed on samples of $22 \times 30 \times 2$ mm dimensions. During the experiment, high temperature tubular furnace, Thermolyne 59300 (USA), was used. The time of the test was determined to be 48 h at 1100°C . Oxidation was performed in the air. After annealing the materials were cooled down in the air. The metallographic specimens were etched in aqua regia and then examined under an optical microscope. Analysis of the composition of the matrix and the surface of the material specimens was carried out using a LEO 1430VP scanning electron microscope (SEM) fitted with EDX-Roentec probe (Germany).

3. RESULTS

Figs. 1a and 1b show the microstructure of M1 and M2 samples before and after computer image analysis. The following geometrical parameters of grains were determined: the area flat cross-section of grain, the shape factor ξ , the grain elongation factor δ and the mean grain diameter F . These parameters were calculated using the following formulae:

$$\xi = 4\pi A / P^2, \quad (1)$$

$$\delta = F_{\max} / F_{\min}, \quad (2)$$

$$F = (F_{\max} + F_{\min})/2, \quad (3)$$

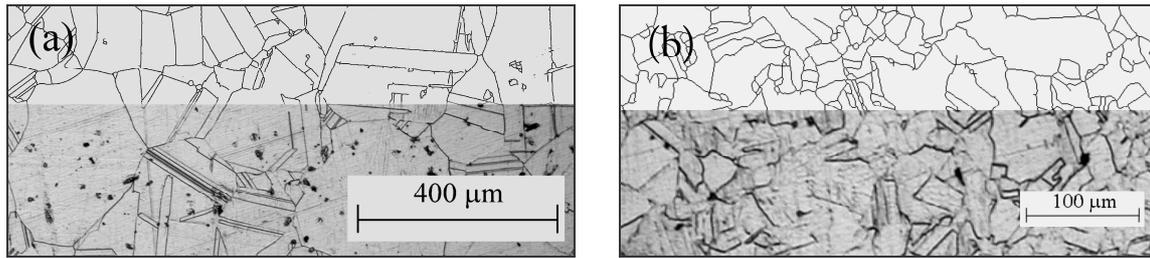


Fig. 1. Microstructure after high temperature oxidation and after computer analysis: (a) M1 alloy and (b) M2 alloy.

where: P is the circumference of the flat cross section of the grain, and F_{max} and F_{min} are the maximum and minimum Feret diameters, respectively. The maximum diameter D was also determined. Table 2 show the mean values of these parameters.

Table 2. Mean values of grain geometrical parameters

Factor	$A (\mu m^2)$	ξ	δ	$F (\mu m)$	$D (\mu m)$
M1	1742	0.34	3.02	36.18	29.09
M2	447	0.37	2.21	23.50	19.41

It was found that annealing of the samples leads to an increase in their average grain area A and elongation parameter ξ and a decrease in the elongation parameter δ . Fig. 2 presents the histograms of the distribution of flat cross-section of grains of M1 and M2 alloys. It may be seen that M2 alloy is characterized by small scatter in the grain area than M1 alloy.

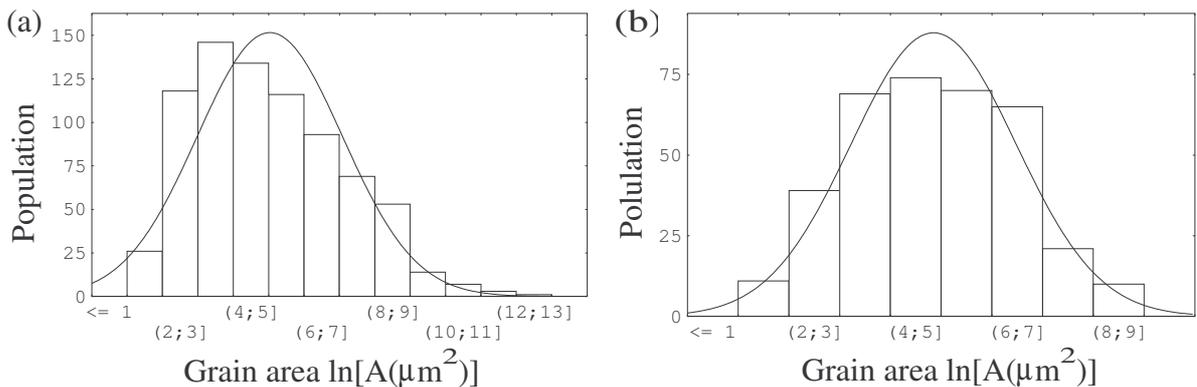


Fig. 2. Distribution of grain areas A : (a) M1 alloy and (b) M2 alloy.

Scale of M1 material after annealing consists of two layers: an upper layer close to the surface and the interior layer. These layers have different compositions, as shown by their EDX spectra in Fig. 3. The surface layer is composed of elements Cr and O (Fig. 3a), while the internal layer is composed of Co, Ni, Mo and O (Fig. 3b). In contrast to the scale of M1 alloy, the scale of M2 alloy consists of only one layer. This scale is composed of Co, Ni, Cr, Mo and O. Moreover, examination of the chemical composition of M1 and M2 materials does not show O in their interior.

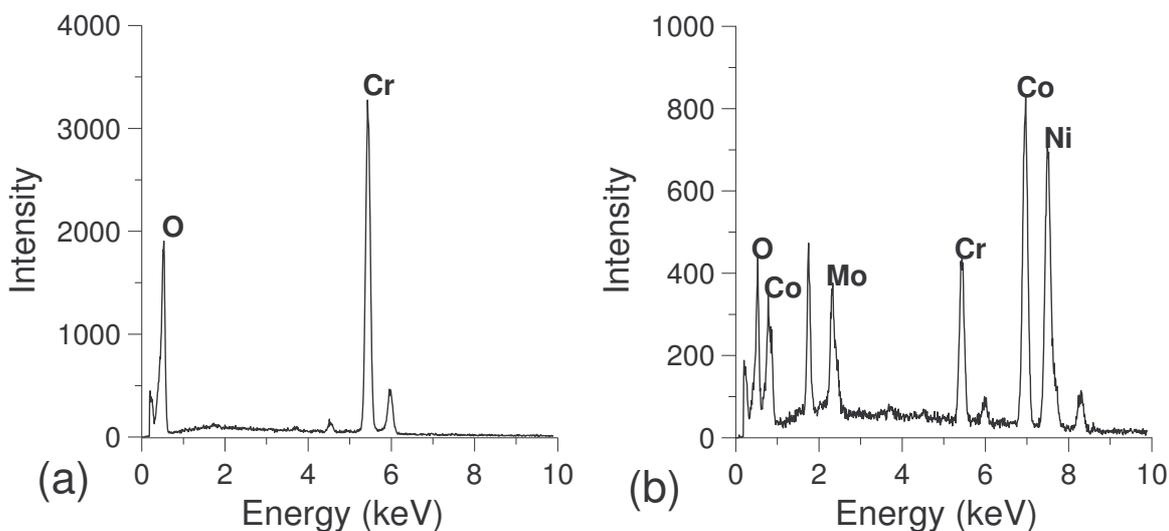


Fig. 3. EDX spectra of (a) outer surface and (b) interior layers of M1 scale.

4. DISCUSSION AND CONCLUSIONS

Annealing leads to recrystallization and recovery of the samples, which occur as a result of nucleation of new grains and their growth. The processes of recovery and recrystallization of M1 and M2 alloys also takes place during their long time annealing. One of the parameters defining these phenomena is the increase in the shape factor of both materials. The materials also show an increase in the grain area. These geometrical changes of the grains affect the heat-resistance and creep-resistance of the alloys [2].

M2 alloy is characterized by significantly smaller grain area $447 \mu\text{m}^2$ than M1 alloy with area $1742 \mu\text{m}^2$. M1 scale consists of two layers. The layer located close to the core contains a larger number of alloy elements, while the surface layer consists mainly of O and Cr. This suggests that the elements contained in the scale can form compounds protecting the material against internal corrosion. Alloy M2 is characterized by a one layer scale with a significant content of alloy elements. This layer is characterized by good adhesion to the base metal but does not protect the native material against oxygen diffusion.

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