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Structure and residual stresses in NiCoFeCrMn and NiCoFeCr HEAs under high temperature irradiation with helium ions

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Abstract. The work presents the results of a study of the elemental and phase composition, internal stresses in NiCoFeCr and NiCoFeCrMn HEAs irradiated with helium ions (40 keV, $2\cdot10^{17}$ cm^{-2}) at a temperature of 700 °C). It has been shown that the elemental and phase composition of NiCoFeCr and NiCoFeCrMn HEAs is resistant to high-temperature irradiation. Irradiation leads to the formation of a large number of blisters on the surface of NiCoFeCr HEAs compared to NiCoFeCrMn, as well as to an increase in tensile stresses and the formation of compressive stresses in the NiCoFeCr and NiCoFeCrMn alloys, respectively. The high radiation resistance of NiCoFeCrMn HEAs compared to NiCoFeCr was revealed.

Keywords: High-entropy alloys, high-temperature irradiation, elemental and phase composition, solid solutions, stress.

1. Introduction

Modern challenges facing the scientific and technological part of nuclear power are associated to a large extent with increasing the efficiency of nuclear power plants by increasing their operating temperatures [1]. Materials for the core and protection of reactors must withstand temperatures up to 500–850 °C [2]. Moreover, such reactors will experience high-dose neutron irradiation. One of the most promising classes of materials for solving such problems is high-entropy alloys (HEA) [3, 4]. They attract the attention of scientists from all over the world, and the works of the Cantor, Senkov, Yeh teams are recognized as pioneers in this field [5, 6].

This work is a continuation of research [7], which compared the stability of the structure of NiCoFeCrMn, NiCoFeCr HEAs and pure Ni under irradiation with helium ions with energy of 40 keV and a helium ion fluence of up to $2\cdot10^{17}$ cm^{-2} at room temperature, as well as changes in stress with increasing fluence. The purpose of this work was to study and compare the radiation resistance of NiCoFeCr and NiCoFeCrMn HEAs when irradiated with helium ions at 700 °C.

2. Material and methods

NiCoFeCr and NiCoFeCrMn alloys were obtained in the Beijing Institute of Technology (China) by the following technology. Bulk ingots were prepared from powders of pure (up to 99.97%) metals by arc melting in a high-purity argon atmosphere followed by casting into copper cuvettes. After their crystallization, annealing was carried out for 24 hours at 1150 °C in order to spheroidize and homogenize the grain structure of the samples. Subsequently, cold rolling was carried out until the thickness of the ingots decreased by 85% and final annealing at 1150 °C for 72 h was carried out in order to reduce the texture and stresses caused by rolling.

The samples were irradiated at the DC-60 heavy ion accelerator at the Astana branch of the Institute of Nuclear Physics (Kazakhstan). Irradiation was carried out with He^{2+} ions with energy 40 keV at a fluence of $2\cdot10^{17}$ cm^{-2} at a temperature of 700 °C.

Analysis of the surface morphology of the samples was carried out using scanning electron microscopy (SEM) using a Hitachi TM3030 scanning electron microscope. The elemental composition of the samples was determined by X-ray energy dispersive analysis using a Hitachi TM3030 microscope.

Phase analysis of the samples was carried out using X-ray phase analysis. X-ray diffraction patterns were obtained on a Rigaku Ultima IV X-ray diffractometer in parallel beam geometry using characteristic CuKα X-ray radiation with a wavelength of λ = 0.154179 nm. The samples were photographed in the Small-angle X-ray diffraction (SAXRD) mode at the angle of incidence of the X-ray beam α to study only the irradiated area of the samples. Internal stresses in the samples were determined by the g-$\sin^2\psi$ method [8].

3. Results and discussion

The results of studying the composition and structure of the initial NiCoFeCr and NiCoFeCrMn alloys are presented in paper [7]. The alloys are single-phase solid solutions (Ni,Co,Fe,Cr) and (Ni,Co,Fe,Cr,Mn) with an fcc lattice, a coarse-grained structure (80–100 μm) and a uniform distribution of elements in depth. In the alloys NiCoFeCr and NiCoFeCrMn, tensile macro- and microstresses were identified, the appearance of which is associated with mechanical processing of the materials at the manufacturing stage.

The radiation resistance of the composition and structure of NiCoFeCr and NiCoFeCrMn HEAs was studied under irradiation with low-energy He ions with an energy of 40 keV and a fluence of $2 \cdot 10^{17}$ cm^{-2} at a temperature of 700 °C.

According to calculations using the SRIM program [9] of radiation damage in NiCoFeCr and NiCoFeCrMn HEAs, the projective range of helium ions in the samples is 146 nm, the maximum energy loss in the region up to 100 nm is 0.22 keV/nm. The maximum concentration of implanted helium and the damaging dose in the HEAs are 16 at.% and 23 dpa for an irradiation fluence of $2 \cdot 10^{17}$ cm^{-2}, respectively [7]. However, SRIM calculations do not take heating effects into account.

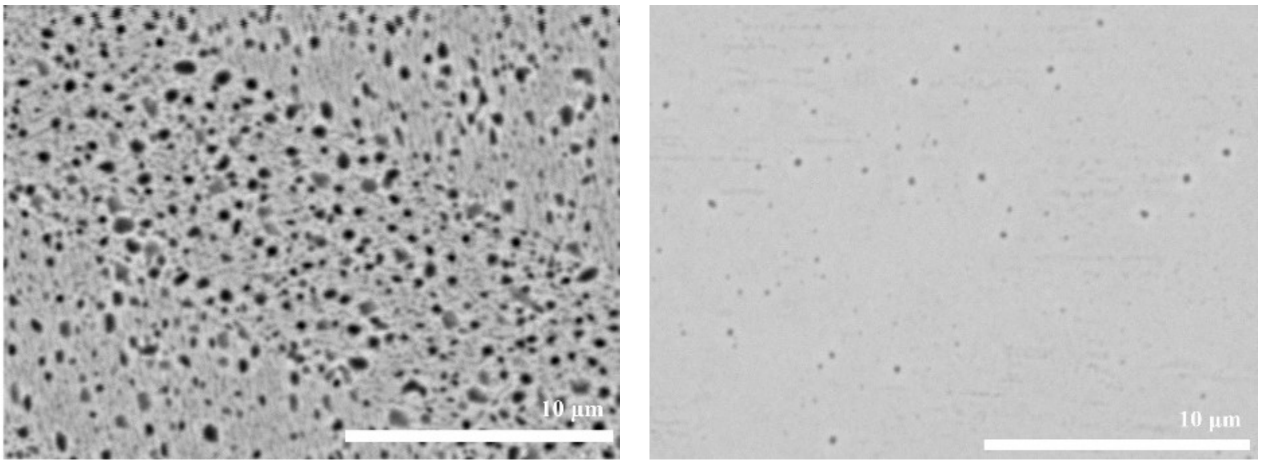
The results of studying the elemental composition of NiCoFeCr and NiCoFeCrMn HEAs irradiated with He ions (40 keV, $2 \cdot 10^{17}$ cm^{-2}, 700 °C) are presented in Table 1.

Table 1. Elemental composition of initial and irradiated with He^{2+} ions (40 keV, $2 \cdot 10^{17}$ cm^{-2}) at 700°C NiCoFeCr and NiCoFeCrMn HEAs.

Sample	**Concentration of elements, at. %**				
	Co	Cr	Fe	Mn	Ni
NiCoFeCr (initial)	24.7	25.7	25.3	-	24.3
NiCoFeCr (He^{2+}, $2 \cdot 10^{17}$ cm^{-2}, 700°C)	24.8	25.9	24.9	-	24.4
NiCoFeCrMn (initial)	19.5	20.3	19.8	20.6	19.8
NiCoFeCrMn (He^{2+}, $2 \cdot 10^{17}$ cm^{-2}, 700°C)	19.5	21.3	21.1	16.6	20.2

As can be seen from Table 1, high-temperature irradiation with helium ions does not lead to a change in the elemental composition of the NiCoFeCr alloy. In this case, irradiation of the NiCoFeCrMn alloy leads to an increase in the concentration of chromium and iron and a decrease in the concentration of manganese, which occurs for several reasons. Firstly, He atoms and defects have different migration energies and diffusion rates near sinks. Fe atoms probably move from the surface deeper into the sample due to exchange with vacancies from a greater depth, as happened when NiCoFeCr was irradiated with Ni ions at a temperature of 500–580 °C [10]. Also, diffusion coefficients through vacancies in CoCrFeNiMn irradiated with Ni at 500C decrease from Mn to Cr, Fe, and Ni which with Co is the least mobile of them, and therefore Mn decreases sharply near grain boundaries [11]. In NiCoFeCr, the migration of Fe/Cr atoms through vacancies requires less energy than the migration of Ni/Co along this path [10]. Secondly, this is likely due to the increase in dislocation density in NiCoFeCrMn, which can form loops and serve as sinks for defects, affecting the diffusion rate of elements [12]. Third, the accumulation and diffusion of mobile helium atoms affect the distribution of HE atoms. In the bcc HEA TiVNbTa irradiated with helium ions at 700 °C, V atoms accumulated, and the remaining elements were depleted near helium bubbles, which is associated with the fact that smaller atoms tend to diffuse as interstices, and large atoms move by exchanging with vacancies, and therefore their concentrations near He bubbles fall [13]. Due to the connection of He atoms with vacancies and the formation of clusters, the diffusion of atoms changes through the vacancy mechanism [14]. As a result, the concentration of elements in irradiated HEA samples remains close to equiatomic, which indicates the resistance of these alloys to the development of concentration gradients and radiation segregation.

Figure 1 shows SEM images of the HEAs surface after high-temperature irradiation with He ions. The results of SEM studies showed that in NiCoFeCr at 700 °C many defects similar to pores are formed, which is probably due to the fact that, at a temperature close to the half-melting temperature of the alloy, helium bubbles can form channels and the surface can become porous. High-temperature irradiation of the NiCoFeCrMn alloy leads to the formation of rare dark spots with a diameter of up to 400 nm relative to NiCoFeCr, which are probably pores or blisters.



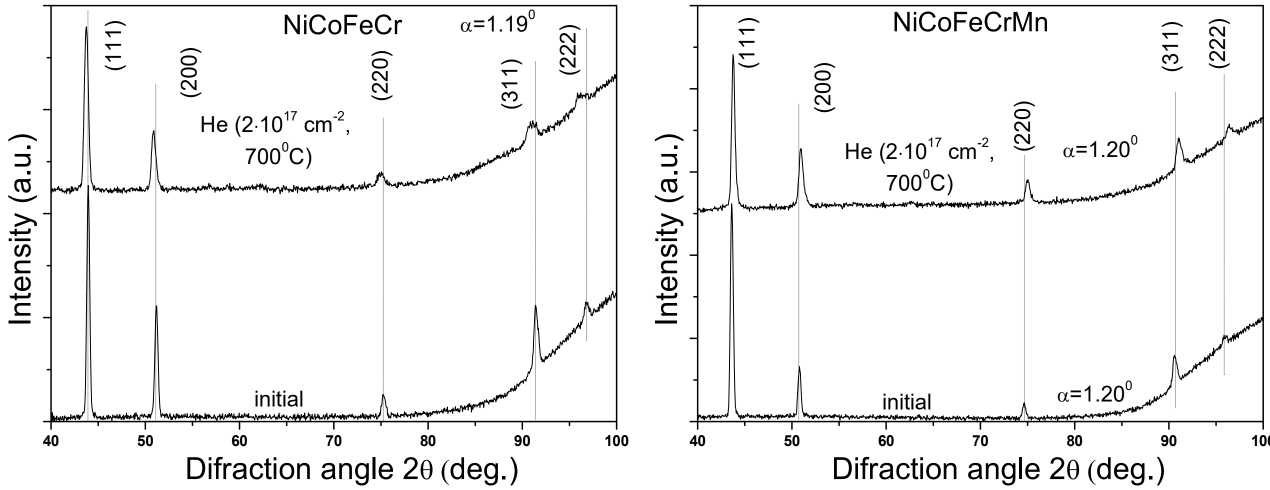
(a) (b)

Fig. 1. SEM images of the surface of NiCoFeCr (a) and NiCoFeCrMn HEAs irradiated with helium ions (40 keV, ion fluence $2 \cdot 10^{17}$ cm^{-2}) at a temperature of 700 °C.

The results of studying the phase composition of HEAs after high-temperature irradiation with helium ions are presented in Figure 2. X-ray patterns were obtained at low angles of incidence of X-ray radiation $\alpha = 1.19$ and 1.20° for NiCoFeCr and NiCoFeCrMn, respectively. Angles $\alpha = 1.19$ and 1.20° correspond to the X-ray penetration depth of 230 nm (the penetration area of implanted helium).

Analysis of X-ray diffraction patterns of samples after high-temperature irradiation with helium ions (Fig. 2) did not reveal the appearance of diffraction peaks corresponding to new phases or the disappearance of existing ones, i.e. there was no decomposition of solid solutions (Ni,Co,Fe,Cr) and (Ni,Co,Fe,Cr,Mn). This indicates the high radiation resistance of the phase composition of HEAs to high-temperature irradiation with helium ions with a fluence of $2 \cdot 10^{17}$ cm^{-2}.

It was found that high-temperature irradiation leads to a shift of the diffraction peaks of solid solutions (Ni,Co,Fe,Cr) to the region of smaller 2θ angles (Fig. 2a), and of solid solutions (Ni,Co,Fe,Cr,Mn) to the region of large angles 2θ (Fig. 2b). The calculations showed that high-temperature irradiation leads to an increase in the lattice parameter of the solid solution (Ni,Co,Fe,Cr) by 0.42% and a decrease in the lattice parameter (Ni,Co,Fe,Cr,Mn) by 0.52%. The increase in lattice parameter of NiCoFeCr could be caused by the accumulation of point defects and their small clusters, which is limited by defect annealing [15], but this is still a microscopic type of swelling [16]. At the same time, high-temperature irradiation improves the recombination of defects and reduces tensile strains of the lattice, so in NiCoFeCrMn HEAs the distorted lattice relaxes [16].



(a) (b)

Fig. 2. X-ray patterns of HEAs of initial and irradiated with He^{2+} ions ($2\cdot10^{17}$ cm^{-2}) at 700°C of NiCoFeCr (a) and NiCoFeCrMn (b) HEAs, taken at an angle of incidence of X-ray radiation α.

To assess the change in internal stresses after high-temperature irradiation, studies of macrostresses in the samples were carried out using the g-sin$^2\psi$ method. The results of determining residual stresses in the original and irradiated samples at α = 1.19, 1.20°, calculated for the (111) plane, are presented in Figure 3.

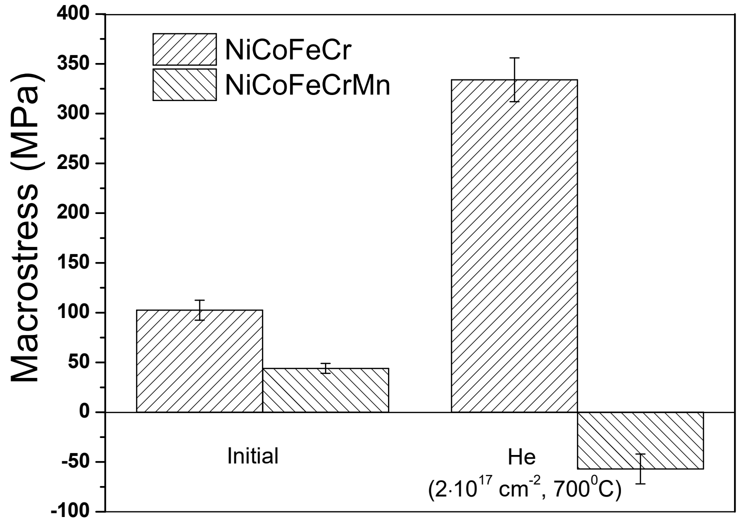


Fig. 3. Macrostresses in the initial and irradiated with He ions at a temperature of 700°C NiCoFeCr and NiCoFeCrMn HEAs.

As can be seen from Figure 3, high-temperature irradiation of the NiCoFeCr alloy with helium ions leads to an increase in tensile stresses in it by 2.26 times. Irradiation of the NiCoFeCrMn alloy leads to the formation of compressive stresses equal to – 57 MPa. The increase in stress in NiCoFeCr alloys is apparently associated with the processes of relaxation and diffusion of radiation defects, primarily with the formation of blisters on the surface, which is confirmed by SEM studies (Fig. 1a). In the case of the NiCoFeCrMn alloy, the formation of blisters is small (Fig. 1b).

Comparison with data on irradiation with helium ions at room temperature [7] showed a decrease in the level of compressive stresses. This is due to the partial formation of blisters, as well as the relaxation of radiation defects at high temperatures (700 °C).

Thus, the elemental and phase composition of the NiCoFeCr and NiCoFeCrMn HEAs under consideration is resistant to irradiation by helium ions (40 keV, $2\cdot10^{17}$ cm^{-2}) at a temperature of 700°C; the formation of new phases has not been detected. The main changes obtained as a result of irradiation of samples are associated with stress relaxation and the formation of blisters.

The obtained data on changes in macrostresses indicate the high radiation resistance of NiCoFeCrMn HEAs under high-temperature irradiation with helium ions compared to NiCoFeCr HEAs.

4. Conclusion

It was found that irradiation of NiCoFeCr and NiCoFeCrMn HEAs with He^{2+} ions with an energy of 40 keV at a fluence of $2\cdot10^{17}$ cm^{-2} and a temperature of 700 °C does not lead to a change in the elemental and phase composition of the alloys.

When irradiated with helium ions at 700 °C, large blisters and pores are formed in NiCoFeCr, which are probably formed by creating channels from helium bubbles. Rare blisters and small pores are formed in NiCoFeCrMn HEAs.

It was revealed that high-temperature irradiation of NiCoFeCr HEAs with helium ions leads to an increase in tensile stresses by 2.26 times and the formation of compressive stresses in NiCoFeCr HEAs.

It has been established that NiCoFeCrMn HEAs are characterized by greater radiation resistance compared to the NiCoFeCr alloy.

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