

THE INFLUENCE OF COPPER ON THE HEAT RESISTANCE OF THIN FOILS OF HIGH-ENTROPY ALLOYS OF THE Cr–Fe–Co–Ni–Cu SYSTEM PRODUCED BY ELECTRON BEAM PHYSICAL VAPOUR DEPOSITION METHOD

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ABSTRACT

The paper investigated the heat resistance of sheet materials based on the Cr–Fe–Co–Ni–Cu system, depending on copper content in the alloy. It is shown that the content of copper in the composition of high-entropy alloys significantly affects the heat resistance of the material: in the case of CrFeCoNiCu alloy foils, the increase in specific mass at a temperature of 900 °C occurs 8 times more intensively than in CrFeCoNi foils, due to activation of the diffusion of copper atoms, its coming to the surface of the foil and formation of scale based on CuO and NiO oxides with a significant number of defects in the structure. CrFeCoNi alloy foils are characterized by higher heat resistance due to formation of scale based on Cr₂O₃ oxide on the surface with fewer defects and greater continuity. The average mass growth rate of the CrFeCoNi alloy sample is about 0.041 mg/(cm²h).

KEYWORDS: high-entropy alloys, electron beam deposition, ingot, thin foils, heat resistance

INTRODUCTION

Sheet materials are required for fabrication of structures with a low specific weight. Among them special attention is given to thermal protection three-layer honeycomb panels, which are considered to be an efficient means for protection of structural elements of aerospace equipment from heating at their interaction with the atmosphere at high speeds. In view of that, the sheet materials used for their manufacturing should have a complex of properties such as heat resistance, strength and low specific weight. Alloys based on Ti–Al [1], Ni–Cr [2] systems and other are traditionally considered as such materials. Thin foils from these materials are usually produced by rolling bulk cast billets, or they are formed by powder metallurgy methods. Such an approach, however, greatly complicates the technology of producing sheet materials and makes it inefficient in terms of power. In this connection, producing thin foil with the required complex of properties and methods of its joining is still a relevant problem.

Over the recent years, considerable attention has been given to the so-called high-entropy alloys (HEA) [3] which are characterized by high strength and thermal stability, wear and corrosion resistance, as well as hydrophobicity and weldability [4–6]. Owing to such features, HEA are regarded as promising materials for producing functional coatings, foils and other components for aviation and automotive industry [7, 8]. At present HEA thin films and coatings are

produced by the methods of magnetron sputtering [9], cathode-vacuum-arc vapour-phase deposition [10], thermal spraying [11] and laser cladding [12]. At the same time, these methods are characterized by relatively low production efficiency.

In earlier works [13–16] the authors showed in the case of CrFeCoNiCu HEA that the method of high-speed electron beam vapour phase deposition (EBPVD) allows producing vacuum foils with a rather wide range of micromechanical characteristics, high damping properties and good weldability. Combination of such properties in the produced foils allows considering such materials as promising for manufacturing structural elements of thermal protection honeycomb panels. At the same time, practical application of such thermal protection panels envisages the possibility of their operation for a long time under higher temperature conditions. In view of that, in this work the heat resistance of foils of HEA of Cr–Fe–Co–Ni–Cu and Cr–Fe–Co–Ni systems made by EBPVD method, was studied.

EXPERIMENTAL

Foils of Cr–Fe–Co–Ni–Cu system alloys with different copper content were produced by electron beam evaporation of the respective ingot-target with subsequent deposition of the vapour phase on the substrate from stainless steel (AISI 302) heated up to specified temperature. Foils of 40–100 µm thickness were deposited at the rate of approximately 100 nm/s at substrate temperatures in the range of 550–750 °C. To ensure foil

separation from the substrate, a thin layer of CaF_2 was first deposited on it. Initial ingots-targets of 50 mm diameter were produced in an induction furnace.

Microstructural studies of the foils and their local chemical analysis were conducted in a scanning electron microscope (SEM) CamScan4, fitted with ENERGY 200 microanalyzer. The foil overall thickness was evaluated by its cross-section in SEM images. X-ray diffractometer DRON-4M (Cu-K_α -radiation) was used to conduct phase analysis.

Heat resistance of the produced foils was studied by the change of specimen specific weight during annealing at the temperature of 900 °C in a shaft-type electric furnace SShOL-2.4/12.5 in atmospheric air.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Prior research showed that foils of CrFeCoNiCu alloy are characterized by a combination of quite high values of microhardness and ductility, as well as damping ability on the level of high-damping materials [15, 16].

When studying the heat resistance of CrFeCoNiCu foils it was established (Figure 1, curve 1) that intensive increase of specific weight occurs during the first 6 hours of heat treatment at the temperature of 900 °C, reaching the values of approximately 8 mg/cm². Further soaking for 30 hours does not lead to any significant growth of the foil specimen weight.

According to the results of scanning electron microscopy, in the initial state the thickness of CrFeCoNiCu foil is approximately 60 μm, and it is characterized by a defect-free structure and uniform distribution of the components over the thickness (Figure 2, a). Chemical composition, averaged over the foil thickness, is given in Table 1. In the initial state the foil structure consists of two FCC-phases, one of which is enriched in copper, and the other is depleted in copper (Figure 2, b) [16]. It should be noted that the two-phase composition is characteristic for foils of this system HEA, deposited at substrate temperature above 750 °C. How-

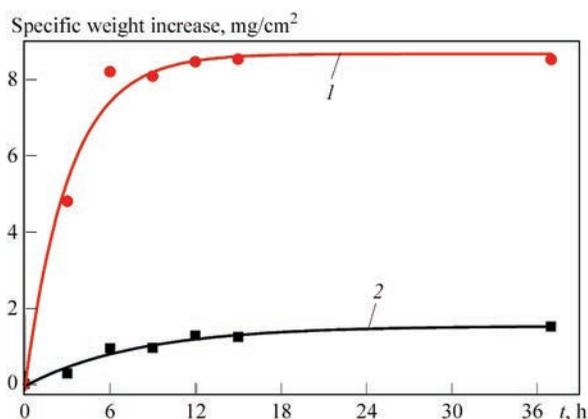


Figure 1. Kinetics of oxidation of CrFeCoNiCu (curve 1) and CrFeCoNi alloy foils (curve 2) at 900 °C in atmospheric air

ever, chemical composition of the phases is somewhat different for HEA produced from the vapour phase and by metallurgical methods: in cast alloys copper content in the copper-enriched phase is more than 80 wt.%, while in vacuum foils its content is not higher than 40 wt.% [15, 16]. By the data of electron microscopy, after CrFeCoNiCu foil soaking in the furnace for six hours at the temperature of 900 °C in atmospheric air, foil thickness increases up to 90–95 μm, and layered scale of 15–20 μm thickness forms on the foil surfaces with a considerable number of defects of the type of pores, delaminations and cracks (Figure 2, c). Chemical analysis of different scale areas (Figure 2, d, Table 1) showed that the surface layers of the scale are represented by iron-based oxides, while deeper-lying scale layers are a complex oxide, which includes all the foil components with the prevailing content of copper. The composition of the foil surface layers is similar which is indicative of the low ability of the formed scale to prevent oxygen atom penetration in-depth of the foil material. Further annealing of samples of CrFeCoNiCu alloy foil at 900 °C temperature for the next 30 hours leads to copper sweating on outer surface of the foil, significant coarsening of the grains and formation of copper oxide-based interlayers and a considerable number of pores of 5–8 μm size (Figure 2, e).

One can also see that nickel-based oxides with loose porous structure and extremely low continuity are present on the scale surface (Figure 2, e). In keeping with the data of X-ray structural analysis, the scale on the foil surface consists of copper oxide (CuO) and nickel oxide (NiO) (Figure 2, f). We noted further “swelling” of foil during high-temperature oxidation (thickness is increased to 100–115 μm) and formation of a layered structure in the foil, which consisted of interlayers of CrFeCoNiCu phase with a lower content of copper, separated by interlayers of a copper-based phase (Figure 2, e). More over, it was found that oxygen is present in a significant amount not only in the surface layers, but also across the entire foil thickness.

It can be assumed that a change in the initial chemical composition of the phases occurs at the initial stages: atoms of other elements are driven from the copper-enriched phase, primarily, those insoluble with it in the solid phase, such as iron and chromium. As a result, iron atoms come to the surface and form scale, leading to rather intensive growth of sample specific weight and increase of its overall thickness (Figure 2, c). As this scale is unstable and is characterized by a loose structure, it breaks up (delaminates) at further heat treatment. It can account for lowering of the intensity of the specimen specific weight increase. In parallel, copper atom diffusion becomes much

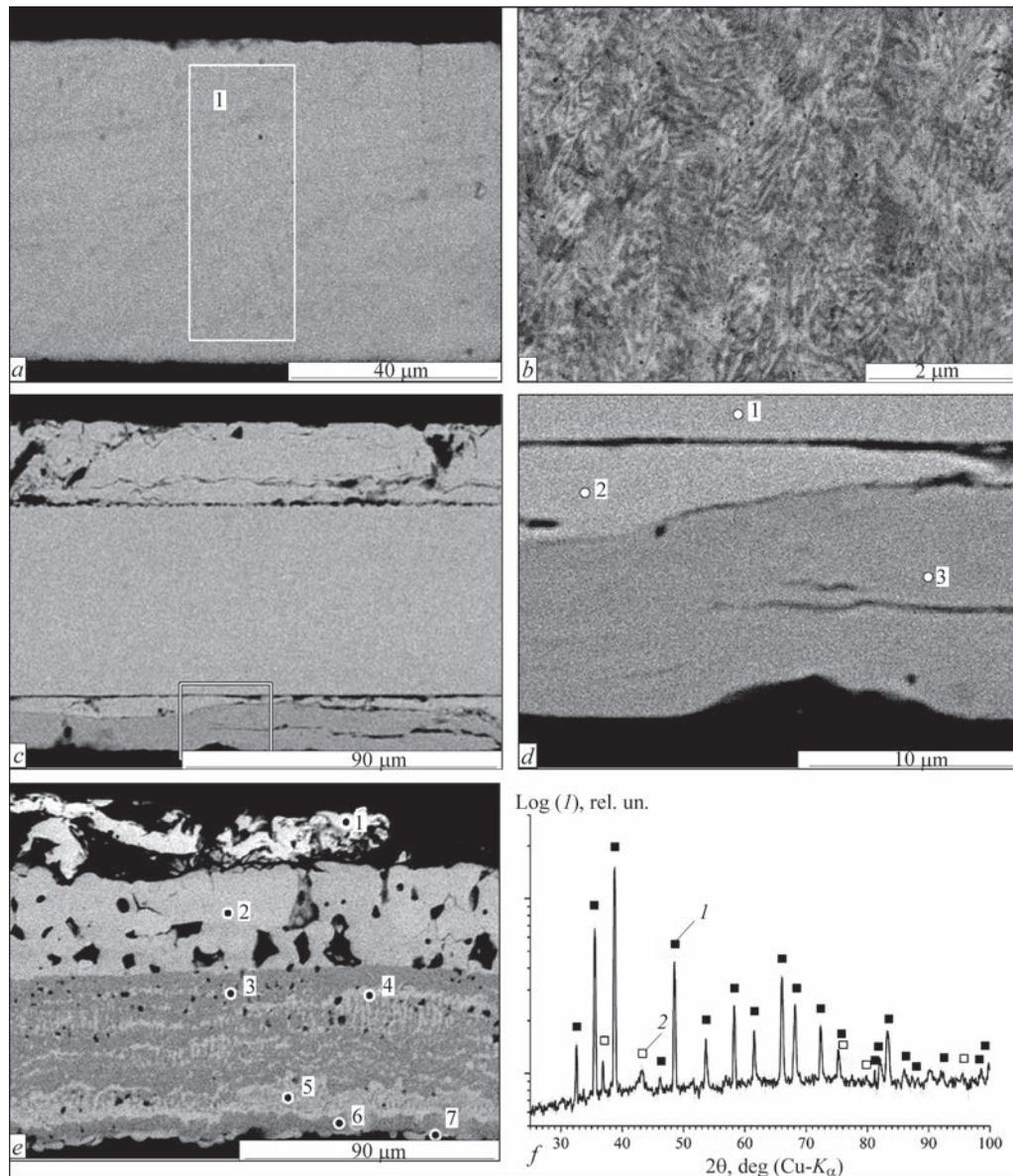


Figure 2. SEM images of cross-sectional microstructure of CrFeCoNiCu alloy foil in the initial condition (*a, b*) after annealing at 900 °C in atmospheric air for 6 h (*c, d*) and 37 h (*e*); diffraction pattern obtained from the foil surface after annealing at 900 °C in atmospheric air for 37 h (*f*): 1 — CuO; 2 — NiO. Numbers show areas where local chemical analysis was conducted (Table 1)

Table 1. Chemical composition (wt.%) of areas of CrFeCoNiCu foil in the initial condition, and after annealing at 900 °C in atmospheric air (Figure 2)

Foil condition	Area	O	Cr	Fe	Co	Ni	Cu	
Initial (Figure 2, <i>a</i>)	1	–	14.12	20.38	23.05	22.53	19.92	
	After annealing for 6 h (Figure 2, <i>d</i>)	1	1.14	11.85	16.01	17.17	17.60	36.22
		2	1.44	8.97	16.87	17.11	18.34	37.26
After annealing for 37 h (Figure 2, <i>e</i>)	3	0.85	0.37	98.78	–	–	–	
	1	1.97	–	0.63	–	97.41	–	
	2	19.57	–	0.46	2.39	2.31	75.27	
	3	25.44	11.36	18.79	15.7	15.63	13.08	
	4	25.99	14.56	18.24	16.37	12.80	12.03	
	5	22.76	11.08	11.54	18.08	20.00	16.54	
	6	26.10	23.68	18.61	17.49	8.91	5.20	
7	14.43	0.58	1.83	1.83	1.20	80.13		

more active under these conditions, coalescence of copper-enriched phase grains and its further refining take place, resulting in copper content increasing up to 93 wt.%.

Thus, structural changes occurring in CrFeCoNi-Cu foils during 37 h of staying at the temperature of 900 °C in air environment actually lead to destruction of the material, essentially limiting the potential

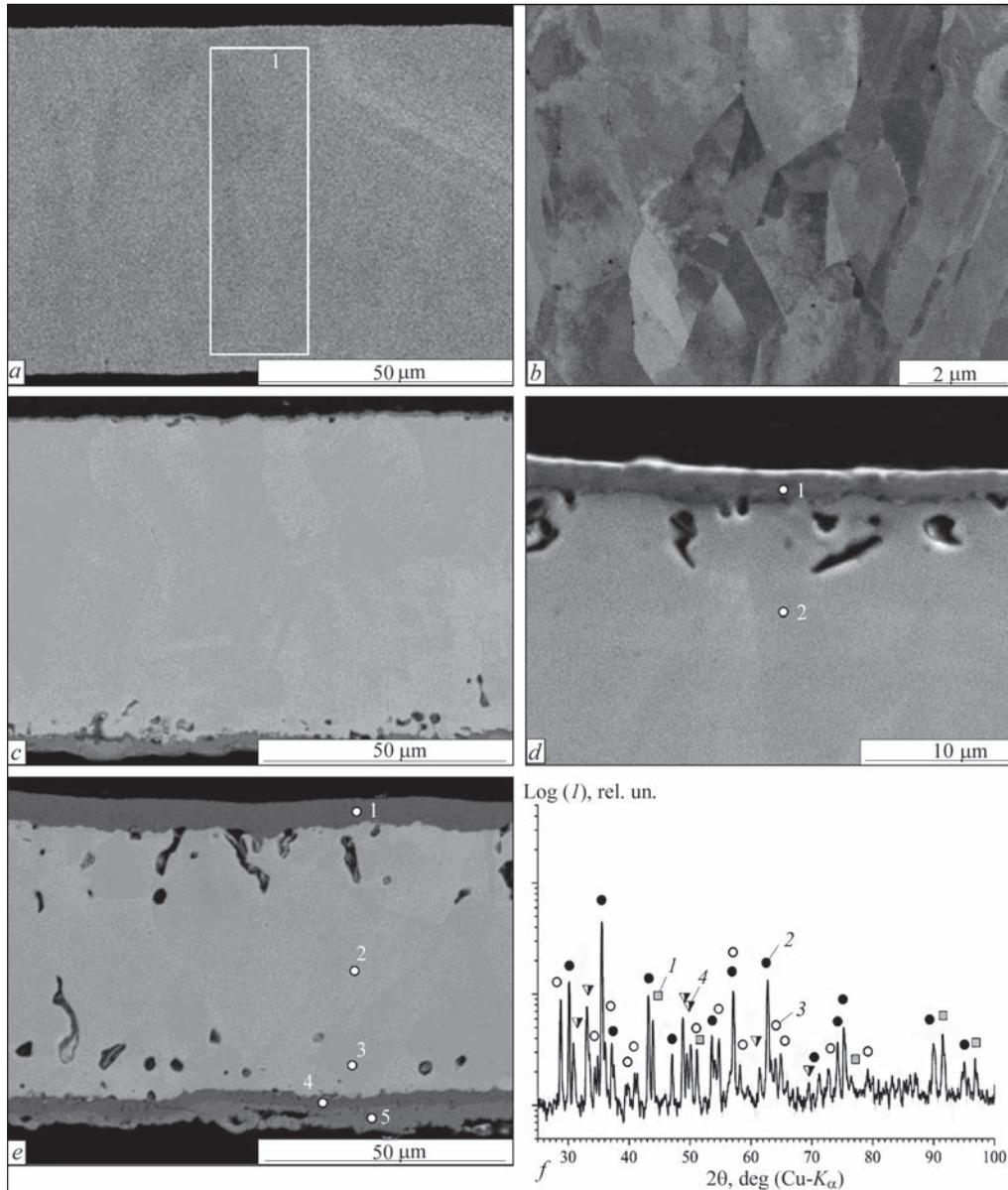


Figure 3. SEM images of cross-sectional microstructure of CrFeCoNi alloy foil in the initial condition (*a, b*), after annealing at 900 °C in atmospheric air for 6 h (*c, d*) and for 37 h (*e*); diffraction pattern obtained from foil surface after annealing at 900 °C in air for 37 h (*f*): 1 — FCC (CrFeCoNi); 2 — Fe_3O_4 ; 3 — Cr_2O_3 ; 4 — $(\text{FeCoNi})\text{O}$. Numbers show the areas where local chemical analysis was performed (Table 2)

Table 2. Chemical composition (wt.%) of areas of CrFeCoNi foil in the initial condition and after annealing at 900 °C in atmospheric air (Figure 3)

Foil condition	Area	O	Cr	Fe	Co	Ni
Initial (Figure 3, <i>a</i>)	1	—	20.49	24.73	18.80	35.99
After annealing for 3 h (Figure 3, <i>d</i>)	1	33.82	58.25	3.01	1.27	3.65
	2	—	20.43	25.35	19.62	34.60
After annealing for 37 h (Figure 3, <i>e</i>)	1	33.23	13.37	27.61	11.23	14.56
	2	—	17.05	25.05	20.47	37.43
	3	—	14.87	23.21	20.92	41.00
	4	34.77	62.08	1.70	0.57	0.89
	5	30.38	13.75	32.07	11.83	11.96

service life of this high-temperature HEA. Analysis of the obtained results shows that the relatively low values of heat resistance of CrFeCoNiCu system alloys can be related, chiefly, to copper content in the foil composition. To verify this assumption under identical conditions, heat resistance testing of foils of CrFeCoNi system HEA was conducted. Investigations were performed in foil of 67 μm thickness, SEM images of the foil cross-sectional microstructure before heat treatment are given in Figure 3, *a, b*, chemical composition is shown in Table 2. It is found that in the first 6 h of annealing, the increase of specific weight of CrFeCoNi foils took place almost 8 times slower, compared to CrFeCoNiCu alloy foils (Figure 1, curve 2). At further soaking of CrFeCoNi alloy foils at the temperature of 900 °C, increase of sample specific weight became considerably slower. Maximum value of specific weight increase for CrFeCoNi alloy foils after heat resistance testing was on the level of 1.5 mg/cm².

SEM investigations showed that scale of 3–7 μm thickness with a high degree of continuity and low defectiveness of the structure forms on the foil surfaces after 6 h of heat treatment (Figure 3, *c, d*). Chemical analysis of the scale revealed that it is a chromium-based oxide with a small content of other foil components (Table 2). No oxygen was found in the foil surface layers. However, pores of up to 5 μm size are observed, forming along the alloy grain boundaries. After 37 h of annealing at the temperature of 900 °C in air, the thickness of scale on the outer surfaces of CrFeCoNi alloy foil increases up to 10 μm . It was found that the scale structure is layered with a small number of defects: outer layer is represented by iron-based oxide, and inner layer is chromium-based oxide (Figure 3, *e*, Table 2).

X-ray structural analysis showed (Figure 3, *f*) that scale is formed on the base of Cr₂O₃ chromium and iron Fe₃O₄ oxides. The diffraction pattern also shows peaks from complex oxide (FeCoNi)O. No oxygen was found in the foil bulk and surface areas. Moreover, a significant increase of the number and size of intercrystalline pores in the foil subsurface layers was noted, which is the consequence of Frenkel effect. Foil swelling is practically absent, foil overall thickness somewhat increased to 70–72 μm . On the whole, obtained results show that such a heat treatment did not have an essential influence on the microstructure and phase composition of the foil material, and the presence of oxygen was revealed only in the subsurface layers in the formed oxide composition.

Thus, it was found that copper content in the composition of high-entropy alloys has a negative effect on the material heat resistance as a result of forma-

tion of scale based on copper and nickel oxides with a large number of defects and low degree of continuity. Copper absence in HEA composition promotes lowering of the rate of high-temperature oxidation at the temperature of 900 °C in atmospheric air by more than 8 times.

CONCLUSIONS

At testing for heat resistance at the temperature of 900 °C in atmospheric air increase of specific weight of CrFeCoNiCu alloy foil takes place 8 times more intensively than in CrFeCoNi foils. More intensive high-temperature oxidation of CrFeCoNiCu foil is associated with significant activation of copper atom diffusion, their coming to the foil surface and formation of scale with a low continuity based on CuO and NiO oxides with a large number of defects in their structure. Foils of CrFeCoNi alloy are characterized by higher values of heat resistance due to formation of scale based on Cr₂O₃ oxide on the surface with lower defect level and greater continuity.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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