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Cu-based shape memory alloys with enhanced thermal stability and mechanical properties

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Abstract

Cu-Based shape memory alloys were developed in the 1960s. They show excellent thermoelastic martensitic transformation. However, the problems in mechanical properties and thermal instability have inhibited them from becoming promising engineering alloys. A new Cu–Zn–Al–Mn–Zr Cu-based shape memory alloy has been developed. With the addition of Mn and Zr, the martensitic transformation behaviour and the grain size can be better controlled. The new alloy demonstrates good mechanical properties with ultimate tensile strenght and ductility, being 460 MPa and 9%, respectively. Experimental results revealed that the alloy has better thermal stability, i.e. martensite stabilisation is less serious. In ordinary Cu–Zn–Al alloys, martensite stabilisation usually occurs at room temperature. The new alloy shows better thermal stability even at elevated temperature ($\sim$ 150°C, $> A_f = 80$°C). A limited small amount of martensite stabilisation was observed upon ageing of the direct quenched samples as well as the step quenched samples. This implies that the thermal stability of the new alloy is less dependent on the quenching procedure. Furthermore, such minor martensite stabilisation can be removed by subsequent suitable parent phase ageing. The new alloy is ideal for engineering applications because of its better thermal stability and better mechanical properties.

Keywords: Martensitic transformation; Shape memory alloys; Cu–Zn based alloys; Thermal stability; Mechanical properties

1. Introduction

Cu-based shape memory alloys (SMA) have been developed in the 1960s. Cu-based shape memory alloys, being cheaper in price, have demonstrated a reasonable shape memory effect. The main problems in the actual utilisation of Cu-based SMAs are mainly due to their low thermal stability and unsatisfactory mechanical strength. They often suffer from martensite stabilisation and finally lose the thermoelastic properties. Moreover, intergranular cracking usually occurs in Cu-based SMA during the manufacturing process and in service [1], hence improving the thermal stability and the mechanical properties are important issues for the prospect of Cu-based shape memory alloys.

Recently, we have added Mn and Zr to Cu–Zn–Al SMA with the aim to improve the thermal stability as well as the mechanical property. Mn addition in Cu–Al–Ni SMA has been proved to enhance the thermoelastic and pseudoelastic behaviours [2]. It has also been reported that minor additions of B, V, Zr and Ti can refine grain sizes in Cu-based SMA [3]. It was found that this Cu–Zn–Al–Mn–Zr alloy would be ideal for engineering applications. This will be further discussed in two perspectives: the mechanical properties and the thermal stability.

2. Materials

A Cu–Zn–Al–Mn–Zr alloy was prepared by melting elements with industrial purity in an induction furnace. The ingots were hot rolled to 1 mm plates and were then cut into small pieces for subsequent examinations. The specimens were solid solution treated at 850°C for 5 min, and then quenched into boiling water. They were kept at 100°C water for 30 min, and then further quenched into ice water at 0°C. This process is usually called step-quenching which intends to improve the resistance to martensite stabilisation due to the

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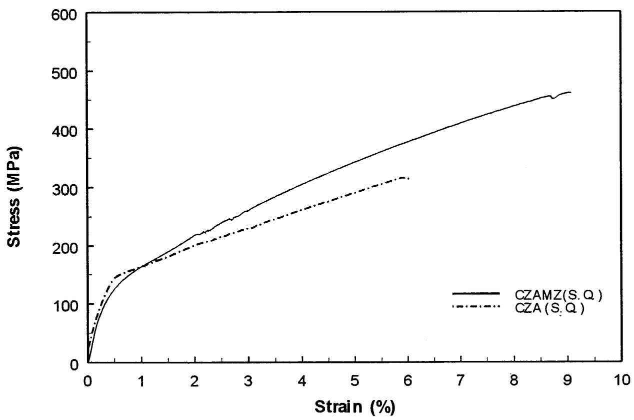

Fig. 1. The stress–strain curves for step quenched (S.Q.) Cu–Zn–A1 (CZA) and Cu–Zn–Al–Mn–Zr (CZAMZ) alloys. The tests were performed at room temperature ($< A_s$) at which alloys were all in the martensite state.

excess quenched-in vacancies. Table 1 lists the information of the alloy after step quenching.

3. The mechanical perspective

Fig. 1 reveals the stress–strain curves of the Cu–Zn–Al–Mn–Zr and ordinary Cu–Zn–Al alloys tested at room temperature (strain rate = 1 mm/min) where the alloys are in the martensite state. The result shows that the Cu–Zn–Al–Mn–Zr alloy possesses significantly higher fracture stress and fracture strain than the Cu–Zn–Al alloy. As revealed from the stress–strain curves, the ultimate tensile strength and the ductility are 460 MPa and 9%, respectively, at room temperature (in the martensite state). These values are much higher than those of the Cu–Zn–Al alloy (Ultimate Tensile Strenght (UTS)) = 315 MPa and ductility = 6%). These are remarkably higher than for the Cu–Al–Ni alloy, which has a typical ductility of only ~1% with UTS of about 300 MPa in the martensite state [4].

The better ductility of the Cu–Zn–Al–Mn–Zr is also shown in the fractographs. Fig. 2 shows the fractographs of the Cu–Zn–Al and the Cu–Zn–Al–Mn–Zr alloys. The Cu–Zn–Al–Mn–Zr alloy shows typical river like characteristics of the ductile failure with transgranular fracture while the Cu–Zn–Al alloy exhibit brittle failure with intergranular fracture.

The improvement in mechanical properties can be attributed to the grain refinement result, from the Zr addition. Significant grain size reduction is found after the doping of Zr in Cu–Zn Al alloys. The grain size was reduced from 300 to 75 μm. The cause of grain refinement should be due to the inhibition of grain growth by the finely dispersed Zr-rich phases [5,6].

The enhanced ductility of the Cu–Zn–Al–Mn–Zr alloy can improve the workability of the alloy. The increase of the ductility from 6 to 9% after Mn and Zr additions can increase the cold working capability of the alloy. This can benefit the processing of the material for engineering application.

4. The thermal stability perspective

Cu-based shape memory alloys usually suffer from thermal instability. The shape memory effect can be destroyed when the alloy is exposed to elevated temper-

Table 1
Information of the Cu–Zn–Al–Mn–Zr alloy after step quenching

	Chemical composition (wt%)					Transformation temperatures (°C)			
	Cu	Zn	Al	Mn	Zr	M_f	M_s	A_s	A_f
Cu–Zn–Al–Mn–Zr	72.9	20	5.6	1	0.5	30	54	60	77

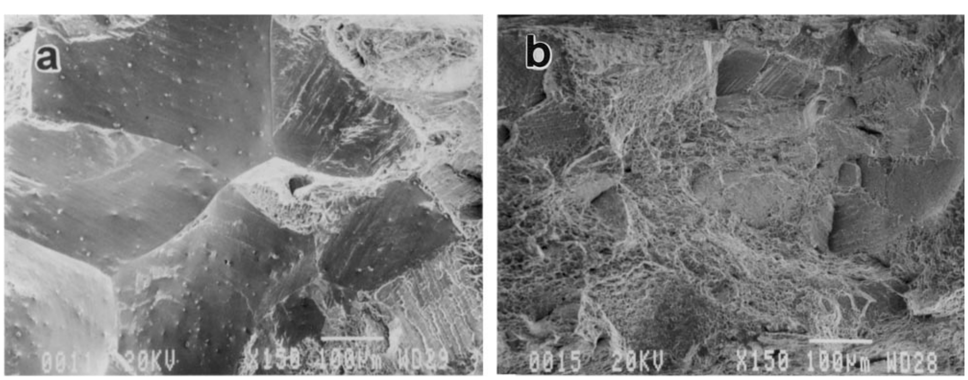

Fig. 2. SEM micrographs of (a) Cu–Zn–A1 and (b) Cu–Zn–Al–Mn–Zr alloys after tensile stressing to fracture at room temperature.

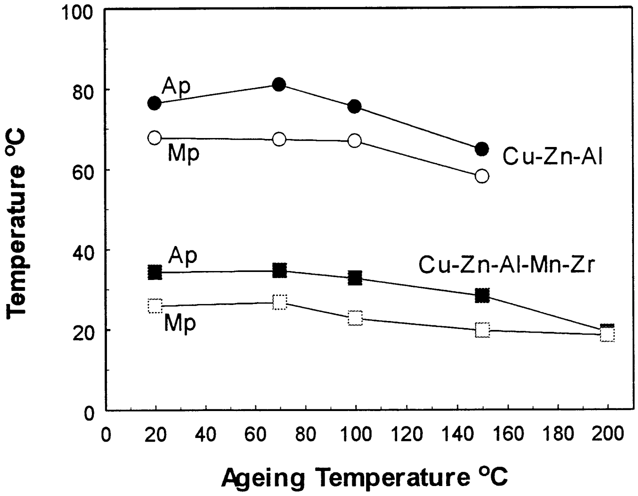

Fig. 3. Peak temperatures for Cu–Zn–Al and Cu–Zn–Al–Mn–Zr during reverse (Ap) and forward (Mp) transformations after different ageing temperatures for 6 h [7].

atures, sometimes even at room temperature. Martensite stabilisation usually occurs when the temperature is low ($< M_f$). The consequences are the increase in transformation temperatures and decrease in the transformation volume. Apart from martensite stabilisation, if the temperature is high enough, precipitation of bainite and equilibrium phases can also take place. This will result in a decrease in transformation temperatures.

Fig. 3 shows the transformation temperatures of Cu–Zn–Al and Cu–Zn–Al–Mn–Zr alloys measured by differential scanning calorimetry (DSC) after the alloys were exposed to different temperatures [7]. For the ordinary Cu–Zn–Al alloy, martensite stabilisation took place in the early stage and gave rise to the increase in the transformation temperature. Then precipitation started and the transformation temperature was decreased. No martensitic transformation could be detected after the alloy had been aged above 150°C. However, for the Cu–Zn–Al–Mn–Zr alloy, martensitic transformation could still be detected even after 200°C ageing although the transformation temperature dropped slightly with ageing temperature. This is a strong evidence that the Cu–Zn–Al–Mn–Zr alloy is more stable thermally when subjected to elevated temperatures. Moreover, the Cu–Zn–Al–Mn–Zr alloy is also less susceptible to martensite stabilisation. When being aged in the martensite phase at 50°C for a month, the transformation temperatures only increased by 2–3°C which signifies that slight martensite stabilisation has occurred. Nevertheless, this minor stabilisation can be removed by a remedial ageing at the parent phase for 30 min [8].

5. Conclusion

A new Cu–Zn–Al–Mn–Zr alloy has been developed. This new alloy shows good mechanical behaviour, with high ultimate tensile strength and relatively high ductility. Moreover, it demonstrates excellent thermal stability against ageing so that the alloy is less susceptible to martensite stabilisation.

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