

Heterogeneous-Structured Refractory High-Entropy Alloys: A Review of State-of-the-Art Developments and Trends

Dingfeng Xu, Xiaodi Wang, and Yiping Lu*

Refractory high-entropy alloys (RHEAs) inspire the development of novel high-temperature structural materials due to their outstanding resistance to softening and phase stability at elevated temperatures. However, they struggle to simultaneously achieve high-temperature strength and room-temperature ductility, while exhibiting insufficient room-temperature strain hardening capability. Heterogeneous structure strengthening possesses a unique plastic self-coordinated ability, which can effectively maintain strain hardening rate to achieve an excellent combination of strength and ductility. Benefiting from slow atomic diffusion, severe lattice distortion, and broad compositional design space, RHEAs with heterogeneous structures can be prepared from both chemical composition and interface structure perspectives. Chemical composition heterogeneity primarily focuses on fluctuations of alloying elements at the nanoscale, along with the formation of heterogeneous precipitates and unique lamellar eutectic structures. While, interface structure heterogeneity manifests in the activation of phase transformation and twin boundaries within grains, along with the formation of grains of vastly different sizes. The trend in RHEAs development is toward structural-functional integration. Heterogeneous structures can also optimize functional properties, such as irradiation resistance, biomedical properties, and high-temperature softening resistance of RHEAs. Finally, a brief outlook is provided on the future development direction of heterogeneous structure RHEAs.

1. Introduction

The rapid development of modern science and technology has accelerated the pace of iteration for novel materials. Higher

demands are placed on high-performance novel metallic materials under complex working and extreme environmental conditions. Traditional metallic materials, after long-term development, have approached their properties ceiling. The limited design space for composition is the main obstacle to further development. This is because they mostly consist of one or two base elements, confined to the corners of the multiphase diagram space. To break through this limitation and explore the central region of the phase diagram space, the concept of high-entropy alloy (HEA), with multiple elements as the principal components, was proposed in 2004.^[1] The fundamental difference between HEAs and traditional alloys is that the former lacks a clear differentiation between solvent and solute elements, whereas the latter has a distinct separation between solvent and solute elements. Meanwhile, HEAs exhibit four “core effects”: the high entropy effect, the severe lattice distortion effect, the sluggish diffusion, and the “cocktail” effect.^[2] They cover almost all crystal structures and types of precipitated phases. Therefore, they have the potential to become materials with integrated structure and function.

Based on crystal structure, HEAs can be classified into face-centered cubic (FCC) structure HEAs, body-centered cubic (BCC) structure HEAs, hexagonal close-packed (HCP) structure HEAs, and mixed structure HEAs. Additionally, various HEA subclasses can be distinguished based on their functional or structural characteristics, such as lightweight HEAs, refractory HEAs (RHEAs), and eutectic HEAs (EHEAs). The development of RHEAs was motivated by the goal of creating advanced high-temperature structural materials. These refractory metal elements offer substantial variation in such properties as melting temperature (1855 ~ 3422 °C), density (4.5 ~ 19.4 g/cm³), and elastic modulus (68 ~ 411 GPa for Young’s modulus). This provides significant flexibility in customizing alloys to achieve desired properties. The two classic RHEA systems are NbMoTaW and TiZrNbHfTa.^[3] The former exhibits superior strength above 1000 °C, while the latter demonstrates better ductility at room temperature. So far, most developed RHEAs are based on these two model alloys. RHEAs also have some notable drawbacks. The high density of refractory metal elements makes them unsuitable for some lightweight applications. In light of

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