

Paragraph Ran in the Queries

Paper Title: Mechanical properties of CoCrFeNi-X (X = Ti,Sn) high entropy alloy and tribological properties in simulated seawater environment

Content :

Phase composition, microstructure and mechanical properties

Fig. 2 shows the XRD patterns of CoCrFeNi-X (X = Ti,Sn) HEA powder, VHPed CoCrFeNi-X (X = Ti,Sn) HEA block. From the XRD patterns, it is found that solid solutions have been formed in both CoCrFeNiTi and CoCrFeNiSn alloy powders, but the diffraction peaks of some alloying elements still exist. It can be seen that the alloying speed of Ti and Sn is slow in the process of mechanical alloying. The reason is that the atomic radii of Ti and Sn are 1.46 Å and 1.72 Å, respectively, which are larger than those of other elements. The alloying elements with larger atomic radii tend to have lower diffusion rates, which results in poor dispersion during mechanical alloying, and larger atomic radii are unable to diffuse uniformly into the positions of other elements in the alloy[40].

For CoCrFeNiTi HEA after vacuum hot press sintering, several other diffraction peaks were detected in addition to the FCC phase diffraction peaks. This indicates the formation of other phases in the FCC phase matrix. According to Table 2, the

$\Delta H_{\{AB\}mix}$

of the atomic pairs between the five elemental elements of Co, Cr, Fe, Ni, and Ti were calculated. It was learnt that the atomic pairs were more easily formed between Ti-Co and Ti-Ni. According to the JCPDS card, they are identified as (1) the R phase, which has a structure similar to that of the rhombic $Ni_{2.67}Ti_{1.33}$ phase; (2) the σ phase, which has a structure similar to that of the tetragonal FeCr phase; and (3) the Laves phase, which has a structure similar to that of the hexagonal close-packed Co_2Ti phase. And the addition of Sn allowed CoCrFeNiSn to generate the Ni-Sn phase with a hexagonal structure similar to that of $Ni_{1.5-1.63}Sn$ on the basis of retaining the FCC structure of CoCrFeNi. From the data in Table 3, the negative

$\Delta H_{\{AB\}mix}$

of Ni-Sn indicates that the bonding between the two atoms is the strongest, leading to the formation of Ni-Sn intermetallic compounds [41], [42], [43]. According to the thermodynamics of materials, the enthalpy of mixing indicates the repulsive force between alloying elements, and when the enthalpy of mixing is negative, it indicates a stronger bonding between elements[44], [45]. Therefore, Sn element is easy to combine with Ni element to form Ni-Sn intermetallic compounds. On the other hand, other possible elements (Co, Cr, Fe) have positive

$$\Delta H\{AB\}_{mix}$$

with Sn, indicating that these elements will not easily interact with Sn.

As shown in Fig. 3(b), the SEM image of the microstructure of CoCrFeNiSn high entropy alloy. It can be found that the surface of the alloy exhibits two regions with different linings, i.e., a light grey region and an irregular dark grey region. The regions E and F marked by yellow dashed boxes in the figure are representative regions. According to the EDS analysis (Table 4), in the E region, the elemental contents of Co, Cr, and Fe are comparable, while the contents of Ni (14.59 %) and Sn elements (7.20 %) are slightly lower. In contrast, the trend of elemental content is reversed in the F region. It is proved that CoCrFeNiSn exhibits a two-phase structure, and based on the XRD results, it can be inferred that CoCrFeNiSn HEA contains FCC phase and Ni-Sn hexagonal phase, which is combined with Fig. 3(b), the grains exhibit a hexagonal structure.

The EDS results of CoCrFeNiTi HEA are shown in Fig. 4(a). The green boxed area is rich in Ti, the blue boxed area is rich in Ni, and the yellow boxed area is rich in Cr. Based on the XRD and EDS analysis, it is assumed that the phase compositions of CoCrFeNiTi HEA are composed of the FCC phase, the R phase, the σ phase, and the Laves phase, respectively. The EDS results of CoCrFeNiSn HEA are shown in Fig. 4(b). Combined with the EDS results, the dark area is rich in Co, Cr and Fe elements, while the grey area is rich in Ni and Sn elements. Combined with the XRD analysis results, it is assumed that the phase composition of CoCrFeNiSn HEA consists of FCC phase and Ni-Sn phase, respectively.

In order to assess the mechanical properties of the alloys, their density, densities and microhardness were tested. The results are shown in Table 5. CoCrFeNiTi HEA was found to have lower density (7.17 g/cm³) and higher hardness (750 HV) as compared to CoCrFeNiSn HEA. Hardness plays a key role in rating the wear resistance of a material, so alloys with higher hardness usually have better wear resistance[50]. The main reasons for the higher hardness of CoCrFeNiTi HEA than CoCrFeNiSn HEA can be attributed to the following three mechanisms. Firstly, the addition of Ti effectively reduces the secondary dendrite arm spacing (SDAS), and the reduction of SDAS increases the hardness and compressive strength of the alloy, which is true for most alloys[51], [52]. Secondly, the addition of Ti promotes the precipitation of hard phases, which helps to improve the overall hardness of the alloy. After sintering, by analysing the phase structure and microstructure, it was found that the precipitation of hard phases (including the Laves phase, the σ phase and the R phase) was not uniform, which further improved the strength of the alloy, but also caused the uneven surface hardness. These precipitated phases also contribute to the increase in hardness of the alloy, which belongs to the second phase dispersion strengthening [53], [54]. Finally, the addition of Ti elements may form solid solution strengthening or intermetallic compounds, which may enhance the grain boundary and dislocation movement hindrance of the alloys and

increase the hardness of the alloys. Comparatively, the addition of Sn elements may lead to weakening of the grain boundary strengthening of the alloys and more prone to grain boundary slip, resulting in relatively lower hardness of the alloys.

Among the mechanical properties of materials, the tensile property is one of the important indexes for evaluating the properties of high-entropy alloy. The tensile stress-strain curves of CoCrFeNi-X (X = Ti, Sn) high entropy alloy at room temperature are given in Fig. 6(b). Compared to CoCrFeNiTi HEA, the tensile yield strength of CoCrFeNiSn HEA is 75.94 % higher. This may be related to the elemental composition, atomic size, solid solubility of the two alloys. The Ti element in CoCrFeNiTi HEA may lead to lattice distortion difficulties generating a hard phase, which improves the compressive strength of the alloy, but also increases the brittleness and reduces its ductility.

Fig. 7 shows the tensile fracture morphology of two high entropy alloys. It can be seen that CoCrFeNiSn high entropy alloy shows a certain toughness fracture morphology during tensile fracture, and the main fracture modes are tough dimple fracture combined with partial quasi-dissociative fracture mode. In contrast, the fracture surface of CoCrFeNiTi high-entropy alloy is relatively flat, with river-like fracture and intergranular cracks, which are the characteristics of brittle fracture, mainly quasi-dissociative fracture and dissociative fracture, and there is also a very small amount of along-granular fracture. The CoCrFeNiSn high-entropy alloy performs better tensile properties compared to CoCrFeNiTi high entropy alloy, probably due to its grain refinement. The grain refinement has a significant effect on the mechanical properties of the material, and usually the smaller the grain size, the strength and ductility of the material may be improved. Fig. 5 shows that the grain size of CoCrFeNiSn HEA is smaller than that of CoCrFeNiTi HEA, so the addition of Sn element can help to reduce the grain size and increase the strength and plasticity of the alloy, which improves the tensile properties of CoCrFeNiSn high entropy alloy.