Intermetallics

Volume 19, No. 1, January 2011   including metallic glasses   ISSN 0966-9795

Effect of grain size on the stress–temperature relationship in a β CuAlBe shape memory alloy

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ABSTRACT

The grain size dependence of the DO_3-18R martensitic transformation start temperature (M_s) and start stress (σ_s) was investigated in a Cu–22.66Al–2.98Be (at.%) alloy. M_s decreases and σ_s increases with the grain size decrease. The σ_s–T relationship is linear, however the slope depends on the grain size. Moreover, the zero stress extrapolated temperature decreases with the grain size decrease and remains lower than M_s. Results are analyzed in a thermodynamical framework.

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1. Introduction

The martensitic transformation (MT) is responsible for the shape memory (SM) properties exhibited by a group of alloys based on the noble metals. In several Cu-based SM alloy the β phase is long range ordered bcc type, and transforms to an 18R martensite [1,2]. The MT can be activated either by temperature, spontaneous transformation, or by stress. The spontaneous transformation starts at the temperature M_s, and occurs without macroscopic shape change with the formation of up to 24 self-accommodated twin-related 18R variants. Applying mechanical stress, the transformation starts at a critical stress σ_s. The induced 18R variants are that with the maximum resolved stress according to the grain constraint (one in a single crystal), and the shape changes. M_s is mainly controlled by the alloy composition, while σ_s depends on the alloy composition, and the test temperature [1–4]. However, both critical values are affected by microstructural defects [5–11]. It is important to control M_s and σ_s because they determine the temperature or stress range over which the SM effect appears.

The aim of this work is to study in detail the effect of the grain size on M_s and σ_s. For that, a Cu–Al–Be alloy with a $DO_3 \rightarrow 18R$

transformation is used. This system has relative advantages when subjected to thermal treatments: i) the grain growth can be well controlled [12], ii) the β phase is highly stable, and then precipitation can be avoided [13], iii) no chemical composition changes are detected under the required thermal treatments. This last point is extremely important considering that M_s increases 114 K each 1 at.% Be decrease [14].

2. Experimental details

The Cu–22.66Al–2.98Be (at.%) ($e/a = 1.483$) polycrystalline alloy was obtained from Trefimetaux (France). The chemical composition was determined by atomic absorption spectrophotometry. Cylindrical samples around 3.5 mm diameter and 10 mm length were prepared for compression test, with slenderness relationship ∼2.8. To obtain different grain sizes, the samples were kept in a resistance furnace at 1073 K for different times, and water quenched at room temperature. Mean grain sizes were determined by the intercept line method [12], with measurements errors smaller than 6.5%. Grains are roughly equiaxed on longitudinal and transversal faces, and sizes between 0.07 mm (as-received) and 1.09 mm have been obtained. Compression tests were performed with a Shimadzu Autograph-DSS-10T-S deformation universal machine with the specimen immersed in a liquid bath at different

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controlled temperatures in the range 270 K−340 K and a constant cross-head speed of 1 mm/min. The sample temperature was monitored using a chromel-alumel thermocouple. To reduce the stress inhomogeneities along the sample during the compression tests, the end faces were covered with a thin teflon film and lubricated with grease. The martensitic transformation temperature M_s was determined by calorimetric measurements with a Rheometric DSC calorimeter, at a cooling rate of 10 K/min. Because of the exothermic DO_3-18R transformation reaction, the M_s was also determined from the slope change in temperature−time cooling rumps at 10 K/s, monitored with a Cole−Parmer data acquisition module. Both techniques provide comparable results.

3. Results and discussion

Fig. 1 shows the compression stress−strain curves obtained at different temperatures for samples with two representative grain sizes, 0.070 ± 0.001 mm (a) and 1.09 ± 0.07 mm (b). They are typical pseudoelastic (PE) cycles, where the first linear part corresponds to the elastic regime of the β phase. The linearity deviation is associated with the β to martensite transformation start; thus, we define σ_s as the stress corresponding to the end of the initial lineal part. A subsequent nearly constant stress−strain slope corresponds to the progress of the martensitic transformation. On removing the load, a hysteresis loop is formed, and an almost complete strain recovery is obtained for PE strains up to around 3% [15,16]. From therein more, strain is increasingly retained on unloading due to retained martensite. In order to assure pure β phase as starting material in each PE cycle, PE strains not beyond 3% were applied. It can be seen from Fig. 1 that σ_s is modified by the grain size as well as by the test temperature.

Fig. 2(a) collects the σ_s−temperature data obtained for the different grain size samples. Two main results are evidenced: i) σ_s increases as the grain size decreases, and ii) σ_s increases linearly with the test temperature increase for all the samples. That larger grain specimens exhibit lower values of σ_s have been also observed under tensile tests of the studied alloy [12]. The measured slope $\partial\sigma_s/\partial T$ is plotted in Fig. 2(b) versus the grain size. It is observed that $\partial\sigma_s/\partial T$ decreases with the grain size increase up to around $d = 0.7$ mm, and maintains values of around 2.4 MPa/K for larger grain sizes. A close value, 2.1 MPa/K, has been reported for a well-oriented CuAlBe single crystal (with high Schmid factor $\mu = 0.482$), and also for a CuAlBe polycrystal with $d \approx 1$ mm, both with similar chemical composition and under tension [16,17]. Fig. 2(c) shows the measured M_s values together with the temperature extrapolated to zero stress, denoted as T^*. An increase in grain size produces an increase of M_s and also of T^*, however T^* remains lower than M_s.

The difference between M_s and T^* decreases as the grain size increases, being ≈ 26 K for the lower grain samples, and 13 K for the larger grain samples. It is worth noting that the stress-induced transformation in the temperature range $T^* \leq T \leq M_s$ becomes hypothetical because the spontaneous transformation takes place at M_s.

An almost linear variation of σ_s with the test temperature has been found in numerous investigations in both single crystal and polycrystalline Cu−Al−Be [16−20], and other copper-based shape memory alloys [21−26]. In a thermodynamic framework, the equilibrium values of σ and T for a single martensite variant in a single crystalline β phase are linked via the chemical free energy difference between the β phase and the martensitic phase ΔG [4]:

$$\Delta G = -(T_0 - T)\Delta S = W_{tr} \qquad (1)$$

where T_0 is the equilibrium transformation temperature, defined at the point where $\Delta G = 0$ for stress-free conditions, ΔS is the entropy difference between β and martensite, and $W_{tr} = \sigma\varepsilon_0 V_m$ is the work of transformation, with ε_0 the transformation strain, and V_m the molar volume. We consider ΔS positive for the forward martensitic transformation. In single crystals the spontaneous transformation starts at M_s, and not at T_0, because the moving interface, except perfect, has to perform a frictional work [4]. When thermally-induced, an overcooling is required for the transformation which is equivalent to an amount of heat $\Delta S (T_0 - M_s)$. In the case of stress-induced transformation, an equivalent work $\Delta\sigma \varepsilon_0 V_m$ is required. In well-annealed Cu-based SMA single crystals, the difference between T_0 and M_s is very low, around 5 K [1,14]. Consequently, the σ_sJ/mol$T$ relationship is usually approached as:

$$\sigma_s = \frac{\Delta S}{V_m\varepsilon_0}\cdot(T - M_S) \qquad (2)$$

Taking into account $\Delta S \approx$ constant for $T > 80$ K [26], eq. (2) leads to $d\sigma_s/dT \approx$ constant.

Our results indicate that it is not straightforward the relationship between σ_s and T for polycrystalline samples. The grain size effects on σ_s can be rationalized introducing an M_s temperature grain size dependant, $M_s(d)$, and an additional stress component which contains the grain constraint effects, σ_{gr} (T,d), modifying eq. (2) as:

$$\sigma_s(d,T) = \frac{\Delta S}{V_m\varepsilon_0}[T - M_s(d)] + \sigma_{gr}(T,d) \qquad (3)$$

If a linear relation between σ_{gr} and T is assumed, the $\sigma_s - T$ slope of Fig. 2(b) can be described as:
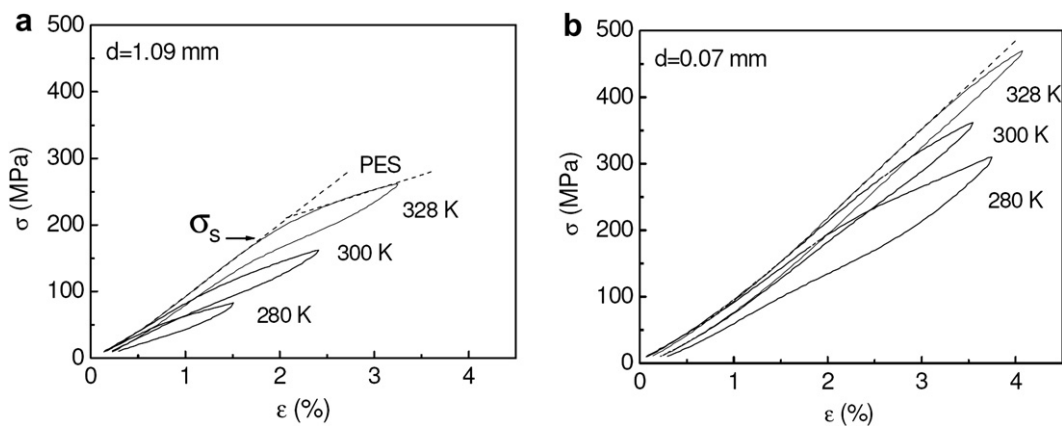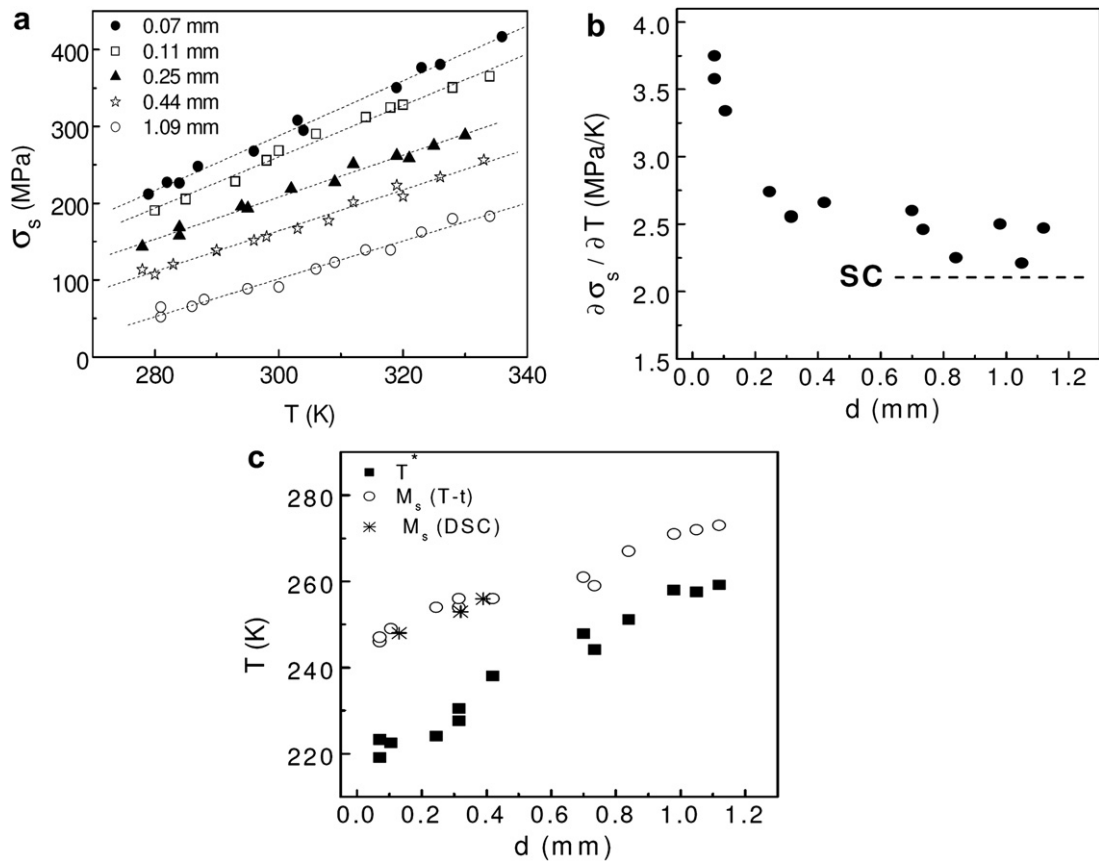

Fig. 1. Stress−strain cycles obtained by compression at different temperatures (σ and ε are considered positive under compression).

Fig. 2. (a) Variation of σ_s with the test temperature for samples with different grain sizes; (b) Grain size dependence of the slope $\partial\sigma_s/\partial T$. Dashed line: single crystal data (SC) from [17] (see text); (c) Temperatures M_s and T^* versus grain size.

$$\left.\frac{\partial\sigma_s}{\partial T}\right|_d = \frac{\Delta S}{V_m\varepsilon_0} + \sigma'_{gr}(d) \qquad (4)$$

where $\sigma'_{gr} = \partial\sigma_{gr}/\partial T|_d$ depends only on d. The increase of $\partial\sigma_s/\partial T|_d$ with the grain size decrease is then ascribed to the increase of $\sigma'_{gr}(d)$. $\sigma'_{gr}(d)$ becomes almost zero for grain sizes 0.7 mm and higher. Considering the samples diameter, 3.5 mm, it corresponds to samples with an average of 5 or less grains per transversal area. It is worth noting that the functional dependence of σ_s with d is not simply. For example, the extensively used Hall-Petch law, a linear relation $\sigma_s - d^{-1/2}$, is not valid in this case. In polycrystals nucleation and growth of martensite to detectable sizes is more difficult because the martensitic plates have to overcome the grain boundary barriers. The decrease of M_s with the decrease of grain size indicates that the self-accommodated martensite formation is disturbed by grain boundaries, and an increasingly overcooling for the transformation start is required. It can be mentioned that linear defects like dislocations strongly reduces the number of martensite variants able to form, leading to a lowering in M_s in Cu−Zn−Al single crystals [5]. By mechanical loading, the transformation occurs under an additional restriction. The variants which nucleates and growth are those most favorably oriented with respect not only to the applied stress but also to the intergranular stress field. This restriction can be considered to be reflected by the non-zero extrapolated start stress at $T = M_s$, $\sigma_s = \sigma_{gr}(M_s,d)$ in eq. (3); or equivalently by the difference between the temperature extrapolated to zero stress T^* and M_s, Fig. 2(c). As a consequence, an
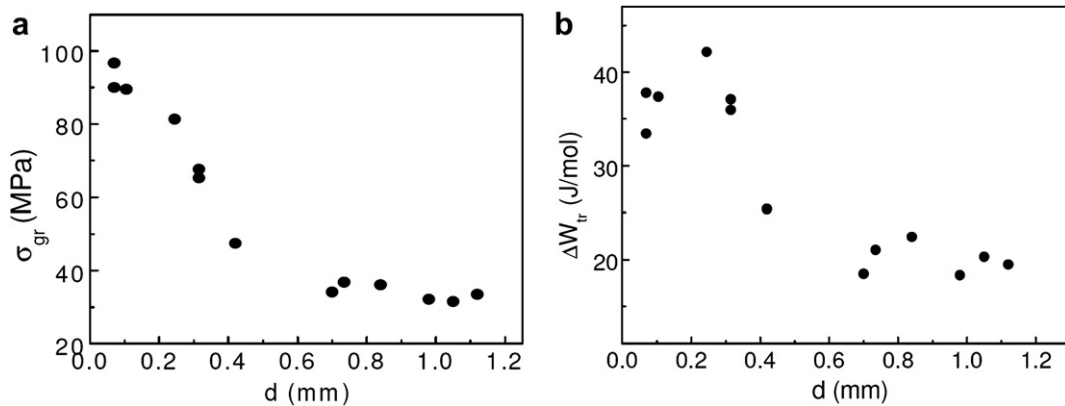
Fig. 3. Stress and additional stress-induced transformation work at $T = M_s$.

additional work $\Delta W_{tr} = \Delta S(M_s - T*)$ seems to be necessary at $T = M_s$ for the stress-induced transformation compared to the thermal-induced transformation, which decreases as the grain size increase. Cingolani et al. [17] report an entropy difference between β and martensite ΔS equal to 1.41 J/mol K. Taking into account ΔS does not seem to vary with the chemical composition for Cu–Al–Be alloys with e/a between 1.48 and 1.49 [14,17], the reported value permits the estimation of the additional work. Fig. 3 shows the values of σ_{gr} and ΔW_{tr} at $T = M_s$, and their grain size dependence. σ_{gr} and ΔW_{tr} decrease as the grain size increases, reaching the lower values around 30 MPa and 18 J/mol respectively for grain sizes larger than around 0.7 mm.

It is interesting to note that in large grain samples $\partial\sigma_s/\partial T$ gives values notably close to that corresponding to well-oriented (high Schmid factor) single crystals, suggesting that the $\sigma_s - T$ slope is strongly related to the largest, and well-oriented grains, which would transform first. However, the start stress remains higher than in single crystals, revealing the grain constraint effect via the $\sigma_{gr}(T,d)$ component.

Finally, the texture evolution during grain growth can be considered. This process, if exists, could modify the $\sigma_s - T$ slope values (Fig. 2(b)). However, it cannot explain the difference between the temperature extrapolated to zero stress T^* and the measured M_s (Fig. 2(c)).

4. Conclusions

The effect of the grain size on M_s and σ_s of a Cu–Al–Be alloy with a $DO_3 \rightarrow 18R$ transformation has been analyzed in detail. The grain size decrease modifies the martensitic transformation producing i) a stress-start increase, ii) a temperature-start decrease, iii) an increase of the $\sigma_s - T$ slope, iv) an increase in the difference between the M_s and the extrapolated temperature at zero stress. A modified stress–temperature relation is proposed containing the grain size effects. The extrapolated required stress and additional transformation work at $T = M_s$ can be considered as a measure of the restriction imposed by grain boundaries to the stress-induced transformation compared to the spontaneous transformation. According to our results, the $\sigma_s - T$ slope for samples with an average of 5 or less grains per transversal area is similar to that of well-oriented Cu–Al–Be single crystals.

The grain size effects not only on the start critical parameters but on the entire transformation behavior deserve further studies, which are in progress.

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