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Paper Title: CALPHAD-aided design for superior mechanical behavior in Ti₄₀Zr₂₀Hf_{40-x}Cr_x eutectic refractory high-entropy alloys

Content :

Results

Fig. 2(a-f) illustrate the microstructure evolution of the Ti₄₀Zr₂₀Hf_{40-x}Cr_x alloys. Fig. 2(a) and (b) show the microstructure of HfCr₁₉ alloys, it can be seen that the HfCr₁₉ alloy is composed of dendritic structure and eutectic structure distributing inter-dendrite regions. The lamellar eutectic region is identified as BCC phase with Zr and Ti elements and Laves phase containing Hf and Cr elements according to the XRD pattern (Fig. 4) and selected area electron diffraction (SAED) analysis (Fig. 5). It can be seen that the elliptic primary phases (BCC phase) are surrounded by the lamellar eutectic structure (BCC and Laves phases) in solidification. It can be observed that the fully lamellar eutectic structure is formed when the Hf/Cr ratio decreases to 16/24, as shown in Figs. 2(c) and (d). Combination XRD pattern (Fig. 4) and EPMA mapping analysis (Fig. 3), the lamellar eutectic structure of the HfCr₂₄ alloy consists of BCC phases with enriched Ti and Zr elements and Laves phases containing Hf and Cr elements. However, when the Hf/Cr ratio reduces to 11/29, it is obviously observed that some irregular lumpy structures occur, and many lamellar eutectic structures have formed around the irregular lumpy structures, as seen in Fig. 2(e) and (f). The irregular lumpy structures are identified as Laves phase enriched Hf and Cr elements according to EPMA point analysis (Table 1), and the lamellar eutectic structure consists of BCC and Laves phase distributing inter-dendrite regions.

The XRD patterns of the Ti₄₀Zr₂₀Hf_{40-x}Cr_x alloys are obtained and shown in Fig. 4, revealing that the HfCr₁₉ and HfCr₂₄ alloys consist of HCP, BCC and Laves phases. However, the HCP phase disappears, and the BCC and Laves phases form in HfCr₂₉ alloy. Fig. 4(b) displays the enlarged view of the XRD patterns in the 34° to 38° range, it can be seen that the intensity of the diffraction peak linked to the BCC phase decreases and the intensity of the diffraction peak linked to the Laves phase increases with the reduction of Hf/Cr ratio. This phenomenon implies that the reduction of Hf/Cr ratio leads to the decrease of the BCC phase and the increase of the Laves phase. The above analysis is consistent with the microstructure evolution analysis (Fig. 1). Additionally, the diffraction peaks of the BCC phase present obviously rightward shift, indicating that the lattice constant of BCC phase is decreased with the decreasing of Hf/Cr ratio. According to the EPMA point analysis (Table 2), it can be concluded that this

phenomenon is mainly due to the reduction of Ti and Zr content in the BCC phase of the $\text{Ti}_{40}\text{Zr}_{20}\text{Hf}_{40-x}\text{Cr}_x$ alloy.

It is evident that the phases in the inter-lamellar regions (IL region) are composed of a few acicular structures and numerous elliptic structures. In order to further analyze the inter-lamellar regions, the EDS mapping and line analysis of the inter-lamellar regions are fulfilled and shown in the Fig. 5(d) and (e). It can be seen that the acicular structure composed of Ti and Zr elements has similar content to the elliptic structure in IL region. Fig. 5(b) presents the corresponding SAED results of the phase in IL regions, which shows that the acicular phase should be $\text{Ti}_{0.5}\text{Zr}_{0.5}$ compounds, with HCP structure along the $[100]$ crystal axis, while the elliptic phase is $\text{Ti}_{0.5}\text{Zr}_{0.5}$ compounds with BCC structure along the $[1$

$\bar{1}\bar{1}\bar{1}$] crystal axis. The formation reason of $\text{Ti}_{0.5}\text{Zr}_{0.5}$ phase with HCP structure will be discussed in the 4.2 section. Fig. 5(f) presents the high-resolution transmission electron microscope (HRTEM) image, enabling the assessment of the interface relationship existing between the HCP phase and the BCC phase. Fig. 5 (g) and (h) show the corresponding inverse Fourier transformation (IFFT) and fast Fourier transformation (FFT) results. It can be seen from Fig. 5(g) that the angle of orientation misfit between the HCP and BCC phases is about $\sim 23.76^\circ$. And the interplanar spacing of $(10\bar{1}2)$ plane is 0.1823 nm (lattice constant of 0.3322 nm) for the HCP phase, and the interplanar spacing of (211) plane is 0.1435 nm (lattice constant of 0.3514 nm) for the BCC phase.

Additionally, some growth twins can be seen in the lamellar regions (La region), as shown in Fig. 5(a). The SAED pattern of twin boundaries reveals the crystallographic orientation relationship between the matrix and the growth twin, with the 180° mirror symmetry relationship between the matrix and twin [29], as seen in the Fig. 5(c). Fig. 6(a) presents the HRTEM image of the twin boundary, and the corresponding FFT images and IFFT images are shown in Fig. 6(b) and (c). It can be found from the Fig. 6(b) that the atoms of the twin plane are located on the nodes of the two crystal lattice, so the prefect matched crystal plane is formed in the alloy. The complete coherent twin with low interfacial energy results in high stability and strength at the twin interface [30]. In addition, it can be seen from the HRTEM image that some intersected stacking faults exist, as shown in Fig. 6(c). The fault formation at the twin boundary is because the dislocation motion in the $\text{Ti}_{40}\text{Zr}_{20}\text{Hf}_{40-x}\text{Cr}_x$ alloy is hindered at the twin boundary.

And the compressive strength and density are compiled in Table 3. All alloys were fractured in the elastic region, that means the ductility of the HfCr19, HfCr24 and HfCr29 alloys were nearly zero at room temperature [31,32]. It is obvious that the compressive strength is increased by 18.8 % from 1387.9 MPa to 1648.7 MPa with the

Hf/Cr ratio decrease from 21/19 to 16/24. However, the compressive strength of the HfCr₂₉ alloys reduced to 1468.1 MPa. The compressive properties of Ti₄₀Zr₂₀Hf_{40-x}Cr_x ERHEAs mainly depend on the microstructure, constituent phases and precipitated HCP phase. The relationship between microstructure evolution and mechanical properties will be discussed in the 4.3 section.

However, it is found that the strength gradually decreases and the compressive strain increases when the compressive temperature rising to 600 °C, as shown in [Fig. 8\(a\)](#). Compressive strength and compressive strain are compiled in [Table 4](#). The compressive strength is increased by 40.9 % from 895.3 MPa to 1261.7 MPa with the Hf/Cr ratio decrease from 21/19 to 16/24. Compared with room temperature, the significant decrease in compression plasticity of HfCr₂₄ alloy at 600 °C may be attributed to the partial transformation of the BCC phase into the HCP phase at this temperature. However, the compressive strength of HfCr₂₉ alloy are reduced to 884.1 MPa. Additionally, all alloys demonstrate a short strengthening and softening stages when the compressive temperature rises to 1000 °C, and then all alloys have followed a prolonged nearly steady-state flow stage, as shown in [Fig. 8\(b\)](#).