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Review Article

Processing, alloy composition and phase transition effect on the mechanical and corrosion properties of high entropy alloys: a review

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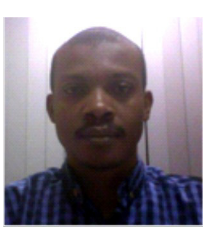
ABSTRACT

This paper reviews from the corpus of literatures on high-entropy alloys (HEAs), their mechanical and corrosion behavior as affected by metallurgical factors such as processing technique, composition, phase formation and transition. HEAs are a promising class of alloys which are designed based on the use of multiple component alloying elements in equimolar or near equimolar ratio. There has been surging interest in this class of alloys on account of their unique property range. Their unique metallurgical characteristics, structures, mechanical and corrosion properties, current and potential areas of applications, and suggestions for future research are discussed in this paper.



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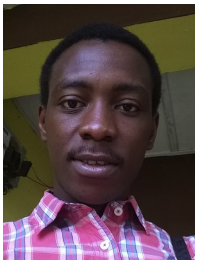

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1. Introduction

The design of HEAs is a relatively new path in the development of advance materials with unique properties unmatched by alloys produced by conventional alloy development approach which is based on only one dominant element [1,2]. High entropy alloys are loosely defined as solid solution alloys that contain more than five principal elements in equal or near equal atomic percent [3,4].

Previous studies [5,6] have shown that HEAs predominantly consist of a simple face centered cubic (FCC), body centered cubic (BCC), or FCC + BCC structure solid solution phase owing to the high entropy of mixing, instead of many intermetallic phases or other complex phases. However, small quantities of intermetallic compound phase/metastable particles have been observed in some HEAs [7]. From Hume–Rothery rules, we recognize the factors that affect the formation of binary solid solutions, which include atomic size difference, valence electron concentration (VEC), crystal structure of the solute and solvent atoms and difference in electronegativity [8]. Besides these factors, enthalpy and entropy of mixing are the most important phase formation parameters for HEAs. Higher entropy of mixing will lead to a lower Gibbs free energy ($\Delta G = \Delta Hmix - T\Delta Smix$) which tends to stabilize the formation of solid-solution phases, rather than intermetallic phases. For multi-component systems, the ratio entropy and enthalpy of mixing ($T\Delta Smix/\Delta Hmix$) would be more important to predict the formation of solid solution phases, and thus, a parameter Ω can be defined $\Omega = TmT\Delta S/\Delta Hmix$ where Tm is the average melting point of the alloy system. Solid solution phase tends to form as long as $\Omega > 1$ is satisfied which means that the effect of the entropy of mixing is greater than that of the enthalpy of mixing at the melting temperature [9].

Zhang et al. [8] and Guo et al. [10] studied the effect of these parameters on the phase formation of HEAs and obtained similar conclusions: the formation of simple or complex phases depends mainly on the enthalpy of mixing, entropy of mixing, and atomic size differences.

Guo et al. [11] investigated the effect of valence electron concentration on stability of FCC or BCC phase in high entropy alloys and suggested the valence electron concentration (VEC) can be used to predict the BCC and FCC structured solid solutions of HEAs. Fig. 1 summarizes the relationship between the structure and VEC, it is observed that BCC structured solid solution forms when VEC < 6.87; while for FCC structure VEC ≥ 8, mixed FCC and BCC phases will co-exist when 6.87 ≤ VEC < 8.0.

The metallurgical nature of HEAs impacts on them rare property combinations which gives them the potentials for use in a wide range of engineering applications. HEAs are known to have good thermal stability [12], high hardness and strength [13,14], excellent wear resistance [15], distinctive electrical, magnetic properties [16] and impressive corrosion resistance [17–19]. HEAs are also reported to possess high hardness and high compressive strength both at room temperature and elevated temperatures [20,21]; and great integrated tensile properties, including both high ultimate tensile strength and reasonable ductility [22]. Some of these spectrums of properties are rarely observed in conventional alloys, making HEAs attractive in many fields. The fact that it can also be used at high temperatures broadens its potential application base even further. For instance, superior structural alloys are in high demand for extreme and highly sensitive engineering service environments, particularly in the nuclear, turbine, and aerospace industries. The properties of HEAs make them suitable candidates for use in such environments.

Overall, it has been reported that the FCC-structured HEAs exhibit low strength and high plasticity, while BCC-structured HEAs show high strength and low plasticity. Thus, the type of crystal structure is a dominant factor for controlling the strength or hardness of HEAs [5,10]. More than 30 elements have been reportedly used to prepare over 300 HEAs, forming an exciting new field of metallic materials [23]. This paper briefly reviews the physical metallurgy of HEAs, including processing routes, areas of application; and effects of production methods and alloying elements on the phase transitions, mechanical properties, and corrosion behavior of HEAs.

2. Processing routes of HEAs

Presently, the processing routes for HEAs can be classified based on the starting states for the alloy preparation [31]. Basically, mechanical alloying followed by isostatic pressing, arc melting and surface coating (plasma spray and laser coating) are used for processing HEAs. Other processing techniques such as electrochemical preparation of HEAs are evolving.

2.1. *Processing by mechanical alloying*

Mechanical alloying is a solid state powder processing technique involving repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill [24]. Mechanical alloying has been reported to have the capability of synthesizing a variety of equilibrium and non-equilibrium alloys starting from blended elemental or pre-alloyed powders [25]. Mechanical alloying is peculiar to metal powder processing, where metal powders are mixed to produce super alloys. Mechanical alloying occurs in three steps. First, the alloy materials are combined in a ball mill and ground to fine powders, this is followed by hot isostatic pressing (HIP) to simultaneously compress and sinter the powders. Finally, heat treatment is carried out to relief existing internal stresses produced during cold compaction. The mechanical alloying