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A brief review of high-entropy films

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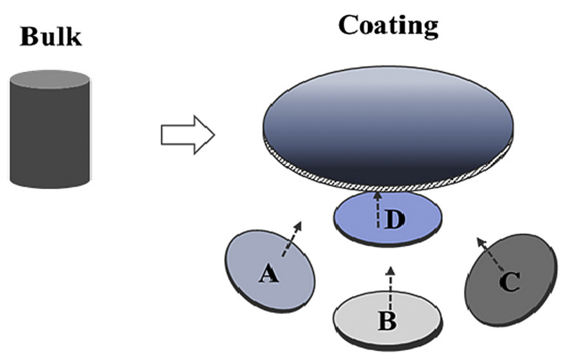
HIGHLIGHTS

- Composition design and processing of high-entropy films are discussed.
- Various properties of high-entropy films are summarized.
- High-entropy films for high-throughput experiments are put forward.

GRAPHICAL ABSTRACT



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ABSTRACT

High-entropy films are a new type of films which have been developed based on high-entropy alloys. It features many excellent properties, such as high strength and hardness with remarkable strain hardening rate, excellent wear and corrosion resistance, thermal stability, irradiation resistance, high toughness for wide-temperature range applications, etc., which traditional films are incomparable with. In recent years, high-entropy films have shown a fast development potential in various fields. This paper reviewed the recent development about high-entropy films. Preparation methods, composition design, phase structures, and various properties are mainly discussed in the paper, and the prospect of high-entropy films for high-throughput experiments is put forward.

1. Introduction

Materials are the foundation of social civilization, and alloy materials occupy an indispensable position. In recent years, high-entropy alloys (HEAs) have attracted a great deal of attention from researchers due to their unique multi-element solid-solution structures, and excellent properties. The high mixing-entropy allows them to have a lower free-energy and higher phase-stability. Therefore, HEAs tend to form a single phase solid-solution structure. This type of multi-component solid-solution has a large solid solubility, and its existence allows HEAs features high strength, excellent corrosion resistance, oxidation resistance, irradiation resistance, and wide-temperature range applications. HEAs have become another new research hotspot, following bulk amorphous alloys and intermetallic compounds.

In recent years, binary or ternary film has been widely explored.

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However, due to the limitations of the alloy entropy, the traditional metal nitride, carbide, and oxide film which are low-entropy films, could not meet the increasing requirements criteria. With the development of HEAs, researchers have focused on study about high-entropy films (HEFs). HEFs not only possess the excellent performance as HEAs, even some of the performances have been enhanced. These alloy films have shown major application potentials in the fields of solar thermal conversion systems [1], high hardness coating [2], corrosion resistant coating [3], diffusion barriers in the integrated circuit (IC) systems [4], etc.

2. Emergence and development of HEFs

Since the concept of HEAs was published in 2004, the study of HEFs has been subsequently developed. HEFs was reported in 2005, when Chen et al. [5] first prepared FeCoNiCrCuAlMn and $FeCoNiCrCuAl_{0.5}$ nitride film through magnetron sputtering, and explored the change of phase structure with the nitrogen flow rate. Then, Huang et al. [6] prepared $AlCoCrCu_{0.5}NiFe$ oxide film, and analyzed the phase structure, hardness, and phase stability. With the continuing development of HEFs, Tsai et al. [7] applied AlMoNbSiTaTiVZr film to the diffusion barrier between Cu and Si wafer. The experimental results showed that the films have major application potential. In recent years, high-entropy coatings prepared by laser cladding have gradually developed. Through laser cladding, Zhang et al. [8,9] prepared $NiCoFeCrAl_3$ and $FeCoNiCrAl_2Si$ high entropy coatings.

At present time, the HEFs are mainly including nitride-films and oxide-films. The principle of the HEFs composition design is similar to that of HEAs. Generally speaking, the elements of HEAs can be divided into “basic element” and “functional element” as shown in Fig. 1. For example, Cr, Fe, Co, Ni, and Cu, along with other elements, can be referred to as the base elements, since they do not have large differences in atomic size, and tend to form simple face-centered cubic (FCC) or body-centered cubic (BCC) solid-solution structures. Meanwhile, Ti, V, and W, which have excellent thermal stability and corrosion resistance properties, can be referred to as the functional elements. According to the performance requirements, the function elements can be added into the base elements. In addition, a number of non-metallic elements, such as C, N, and B, can also be added, which can fill interstitial positions of films, in order to improve the hardness characteristics.

3. Preparation of HEFs

The preparation methods of films can mainly be divided into two categories: physical methods, and chemical methods, which are shown in Fig. 2. Physical preparation mainly refers to physical vapor deposition (PVD), including vacuum sputtering, vacuum evaporation, and ion plating. Meanwhile, chemical preparation mainly includes chemical vapor deposition (CVD), and the liquid phase deposition (LPD).

At the present time, the following methods of preparing HEFs have been reported: magnetron sputtering method [10–13], laser cladding [8,9,14,15], electrochemical deposition [16], arc thermal spraying [17], cold spraying [18], electron beam evaporation deposition [19], and plasma cladding [7]. Among them, magnetron sputtering and laser cladding are the most mature techniques for the preparation of HEFs. Table 1 summarizes the characteristics of the two technologies.

The principle of magnetron sputtering deposition is a sputtering effect. The high energy particles bombard the surface of the target (Fig. 3), making the target atoms escape and move along a certain direction, and eventually thin film forms on the substrate [20]. The dual function of magnetic and electric fields increases the collision probabilities of the electron, charged particles, and gas molecules.

In the usual cases, the magnetron sputtering target material is prepared by the arc melting and powder-metallurgy methods. If the melting point of each principal component is relatively different, a powder metallurgy method is usually the priority choice. Also, it is difficult to obtain an equiatomic ratio thin film, since the different elements have different sputtering output capacities. Therefore, the “multi-target sputtering” has been proposed [21]. According the composition design of HEFs, many single element targets or alloy targets can be prepared, and the atomic ratio of elements can be controlled by adjusting the target sputtering power.

Laser cladding technology is pointed out that melting metal powder which features certain physical, chemical, or mechanical properties by high-power and high-speed laser. A layer combining with the matrix in the way of metallurgy bonding can improve the mechanical properties between the layer and matrix. Laser cladding technology is divided into two types of methods, referred to as pre-powder and synchronous feeding, as shown in the schematic diagram of Fig. 4.

4. Phase structure

The composition design of the HEFs is consistent with the HEAs. Therefore, the HEFs also has a “high entropy effect”. In addition, the film cooling rate is relatively fast, and it tends to form an amorphous phase or simple FCC, BCC solid solution phase. In this section,

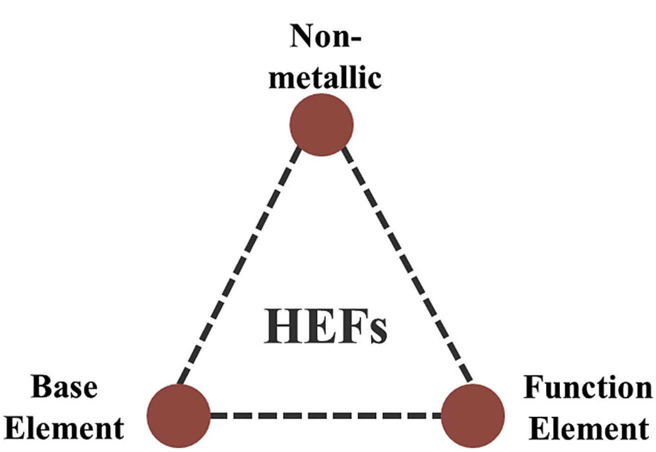

Fig. 1. Composition design of HEFs.

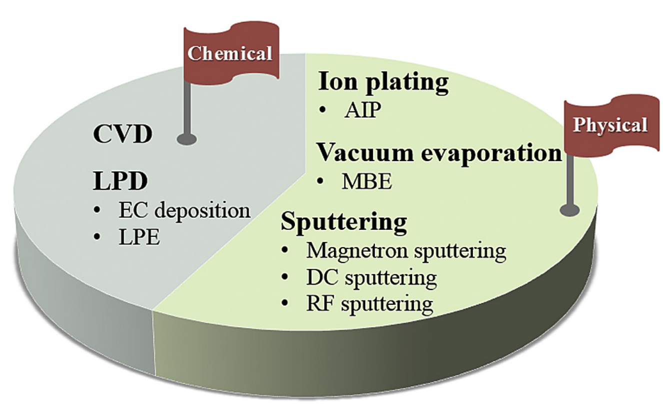

Fig. 2. Classification of thin film processing (Electrochemical (EC) deposition, Liquid phase epitaxy (LPE), Arc ion plating (AIP), Molecular beam epitaxy (MBE), Direct current sputtering (DCS), Radio frequency sputtering (RFS)).

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