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Phase Formation and Structural Analysis via X-Ray Diffraction: Insights into Material Stability and Properties

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This review investigates thin films of CoCr-based high-entropy alloys, focusing on their contributions to physics through the study of phase formation and their analysis using X-ray diffraction. By leveraging the principles of crystallography and solid-state physics, the project addresses critical challenges in understanding phase transitions and microstructural evolution in CoCr-based high-entropy alloy system. X-ray diffraction provides key insights on lattice parameters, crystallite size, and strain, linking these parameters to material properties and stability. The integration of computational modeling and experimental techniques emphasizes the project's role in advancing knowledge of phase behavior and its applications in automotive, hard coatings, and even semiconductor. This concise assessment highlights the importance of X-ray diffraction-driven studies in shaping future directions in materials science and physics research.

topics: high-entropy alloy (HEA), X-ray diffraction (XRD), phase structure, thin films

1. Introduction

In the last century, high-entropy alloys (HEAs) have combined multiple elements to form a new material with enhanced properties. Such materials are gradually being developed and used for common and special applications, usually in association with a metal or a combination of metals [1, 2]. The first HEAs were introduced by Yeh et al. [3] (see also [4]) and represent a novel class of materials characterized by a random mixture of five different elements with atomic percentage usually between 5% and 35% [5]. Among the most well-know HEAs is the Cantor alloy, which is a combination Co-Cr-Fe-Mn-Ni. It crystallizes in a FCC lattice (FCC — face-centered cubic) and is renowned for its balanced strength and ductility [6]. The success of bulk HEAs, as mentioned beforehand, was built on the scientific findings involving these alloys. However, there is limited research on thin films HEAs that could be accessible to the general public. The fabrication of HEA thin films may allow researcher to explore novel phase formation mechanisms, grain structure, crystal size, strain, as well as to explore material properties and stability that are challenging to achieve in bulk HEAs. In terms of occurrence, MoNbTaW is an example of the element most often discovered in thin films [7].

Among the studies on HEA thin films, CoCr-based HEA has been explored by Dolique et al. [5] using varying target power settings during sputtering deposition on FeCoNi as a target system see also [8]. Several years ago, it was observed that the system synthesized by magnetron sputtering techniques has shown an interesting transition in the structure of HEA thin films [9]. These innovations have expanded the potential application of HEAs, particularly in the areas demanding protective, automotive, and semiconductor coatings [10, 11].

The successful application of HEA thin films encourages better understanding and control of the early stages of the phases and compositional changes. Hence, it is compulsory to provide studies with an in-depth analysis on the development of HEA-based thin films, with respect to material properties and stability.

2. XRD and TEM

The phase structure and crystallographic orientation of the HEA thin film were examined using X-ray diffraction (XRD) testing. Previous study [8] on as-deposited HEA thin films with thicknesses ranging from 300 to 1400 nm revealed that, as the film thickness increased, a strong and sharp peak was observed around 43.4° , corresponding to the (111) peak (see Fig. 1). It indicated the presence of face-centered cubic (FCC) phase structure, which allows for better thermal and mechanical stability. This finding was supported by the previous synchrotron XRD research of CoCr-based HEA thin films, which showed the presence of two distinct and sharp peaks at around 43.5° and 44.9° , corresponding to the FCC (111) and BCC (110) dualphase structure [10] (BCC — body-centered cubic). The FCC (111) and BCC (110) peaks exhibited a slight rightward shift with increasing annealing temperature, which reflected the decrease in the lattice parameters of both phases. Figure 2 shows the atomic arrangement for FCC and BCC structure in the normal state. The previous study [11] proven a different packing fraction for the FCC structure (0.74) than for the BCC structure (0.68). The packing fraction (PF) can be defined as [11]

$$PF = \frac{n\frac{4}{3}\pi r^3}{\alpha^3}.$$
(1)

In (1), ρ represents the intrinsic alloy density $[g/cm^3]$, n is the number of atoms/cell, $\frac{4}{3}\pi r^3$ is the volume of an atom, and α is the volume of an unit cell. The equation was attributed to heat recovery, where residual stress in the as-deposited films was relieved through enhanced atomic diffusion at high temperatures, particularly due to differences in atomic size of the alloying elements [12]. Chou et al. [13] reported that the electrical conductivity (σ) decreases with increasing the percentage of Al addition in the single-phase of either FCC or BCC regions. FCC and BCC phases tend to appear more readily in HEA thin films compared to bulk HEA due to thermodynamic stability and the influence of conditions on the growth of films according to their unique properties.



Fig. 1. XRD pattern of CoCr-based HEA thin films. Reprinted with permission from [7] (Copyright 2020 Elsevier).



Fig. 2. Schematic illustration of the (a) FCC and (b) BCC crystalline structure. Reprinted with permission from [12] (Copyright 2013 Elsevier).

Regarding the microstaining of HEA thin films, as proven in the previous study [9], it can also affect the phase stability because of the lower energy configuration under strain compared to other phases. This resulted in the dominance of FCC or BCC phasee, which tend to be more sensitive to strain. The residual stress in the deposited thin films was relieved through heat recovery, which accelerated the atomic diffusion at high temperatures. This, in turn, impacted the thermal expansion of the material and its electronic properties due to the changes in the lattice parameter during phase transitions [11].

The reduction in peak intensity, as depicted in Fig. 1 by Z. Wang et al. [7], can be attributed to the increased lattice distortion in crystalline phases and amorphous characteristics of thin films with increasing additive concentration. The authors of [14] observed smaller grain size along with larger dislocation and twinning density at high addition content [12]. This film transformed from an amorphous state into a crystallized FCC solid solution structure with a lattice parameter of a = 0.3613 nm.

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Fig. 3. (a) TEM bright-field image and (b) selected-area image for thin films without Al addition. (c) TEM bright-field image and (d) selected-area image for thin films with Al addition. Reprinted with permission from [16] (Copyright 2014 Elsevier).

It was also reported that a similar crystalline structure was observed under the influence of the Al content in CoCr-based HEA [15]. The equation from the previous study [16] showed the temperature dependence of resistivity can result in the resistivity expression of the form [16]

$$\rho = \rho_0 \left| 1 + \alpha \left(T - T_0 \right) \right|. \tag{2}$$

In (2), ρ is the resistivity at temperature T, while ρ_0 is the resistivity at a reference temperature T_0 , and α is the temperature coefficient of resistivity, indicating how the resistivity changes with temperature — in our case it is like $(T)^{-1}$. The occurrence of this phase transition and crystal structure was noted as a change of the dual-phase from amorphous to crystalline phases, which resulted in grain refinement and further enhance the properties and stability of thin films during the transition [13].

In addition to XRD results, transmission electron microscopy (TEM) is used to gather more detailed crystallographic information and grain size data of HEA thin films. The phenomenon observed in HEA thin films, in which the growth condition became more energetic at high bias voltage, can lead to the relocation of adsorbed atoms toward grain boundaries [17]. In Fig. 3b, the TEM bright-field image reveals an FCC-like structure, and Fig. 3c shows a BCC-like crystalline structure. Both the FCC and BCC structures can be explained by two arguments, i.e., the observed phase structures suggest that even a slight variation in chemical composition can affect the structural transformation from FCC to BCC or inversely [15]. At present, in all the reported HEAs, there is no hexagonal tightly packed (HCP) structure, which is present in structured HEAs except FCC and BCC. Most researchers usually assumed that the influence of the increasing percentage of additives such as aluminium is manifested in that there is a phase transition from FCC to BCC [10, 16]. Variation of mechanical properties of HEA thin films with diverse temperatures can be attributed to Hall–Petch effect as [15]

$$\sigma_{\gamma} = \sigma_{\gamma} + k \, d^{-\frac{1}{2}},\tag{3}$$

where σ_y represents the yield stress, which is the stress at which the material begins to deform, σ_0 is a frictional stress required to move dislocations within the material's crystal structure, k refers to the Hall– Petch slope, and d is the grain size used to define the material's strength, since smaller grains generally lead to higher strength due to grain boundary strengthening [17, 18].

In previous research [18], it was shown that an increase in grain size reduces material strength, resulting in lower hardness and elastic modulus values [19]. The average grain size incressed after 24 h of annealing, while the FCC phase lattice parameter reduced with longer annealing time due to heat recovery and recrystallization. Phase structure governs electronic properties such as metallic or semiconducting behavior including entropy. Entropy is responsible for phase stabilization, and also influences the phase transition of the material. However, a few studies have shown interest in computational modeling of HEA to learn the structure, kinetics and mechanical properties, such as semiconductors application, by using CALPHAD (an acronym for CALculation of PHAse Diagrams) method. It is a simulation technique used to predict the mechanical stability of HEAs by simulating phase diagrams and calculating thermodynamic properties. CALPHAD also ensures stability and performance under various operational conditions by allowing for the computation of electronic and vibrational contributions to entropy by [16]

$$\operatorname{Sel}(V,T) = -2k_{\mathrm{B}} \int_{-\infty}^{\infty} d\varepsilon \ n_{el(\varepsilon,V)} \left[f_{\mathrm{FD}} \ln(f_{\mathrm{FD}}) + (1 - f_{\mathrm{FD}}) \ln(1 - f_{\mathrm{FD}}) \right].$$
(4)

Here, Sel represents the entropy from conduction, while $f_{\rm BE}$ and $f_{\rm FD}$ denote the Bose–Einstein and Fermi–Dirac distribution functions, respectively. Thus, these kinds of HEAs can be used in transportation or semiconductor industry and need further studies. As the entropy value increases, it may stabilize certain phases (FCC or BCC) and enhance the ability of HEA thin film to conduct electricity or exhibit semiconductor-like behavior [16].

3. Conclusions

The focus of this review is on the next generation of HEA materials, especially thin films, which have greatly captured the attention of researchers due to their growth and unique properties, demonstrating strong interrelation. Thin films influence the phases and crystal structure in a way distinct from bulk materials. With different elements and methods, findings related to phase transition, crystal structure, and morphology enhance the properties and stability of HEA thin films. By controlling the parameters and treatments, CoCr-based HEA thin films can become reliable for demanding applications, providing better and more extensive functions such as protective coatings and even semiconductor applications. Moreover, future understanding is required to advance the technology by addressing existing knowledge gaps and challenges to discover the full potential of HEA thin films.

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