Metastable states and physical properties of Co-Cr-Fe-Mn-Ni high-entropy alloy thin films

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Introduction

About 17 years ago, the first papers on the study of high-entropy alloys (HEAs) were published. The HEAs are composed of at least 5 major components with equiatomic or nearly equiatomic concentrations which are between 5 and 35 at.%. Choosing a number of components and their concentration allows one to achieve an increased entropy of mixing, which remains not only in the melt but after solidification. Because of the high entropy, usually simple substitutional solid solutions with BCC or FCC crystal lattices are formed during the solidification of such alloys. The HEAs are characterized by many useful characteristics, such as hardness, wear resistance, resistance to oxidation, corrosion, and ionizing radiation, biocompatibility, and high thermal stability. At the same time, the majority of HEAs were investigated in the as-quenched or homogenized state, whereas much less attention was paid to the study of thin films of high-entropy alloys.

Materials and methods

In this study, $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ HEA thin films have been synthesized by the modernized method of three-electrode ion-plasma sputtering of composite targets. The targets were parallelepipeds of pure (not less than 99.99%) metals 20 × 20 mm in size and 5 mm in height, separated by barrier cells with the function of electrostatic lenses, which allowed a 5-7-fold increase in the velocity of atoms sputtered from the target before a collision with the substrate, on which deposition was carried out. The cooling rate, which is connected with the relaxation time of individual atoms on the substrate, was in this case theoretically evaluated to be 10^{13}-10^{15} K/s, that on 7-8 orders of magnitude higher than the maximum cooling rates that are realized during the quenching from the liquid state. In fact, there occurs a vapor quenching. Sputtering was carried out on the sitall substrates, as well as on a fresh cleavage of NaCl single crystal. To estimate the compositions of the films, a special procedure was used , which took into account the relationship between the relative atomization area occupied by the element and its content in the deposited film. This technique allows us to determine the film composition to within ± 2 at.%

The sputtering deposition process was carried out at room temperature with pure Ar atmosphere, the working pressure was controlled at $5 \cdot 10^{-2}$ Pa. The deposition rate for the HEA thin film was 0.19 nm/s. The as-deposited HEA film thickness was estimated to be ~ 110 nm. Films deposited on single-crystal substrates after a dissolution of the salt were used for structural studies by X-ray diffraction analysis (with a photographic registration, in a Debye camera on the URS-2.0 diffractometer in filtered Co K_α radiation). Debyegrams were digitally microphotometred and processed using a qualitative phase analysis software Qualx2. Films obtained under identical conditions of deposition on the sitall substrates were used to study the thermal stability and physical properties of nonequilibrium structures. The polytherms of the surface electrical resistance of films were measured by the four-point technique upon continuously heating in the high vacuum with a pressure of $4 \cdot 10^{-2}$ Pa. The heating rates from room temperature to ~ 870 K were 9 K/s and 4.5 K/s. Calculation of the activation energy of the beginning of phase transitions was carried out by Kissinger method. Using the temperature dependence of the relative resistance $R(T)/R_0$ at different heating rates we can construct the function $\ln(T^2/V)$ from $F(1000/T)$. This relationship satisfies the Arrhenius equation. The activation energy of phase transition was estimated by the slope of this line. The magnetic properties of the films were measured by a vibrating sample magnetometer at room temperature with the magnetic field applied parallel to the film plane.

Results

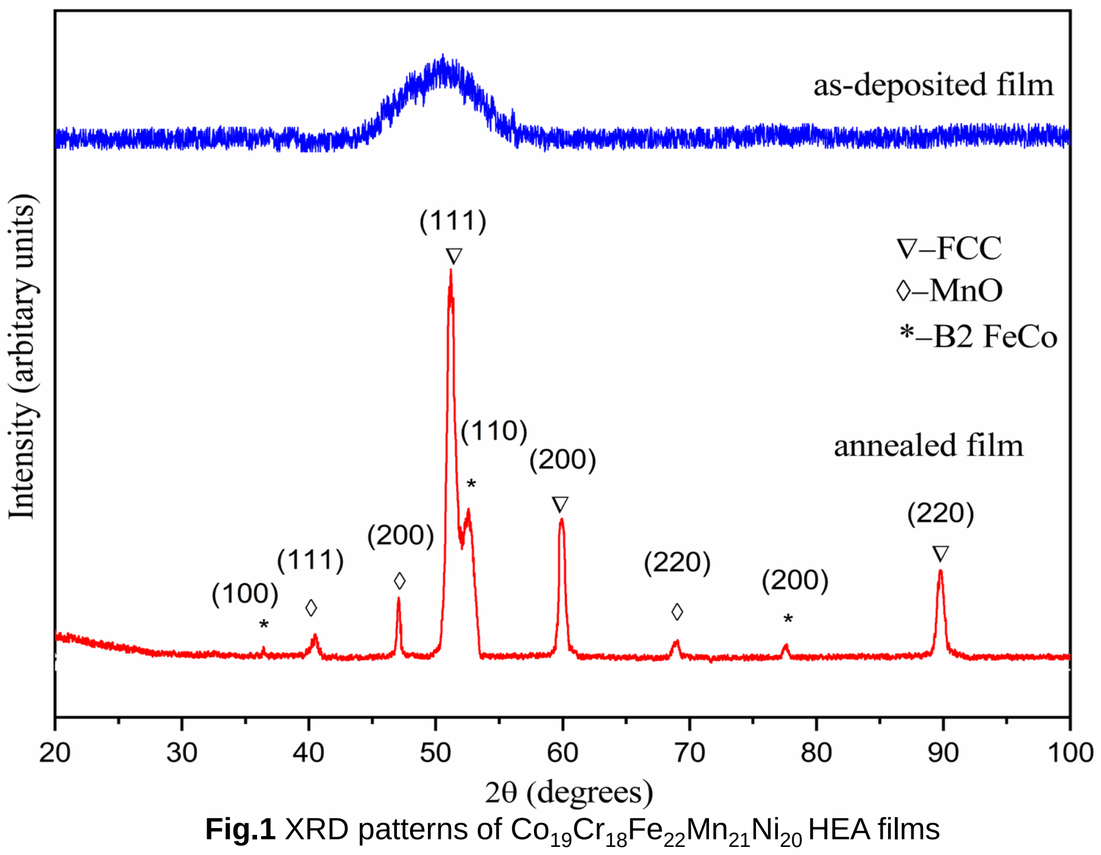

Fig.1 XRD patterns of $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ HEA films

The XRD patterns of the films are shown in Fig. 1. Single diffuse halo observed on the XRD patterns of the as-deposited films confirms their amorphous structure. The coherently scattering domain size (crystallite size) of films estimated by the Sherer equation ($L = K\lambda/\beta\cos\theta$) is ~ 4 nm. Some of the thin films annealed at 900 K in a vacuum furnace were identified to be oxidized by the small amount of oxygen in the chamber (all the as-deposited thin films contained 7–8 at % oxygen which was from the deposition process). These films transform from an amorphous state into a crystallized FCC solid solution structure with the lattice parameter a=0.3613 nm with coherently scattering domain size ~30 nm. Such crystalline structure was reported earlier for the bulk as-casted samples and thin films (with the lattice parameter of 0.359 nm for the as-casted sample) of CoCrFeMnNi alloy. The cubic B2 phase of FeCo with a lattice parameter of 0.2857 nm is also formed in the annealed films. The occurrence of this phase was noted in the study of CoCuFeNiMn samples subjected to prolonged annealing at 500°C. As a result of oxidation processes, a dispersed phase of cubic FCC manganese oxide MnO is also formed after annealing because of diffusion of atoms and oxidation.The study of electron diffraction patterns confirms the results of X-ray structural studies.The as-deposited HEA film exhibits the soft magnetic properties and the saturation magnetization (*Ms*), and coercivity (*Hc*) are 29.4 A·m²/kg and 400 A/m. After annealing the values of these parameters increase, respectively, to 57.6 A·m²/kg and 8760 A/m (Fig.2) . So the annealed films can be referred to hard magnetic materials. As can be seen from the dependence of the relative electrical resistivity of the films $R(T)/R_0(300\ K)$, the temperatures of the single-stage phase transformations (crystallization processes) in $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ films are ~ 540 K for heating rate 4.5 K/min and ~ 580 K for heating rate 9 K/min. The films in the initial amorphous state are characterized by a very low value of the temperature coefficient of resistance (average value ~$3.5 \cdot 10^{-5}$ 1/K, while after crystallization it increases up to $5.1 \cdot 10^{-4}$ 1/K.

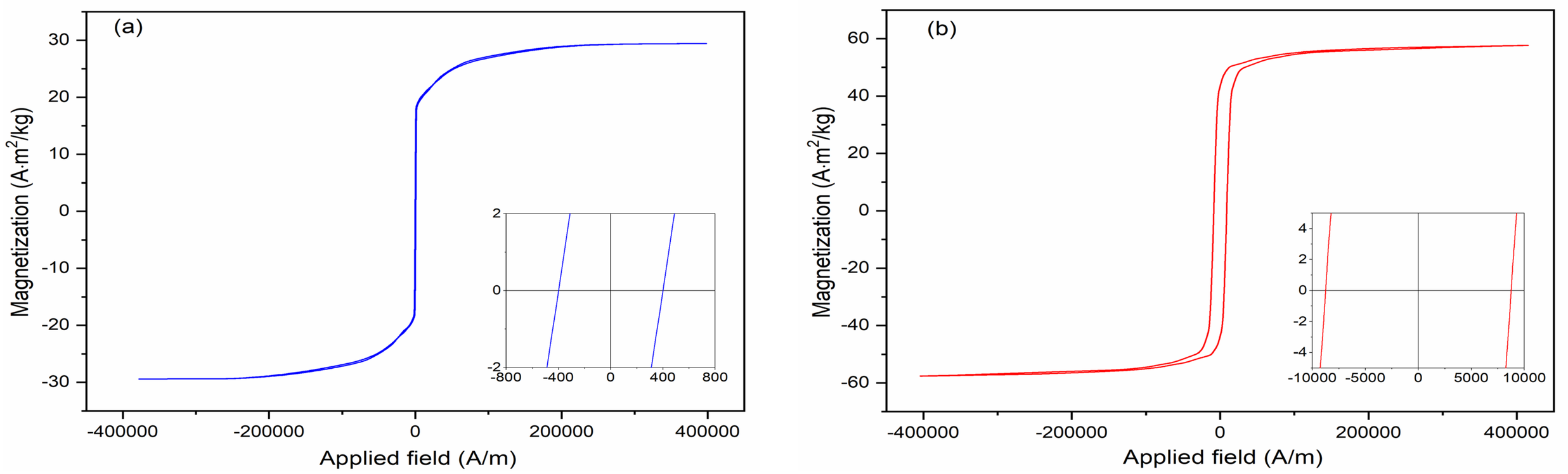

Fig.2 Hysteresis loops of $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ HEA films. **a-** as-deposited; **b-** annealed

Conclusions

In this study, a new $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ HEA thin films have been synthesized by the modernized method of three-electrode ion-plasma sputtering. The as-deposited films the films have an amorphous structure and soft magnetic properties, while the annealed films transform into a crystallized FCC solid solution. A minor phase of manganese oxide is also formed after annealing together with the B2 phase of FeCo. Annealing also improves the magnetic properties of $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ HEA thin films, increasing the magnetization and coercivity. Investigations of the temperature dependence of electrical resistivity have shown that the films in the initial amorphous state are characterized by a very low value of the temperature coefficient of resistance.