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Ageing study of Cu–Al–Be hypoeutectoid shape memory alloy

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ABSTRACT

Thermal ageing at constant temperature (350 °C) and under systematically designed temperature-varying conditions were performed on the metastable austenitic phase of hypoeutectoid Cu–Al–Be shape memory alloy. Thermal precipitations and their effects on the alloy global microstructure were studied by DSC, XRD and SEM techniques. Precipitations of equilibrium phases ($\alpha+\gamma_2$) within the temperature range of 330–370 °C, and their generalization by a discontinuous mechanism for an ageing time of 864 ks (240 h), were identified and analyzed. The results of this study are expected to benefit the applications of copper-based shape memory alloys under various thermal conditions.

1. Introduction

Because several copper-based alloys have demonstrated shape-memory effect, such as Cu–Al–Ni and Cu–Al–Be shape memory alloys, the understanding of thermal behaviours and microstructure evolutions embedded in them will bring significant impact on their applications.

Near the eutectoid point of the binary Cu–Al alloy system, the disordered austenite β phase is stable above 565 °C. Below this temperature, the equilibrium phases are face-centered-cubic α phase and Cu_9Al_4-γ_2 phase. During rapid cooling (quenching), the high-temperature β phase may evolve into a DO_3 ordered-structure (metastable β_1-phase) and can further transform into a martensite phase of 18R microstructure.

The addition of the third element "X" into the binary Cu–Al alloy system favours the DO_3 ordered-microstructure for chemical compositions near $(CuX)_3Al$ where the Cu and X atoms are interchangeable in their lattice positions and the Cu is dominant. If X concentration increases, the microstructure evolves toward Heusler $L2_1$ type with a Cu_2XAl stoichiometry. Therefore, some ternary Cu–Al–X alloys, according to their respective chemical compositions, adopt either a DO_3 or a $L2_1$ order. Likewise, there are several other order–disorder transitions observed in the Cu–Al–X alloys, as in the Cu–Al–Ni where different studies [1–4] show the presence of two order–disorder transitions and the $L2_1$ type order crystalline phase near the room temperature. For the Cu–Al–Be alloy, a recent study [5] confirmed prior studies [6,7] revealing only a DO_3 type transition, where a $Cu_{0.75}Al_{0.22}Be_{0.03}$

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alloy shows that DO_3 is more likely from a stoichiometrical composition, i.e. a copper/aluminium atomic ratio of 3:1, with beryllium atoms substituting a small proportion of copper atoms. The phase of martensite, which is responsible for the shape memory effect, derives from β phase through a diffusionless reversible phase transformation with self-accommodating atom displacements. Either cooling or mechanical stress can induce martensite [4,8].

Cu–Al–Be alloys have revealed characteristics similar to that of other copper-based shape memory alloys. Beryllium addition is responsible for the extraordinary decrease of martensite transformation, i.e. M_s temperature, while aluminium composition and β phase stability are not affected significantly. This allows the martensitic transformation to maintain the same mechanism. However, the eutectoid temperature is lowered by the beryllium addition (Fig. 1), even if the temperature of β solution treatment remains the same [9].

In the Cu–Al–Ni system, M_s temperature has never been under 60 °C, owing to the stability of the aluminium content. An excess of aluminium would induce γ_2 precipitations which lead to the formation of martensite of a 2H microstructure instead of a 18R microstructure and causes brittleness and shape memory effect deterioration. With nickel addition, while the eutectoid temperature remains around 565 °C, the material experiences eutectoid composition variation affecting the martensite microstructure [10].

Generally, the rich copper part of the Cu–Al system exhibit three types of alloys, namely, hypoeutectoid, eutectoid and hypereutectoid; the stability limit of the β phase must be well established in order to avoid precipitation of stable phases in particular the Cu_9Al_4-γ_2 phase for an hypereutectoid alloy. Thus, the eutectoid composition should be ideal for a shape memory alloy, even though, the slightly hypoeutectoid one may be considered as a compromise.

The shape memory effect may deteriorate for many reasons. Dune et al. [11] had shown that martensite stabilization could occur through air-cooling from the high-temperature austenite phase, with a dominant mechanism of vacancy pinning. After the reheating afterwards which produces the β phase, vacancies, dislocations, heterogeneous stress and disorderness rapidly evolve until saturation. It is well known that precipitate formation is one of the main reasons for shape memory effect deterioration. Different types of precipitates have been observed in copper-based shape memory alloys after ageing treatment.

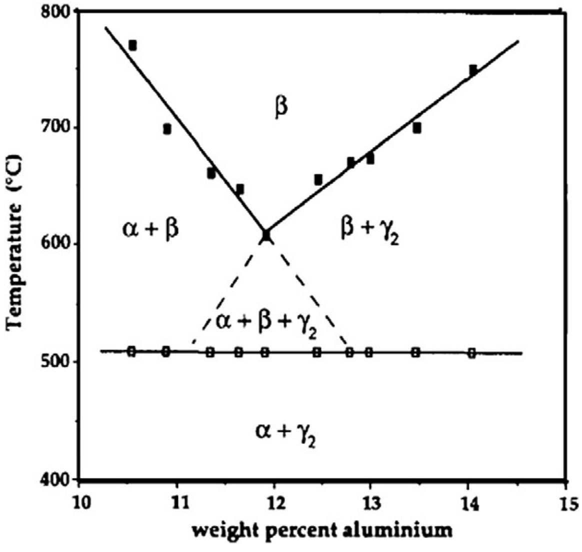

Fig. 1 – The quasi-binary Cu–AI phase diagram with 0.47 wt.% [9].

Kuo et al. [12] had studied a Cu-10 wt.% Al-0.8 wt.% Be alloy in which precipitates were found to be plate shape α_1 phase and γ_2 phase when aged at 200 °C for various amounts of time (20–160 h). For other systems such as Cu–Al–Ni hypoeutectoid alloys [4,13], it is demonstrated that, between 220 and 350 °C, precipitation occurs by a continuous mechanism (saturated $\beta_1 \rightarrow \beta_1 + \text{AlNi}$) with an energy of around 7 J/g.

The aim of this study is to explore the ageing effect on non-equilibrium β_1 phase at 350 °C for various amounts of time or for systematically designed temperature-varying conditions. The temperature range of study was designed based after a preliminary investigation by DSC. The results and analysis are expected to bring insight about the thermal behaviour of copper-based shape memory alloys for the better control of their performance in applications.

2. Experimental Procedures

All measurements were performed on a Cu–Al–Be polycrystalline ingot, with nominal composition of Cu-11.4 wt.% Al-0.52 wt.% Be (Cu-22.7 at.% Al-3.1 at.% Be). After betatizing for 30 min at 750 °C, the ingot was water quenched to obtain the metastable β_1 phase at room temperature. The martensite transformation start (M_s) temperature for this alloy was determined by DSC to be −37 °C. For thermal treatments and calorimetric measurements, rod-shaped samples (3 mm diameter, 1.5 mm thick) were cut from the original rod using a low speed diamond saw which only brought minimal damage to the sample microstructure. In the case of the isothermal treatment, the samples were first heat treated at 350 °C for 0.3 to 864 ks (240 h), (two samples each time), and subsequently air-cooled. The first sample group was treated inside a Setaram DSC 131 calorimeter, under nitrogen atmosphere, with the rate of 5 °C/min between the room temperature and the temperature of −55 °C and vice-versa. For the second sample group, a phase identification was first carried out with a Seifert XRD 3003 PTS diffractometer (Cu Kα radiation), then with a scanning electron microscope (Jeol JSM-5800 LV) and an optical microscope.

For the temperature-varying conditions, the sample was studied with the DSC under nitrogen atmosphere at variable rates. Four cycles were performed. From room temperature, β_1 phase sample was cooled to −55 °C, at 5 °C/min, heated back to room temperature at the same rate, and then heated to 350 °C at 10 °C/min. After maintaining at 350 °C for 0.3 ks, the sample was cooled to room temperature at 10 °C/min.

3. Results and Discussion

Fig. 2 shows the DSC thermogram from the reference state (non-equilibrium room temperature β_1 phase) to 550 °C,