Paragraph Ran in the Queries

Paper Title: Nanoprecipitates enhanced the yield strength and output work of (TiHfZr)50(NiCu)50 high-entropy shape memory alloys
Content :

Mechanical properties

Fig. 7 shows the compressive engineering stress – strain curves of the fifteen as-cast and aged samples. Each sample exhibits the typical double yield shape characteristic of superelastic alloys. The results show that alloy composition and aging treatment have great influences on its mechanical properties. With increasing Zr content, the fracture strength (σ_{max}) and fracture strain (ε_{max}) decrease due to the increase in secondary phase precipitation during solidification, but the yield strength (σ_s) and the critical strength (σ_{LC}) of stress-induced martensite transformation increase significantly. For the as-cast alloys, ternary TiNiCu alloys have the highest σ_{max} (3391.6 MPa) and ε_{max} (44.2 %), but their σ_{LC} (310.2 MPa) and σ_s (660.5 MPa) are the lowest. The σ_{max} (2863.1 MPa) and ε_{max} (33.4 %) of the quaternary Zr0 alloy decrease, but σ_s and σ_{LC} increase greatly, reaching 481.2 MPa and 1530.1 MPa, respectively. With the increase in Zr, the σ_s and the σ_{LC} of HESMA continue to increase (Fig. 7(f)), and the σ_s of alloys Zr1, Zr5, and Zr10 reach 1500.2 MPa, 1760.5 MPa, 1870.3 MPa, respectively, and σ_{LC} reaches 373.5 MPa, 570.1 MPa, and 648.5 MPa. This should be due to the combined effect of the enhanced solid solution strengthening effect caused by the increase in Zr content and the enhanced dispersion strengthening effect caused by the increase in the solidified secondary phase

Moreover, due to the precipitation of the nanoscale phases, the σ_s and σ_{LC} of aging alloys (especially for the samples aged at 400 °C) increase obviously, but the plasticity decreases, which is more obvious in HESMAs. The reason for the more significant decrease in plasticity of alloy HESMAs, may be that the number and size of nanoprecipitates is larger, so the hindrance effect on dislocation slip is stronger when the alloy undergoes plastic deformation. Compared with the as-cast alloys, the σ_s of the Zr1–300 and Zr5–300 samples increases by 10.4 MPa and 110.2 MPa, and the σ_{LC} of the Zr1–300, Zr5–300, and Zr10–300 alloys increases by 7.1 MPa, 60.0 MPa and 113.5 MPa, respectively. For the alloys aged at 400 °C, the σ_s of the Zr1–400, and Zr5–400 samples increases by 205.4 MPa and 180.2 MPa, and the σ_{LC} of the Zr1–400, Zr5–400, and Zr10–400 samples increases by 43.1 MPa, 310.0 MPa, and 350.5 MPa, respectively. The reason is that the quantity and scale of the nanoprecipitates in HESMAs aged at 400 °C (approximately 45–50 particles per μm^2 and 80–150 nm in length) are much larger than the samples aged at 300 °C (approximately 5–10/μm^2 and

40–80 nm in length) (as shown in Fig. 3), so the dispersion strengthening effect of the nanoprecipitates is stronger.

Superelasticity properties

Fig. 8(a)-(e) show the loading — unloading compressive curves of the five as-cast shape memory alloys with prestrains from 2 % to 15 %. For the first five cycles, the strain step size is 2 %, and for the last five cycles, it is 1 %. Fig. 8(f)-(i) show the evolutions of total recoverable strain (ε_r), superelastic recovery strain (ε_{SE}), elastic recovery strain (ε_E), residual strain (ε_i), and shape recovery rate (η) during cyclic compression. Fig. 9, Fig. 10 show the corresponding results of HESMAs aged at 300 °C and 400 °C, respectively. The results of Fig. 8, Fig. 9, Fig. 10 indicate that the load prestrain has a significant effect on the superelasticity behaviors during cyclic compression. With increasing prestrain, the ε_r and ε_{SE} increase significantly at first, and then increase slowly or even decrease slightly. For example, as the load strain increases from 2 % to 10 %, the ε_r of the as-cast Zr5 sample increases from 1.1 % to 7.7 %, and ε_{SE} increases from 0.3 % to 4.9 %. When the loading strain increases from 10 % to 15 %, ε_r increases from 7.7 % to 8.7 %, and ε_{SE} decreases from 4.9 % to 4.8 %. On the one hand, the amount of austenite participating in the stress-induced martensite transformation gradually increases with the increasing prestrain; therefore, the ε_r and ε_{SE} increase with the loading prestrain at the initial stage. However, with a further increase in load strain (more than 10 %), the increment of newly added austenite participating in stress-induced martensitic transformation gradually decreases, and the deformation gradually exceeds the elastic deformation limit of the alloy, so the increase rates of ε_r and ε_{SE} decrease and tend to be gradually stabilize. On the other hand, with increasing loading strain, the plastic deformation of austenite and martensite and the dislocation accumulation in the cyclic compression process hinders the reverse transformation of stress-induced martensite, which may result in the stabilization of stress-induced martensite [48], [49], [50], [51], [52], so ε_r and ε_{SE} may drop slightly.

Moreover, the results in Fig. 8, Fig. 9, Fig. 10 also indicate that the superelasticity of the $(Ti_{40-x}Hf_{10}Zr_x)_{50}(NiCu)_{50}$ HESMAs is much better than that of the ternary alloy and further improved after aging. Taking the as-cast alloys as an example (Fig. 8), the maximum ε_r and ε_{SE} of the ternary TiNiCu alloy in the cycle process are only 2.6 % and 0.9 %, respectively, ε_i reaches 12.4 % and the maximum η is only 52.3 % in the cyclic process. While the ε_r of $(Ti_{40-x}Hf_{10}Zr_x)_{50}(NiCu)_{50}$ HESMAs is 7.2–8.8 %, the ε_{SE} is 3.6–4.8 %, and the maximum η can reach 75.5–77.8 %. For the results of the aged samples at 300 °C (Fig. 9), the maximum ε_r and ε_{SE} of the ternary TiNiCu-300 samples in the cycle process are only 3.9% and 1.8 %, while the corresponding values of HESMAs are 6.4–9.7 % and 2.4–5.4 %, respectively. For the results of the aged samples at 400 °C (Fig. 10), the maximum ε_r and ε_{SE} of the ternary TiNiCu-400 samples are only 4.2 %

and 2.1 %, while the corresponding values of HESMAs are 7.1–9.3 % and 3.2–5.1 %, respectively. Similar to the mechanical properties, the memory performances of HESMAs are better than those of ternary Ti-Ni-Cu and quaternary Zr0 samples, possibly for two reasons. First, the solution strengthening effect of HEAs is enhanced by the increase in Zr content; second, the dispersion strengthening effect caused by the secondary solidification phases is enhanced with the increase in Zr content. The reason for the further improvement of the aging sample is due to the dispersion strengthening effect of nanoprecipitates. It should be noted that among all the samples, the Zr5 cast and aged HESMAs samples have the best superelasticity properties, and their maximum ε_r and ε_{SE} are 8.8–9.7 % and 4.9–5.4 %, respectively. In addition, the precipitation of coherent compound phases shown in Fig. 5 may also be one of the reasons for its strengthening. In addition to the above reasons, there is another possible reason for the better performance of Zr10 and Zr5 HESMAs. We measured the compositions of the 400 °C aged samples containing O through EDS. The oxygen contents of alloys TiNiCu-400, Zr0–400, Zr1–400, Zr5–400 and Zr10–400 are 4.8 %, 4.8 %, 4.96 %, 7.76 %, and 5.51 %, respectively. The results indicate that the Zr5–400 and Zr10–400 alloys with the best performance have the highest oxygen content. Ambient oxygen can also enter the HEA lattice as interstitial impurities, causing the formation of ordered oxygen complexes that can enhance both the strength and ductility of the alloys [53], [54], [55]. Therefore, the strength effect of interstitial oxygen may be one of the reasons for strengthening Zr5 and Zr10 HESMAs. However, further research is needed on the existing form and strengthening mechanism of oxygen in alloys in the future.

It should be noted that, compared with the increase in yield strength, the improvement in ε_r and ε_{SE} of HESMAs after aging treatment is slightly lower. One possible reason is that the phase transformation of the superelastic alloy in the cyclic loading process must be completed by the phase boundary migration of austenite and martensite. However, grain boundary migration is sometimes hindered by some factors, such as the precipitated phase [56], [57], [58], antiphase boundaries [59], or twin boundaries [60], [61], [62]. In this article, the nanoscale precipitates pin the phase boundary and hinder its migration, leading to the stabilization of martensite during reverse transformation [56], [57], [58], thus reducing the ε_r and ε_{SE} of the aged HESMAs to a certain extent. To understand the fracture mechanism of the prepared alloys, the samples after cyclic compression with 2–15 % prestrain were compressed to fracture and the morphology of the compression fracture surfaces is shown in Fig. 11. Most alloy samples exhibit cleavage fracture morphology, but due to the presence of vein-like fractures, a small amount of plastic slip traces can also be observed. In addition, it was found that aging treatment and an increase in Zr content both led to a decrease in vein patterns and a small increase in cracks. It should be noted that the Zr10–300 and Zr10–400 samples exhibit only brittle fracture morphology with no plastic slip traces visible, which is consistent with the mechanical performance test results.

Superelastic SMAs are widely used in medical devices, seismic structures, mechanical connections, damping devices, and other fields. Output work (W_{out}) is one of the important indicators to measure its performance, which is equal to the product of applied stress and recoverable strain ($W_{out} = \sigma_{out} \times \varepsilon_r$) [26], [35], [44]. Fig. 12 shows the comparisons of W_{out} of the three groups of samples during cyclic compression. Compared with the as-cast alloys, the compressive strength (σ_{out}) of all alloys and the recoverable strain (ε_r) of most alloys are improved after aging, which can lead to a higher W_{out}. For example, when the compressive prestrain is 15 %, the σ_{out} of the aged Zr5 alloy reaches 1693.8–1976.2 MPa, ε_r reaches 9.1–9.7 %, and W_{out} reaches 179.6–188.5 J/cm3, while the corresponding values of the as-cast alloy are 1591.4 MPa, 8.7 %, and 163.7 J/cm3, respectively. Moreover, in comparison to reported HESMAs and SMAs [15], [23], [24], [25], [26], [28], [29], [31], [32], [35], [44], [63], [64], [65], [66], [67], [68], [69], [70], [71], [72], [73], [74] shown in Fig. 13, the $(Ti_{40-x}Hf_{10}Zr_x)_{50}(NiCu)_{50}$ HESMAs show an excellent combination of maximum output work (W_{Mout}) and maximum recoverable strain (ε_{Mr}). The W_{Mout} and ε_{Mr} of TiNiCu samples are only 17.4–35.8 J/cm3 and 2.6–4.2 %, respectively, which are close to the values reported in the literature. The results of the Zr0 and Zr1 samples are relatively close and obviously higher than the literature values. The value of W_{Mout} reaches 99.8–146.8 J/cm3 and ε_{Mr} reaches 6.4–7.98 %. The Zr5 and Zr10 samples have the highest W_{Mout} (151.7–188.5 J/cm3) and ε_{Mr} (7.9–9.7 %), respectively. In summary, the HESMAs have much higher W_{Mout} and ε_{Mr} than the existing TiNi-based memory alloys due to the combination of high strength and large recoverable strain. The reason for the high W_{Mout} is that the lattice distortion effect of HEAs increases the strength of the alloy, and the dispersion strengthening effect of nanoprecipitates after aging further increases the critical stress and yield strength, making the HESMAs possess both high strength and large recoverable strain, thus possessing high W_{out}. Moreover, the load strains in this paper are higher than most of the literature values due to the good plasticity and high yield strength of the HESMAs, which also leads to the possibility of higher ε_r. However, it should be noted that the performance of the Zr1 sample is not significantly improved compared with that of Zr0, which may be due to the weak lattice distortion caused by the low Zr content, so the solution strengthening effect is also weak. In addition, the performance of the Zr10 alloy decreased compared to that of the Zr5 alloy, possibly due to a decrease in plasticity caused by more secondary phase