



Microstructure and electrochemical properties of high entropy alloys—a comparison with type-304 stainless steel

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Abstract

High entropy alloys (HEAs) are a newly developed family of multi-component glassy alloys composed of several major alloying elements, such as copper, nickel, aluminum, cobalt, chromium, iron, silicon, titanium, etc. The HEA studied had a nearly amorphous structure as proven by X-ray diffraction (XRD), selected area diffraction (SAD), and differential scanning calorimetry (DSC) analysis. The dendritic phase was composed mainly of a non-crystalline phase with a little body centered cubic (BCC) structure whereas the interdendritic phase had an amorphous structure containing small amounts of nano-scale precipitates. The HEA had a high degree of atomic disorder with mechanical properties comparable to that of glass and it was therefore hard but brittle. Its hardness (Hv860) was much higher than that of type-304 stainless steel (Hv265). The anodic polarization curves of the HEA, obtained in aqueous solutions of NaCl and H₂SO₄, clearly indicated that the general corrosion resistance of the HEA at ambient temperature (~25 °C) is superior to that of 304S, irrespective of the concentration of electrolyte in the range 0.1–1 M. On the other hand, the HEA's resistance to pitting corrosion in a Cl⁻ environment is inferior to that of 304S, as indicated by a lower pitting potential and a narrower passive region for the HEA. Tests in 1 N sulfuric acid containing different concentrations of chloride ions showed that the HEA has least resistance to general corrosion at a chloride ion concentration of 0.5 M (close to the concentration in seawater). The

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lack of hysteresis in cyclic polarization tests confirmed that the HEA—like 304S—is not susceptible to pitting corrosion in chloride-free 1 N H₂SO₄.

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1. Introduction

Conventional engineering alloy systems are mainly made up of iron, copper, aluminum, magnesium, titanium, zirconium, etc. Also, superalloys are classified as iron-based, nickel-based and cobalt-based, etc. These alloys all have crystalline structures. During the 1930s, Kramer et al. produced the first amorphous alloy using vapor deposition [1,2]. In the 1950s, Bremer et al. manufactured a Ni–P non-crystalline alloy by electrodeposition methods [3]. However, neither of these approaches produced an alloy that was cooled directly from the liquid phase to produce an amorphous phase. It was not until the 1960s, that Duwez obtained an Au–25 at.%Si amorphous alloy by rapid solidification, and confirmed that it was possible to obtain the amorphous phase if the cooling rate was fast enough to suppress the nucleation and growth of crystals [4]. However in the 1960s, a very rapid cooling rate (about 10⁶ K/s) was necessary in order to suppress the crystal nucleation and growth. Such a high cooling rate limited the specimen geometry: only thin films of a thickness of 50–100 μm could be formed, which could not be used as a structural material. Also, the thermal stability of these amorphous alloys was poor making them unstable for use near the glass transition temperature. In 1984, Kui et al. successfully produced a bulk Pd₄₀Ni₄₀P₂₀ amorphous alloy of 10 mm in diameter by using a fluxing method to remove heterogeneous nucleation [5]. And, during 1989–1998, Inoue et al. investigated several alloy systems with a highly stable supercooling liquid region, which had good glass-forming ability comparable to Pd₄₀Ni₄₀P₂₀ [6–10]. The alloy design approach was to select components that allowed the alloy composition to approach the eutectic composition. In this way, an amorphous alloy could be produced at a slower cooling rate. However, the designs of these alloys, as mentioned above, relied on the concept that the matrix was composed of a single major element. For example, even Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} [8], is consistent with the “one major alloy element” framework. In order to break away from the traditional alloy design conventions, a novel high entropy alloy (HEA) or a bulk glassy alloy was developed, which was a combination of many major elements, e.g., Ti–Zr–Hf–Cu–M (M = Fe, Co, Ni) [11].

In general, the corrosion resistance of crystalline alloys, like stainless steels (SS), depends on the formation of a protective surface oxide film. This observation suggested that an HEA composed of elements similar to SS might also possess good corrosion resistance. Because of the binding enhancement (binding strength among the component elements) and the fact that there are no dislocations within a fully amor-

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