Grain size effect on the thermal-induced martensitic transformation in polycrystalline Cu-based shape memory alloys

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Abstract

In Cu-based SMA alloys, the grain size ($d$) effect on the martensitic transformation temperature was investigated for a wide range of $d$. Specimens were prepared by different heat treatments in order to create a range of grain sizes, from about 500 nm (ribbons and tapes obtained by rapid solidification techniques) up to 6 mm diameter single-crystals (grown by the Bridgman method). Information obtained from the literature was also included in the set of analyzed experimental data. The reduction of grain size shifts the forward transformation temperature downwards. These grain-size effects are observed in specimens with $d$ below ~ 100 $\mu$m, and become more pronounced for $d$ below ~ 20 $\mu$m. An empirical expression was obtained that describes the grain-size effect over the whole temperature range. The obtained curve differs considerably from the Hall-Petch behaviour reported in the literature by some other investigators.

Keywords: Cu-based SMA; polycrystals; grain size effects

1. Introduction

Since polycrystalline Cu-based SMAs with coarse grains are extremely brittle, many attempts have been made over the past decades to improve their ductility and fatigue strength by grain refinement [1,2]. A fine grain structure suppresses intergranular fracture, although the recoverable strains and phase transformation temperature decrease. Also, grain constraints affect the transformation stress and resulting strains [3]. Therefore, for Cu-based SMAs the

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grain size must be properly controlled to attain a balance between ductility and shape memory properties. Moreover, how grain size impacts the SMAs transformation behaviour provides valuable information for understanding the size-scale dependence of martensitic transformations (MT). Such size effects are critical in the design of micro- and nano-scale devices that employ SMAs [4]. The present investigation focuses on the lowering of the $M_s$ temperature as the grain size decreases. Prior measurements have shown that $M_s$ is generally independent of $d$ when grain sizes are greater than 100 $\mu$m, but decreases when $d$ is below this value [5,6,7].

In Cu-based alloys, the high temperature parent phase with an ordered L2$_1$ structure (called $\beta_1$) can transform at lower temperatures than the martensite 18R or 2H for some alloy compositions. The type of martensite structure and transformation temperatures depend mainly on the chemical composition ($Q$). However, $M_s$ is also affected by other factors such as concentration of vacancies ($X_v$), degree of long range order ($S$), density of antiphase boundaries [8], and dislocation density ($\rho^{dis}$) [9]. Accordingly, the martensitic transformation temperature can be expressed as

$$M_s(Q,d,X_v,S,\rho^{APB},\rho^{dis},d) = M_s^{SC}(Q,X_v,S,\rho^{APB},\rho^{dis}) + F(d)$$

Where the term $M_s^{SC}$ is inherent to the “bulk” material condition, corresponding to the transformation temperature of a millimetre-size single-crystal, and $F(d)$ introduces the related grain-size ($d$) contribution. For the latter term, it has been proposed that $M_s$ depends linearly on the inverse of the square root of the grain size [5,10], i.e. in a similar way as in the Hall–Petch relationship. However, the Hall–Petch relationship was derived by analyzing specimens spread over a narrow range of grain sizes [5, 10-12]. In this paper, we examine specimens with grain sizes ranging from about 500 nm to a few millimeters and a new empirical relationship valid over this entire range is proposed.

2. Experimental details

Cu-Al$_{13}$Ni$_5$, Cu-Al$_{13}$Ni$_6$Ti$_1$ and Cu-Al$_{13}$Be$_{0.5}$ (at.%) sheets (thickness~500 $\mu$m) and ribbons (thickness~50 $\mu$m) were obtained by two different rapid-solidification methods: Melt-Spinning (MSp); and Twin Roll Casting (TRC) [13]. Thermal annealing at different temperatures (T>700 $^\circ$C) was performed in order to modify the grain size ($d$) in order to study a wide range of $d$ (1 $\mu$m < $d$ < 100 $\mu$m). After the annealing treatments all the samples were ice-water quenched. A second thermal treatment at 200 $^\circ$C for 15 min, followed by air cooling, was performed in order to promote ordering and to eliminate an excess of vacancies. This final ageing in the parent phase stabilizes the MT temperatures [14]. The grain size was determined by the line intersection boundary method from SEM, TEM and OM images. The MT temperatures were measured by DSC with a Shimadzu DSC-60 calorimeter and by four-probe resistivity tests in a.c. mode, using an SR-530 lock-in amplifier, at cooling/heating rates of 5 K/min. Three runs for the forward and reverse transformation were performed to verify data reproducibility.

3. Results and discussion.

Fig. 1(a) shows the experimental data obtained in this work and by other authors [5,10,11,12,15,16]. $M_s$ has been plotted against the inverse of the square root of the grain size $d^{-1/2}$ in order to evaluate the consistency between the collected data and a Hall–Petch type relationship ($M_s = k.d^{-1/2}$). This figure shows that for materials of similar composition, e.g. data in blue (see the on-line version), the constant $k$ (Hall–Petch relation parameter) can differ by one order of magnitude when data are evaluated at the extremes of the grain-size range. Moreover, when we assess a set of somewhat widespread data, they do not follow a linear dependency. This can be seen in Fig. 1.

In light of these facts, we propose an alternative method to assess the term $F(d)$ in eq. (1), which introduces the contribution of grain size to the $M_s$ temperature. To make the evaluation independent of the “bulk” material ($M_s^{SC}$) contribution to $M_s$, it is helpful to work with the derivative $\partial M_s/\partial d = \delta F(d)/\delta d$. Now our purpose is to determine $\partial M_s/\partial d$ on the basis of an analysis of all the available experimental data, and then fit this data with an empirical function. It is then possible to find the antiderivative function $F(d)$ plus an additive constant. Keeping this in mind, from a set of $n$ experimental data ($M_s$ vs. $d$) associated with each sample, we can approximate $\partial M_s/\partial d$ vs. $d$ as follows:
(\frac{\partial M_s}{\partial d})_i = \frac{(M_s)_{i+1} - (M_s)_i}{d_{i+1} - d_i}
(2)

\quad \bar{d}_i = \frac{d_{i+1} - d_i}{2}
(3)

where \(i=1,2,\ldots n\) represents different \(M_s(d)\) data points associated with a single sample. In this way, it is possible to obtain \((n-1)\) experimental points with the form \(\left(\frac{\partial M_s}{\partial d}, \bar{d}\right)\) for each analyzed sample. By processing all the available data, we obtain the graphic representation shown in Fig. 1(b), where a regular behavior is observed for \(\partial M_s/\partial d\), since no steps or disruptions in slope are observed. This data treatment allows us to obtain an empirical expression for \(\partial M_s/\partial d\) (or \(\partial M_s/\partial d\)). By fitting the experimental data in Fig. 1(b) with a power law \(f(x) = a \cdot x^b\), the fitting parameters \(a\) and \(b\) were obtained by a least-square procedure, leading to the expression: \(\frac{\partial F(d)}{\partial d} = 48.9 \frac{^\circ C}{\mu m} (\frac{d}{\mu m})^{-1.11}\). Then the antiderivative function results: \(F(d) = -445 \frac{^\circ C}{\mu m} (\frac{d}{\mu m})^{-0.11} + c\), where \(c\) is an indeterminate constant. Such indeterminacy is solved by using the experimental data that show a negligible effect of grain size on \(M_s\), for \(d < 100 \mu m\). So the constant \(c\) is determined such that \(F(100 \mu m) = 0\). In this way, the empirical expression that describes the \(M_s\) behavior as a function of grain size (for \(d < 100 \mu m\)) becomes:

\[M_s(d) = M_s^{SC}(Q, X_v, S, \rho^{APB}, \rho^{dis}) - 445 \frac{^\circ C}{\mu m} (\frac{d}{\mu m})^{-0.11} + 268 ^\circ C\]
(4)

This expression is plotted with a green dashed line in Fig. 2 and represents the \(M_s\) vs. \(d\) behavior over the whole grain size range. Using this function as a guide, in Fig. 2, the experimental data \((M_s,d)\) from each sample were located to match the green dashed curve. In order to achieve the matching, the data sets of each sample were shifted in the temperature axis by imposing \(M_s^{SC} = 0\) as a common reference condition. So, Fig. 2 must be regarded as the experimental \(\Delta M_s\) variation as a function of grain size \(d\) where differences in composition and the other parameters inherent to the “bulk” are compensated for (equals \(F(d)\)). As can be seen, expression (4) provides a suitable description of \(M_s\) behavior for a wide range of \(d\) in Cu-based SMAs polycrystals. Grain-size effects are already observed in specimens with \(d\) below \(\sim 100 \mu m\), and they became more noticeable for \(d\) below \(\sim 20 \mu m\), giving rise to a pronounced drop in the transformation temperature. According to the curve, a reduction of more than 200 \(^\circ C\) in \(M_s\) with respect to the single-crystal condition takes place if grains are refined to an average value of \(\sim 1 \mu m\). It should be emphasized that expression (4) is defined for grain-size values of \(d < 100 \mu m\). Above this value no appreciable size effects are observed [5,6]. Finally, it is worth stressing that the \(M_s\) vs. \(d\) behavior is not described by a Hall-
Petch type relationship. The fitting with a power law $d^{-1/2}$ previously reported in the literature may have produced suitable results because it was applied over a narrow range of $d$, and for grain sizes well above $10 \, \mu m$ [5,10].

![Fig. 2. Variation of transformation temperature $\Delta M_v$ vs average grain size of the samples. (dashed green curve corresponds to the antiderivative of the fitting curve displayed in Fig. 1(b), see text for details).](image)

### 4. Conclusions

How grain size ($d$) affects the martensitic transformation temperature in Cu-based SMA alloys was investigated for $d$ values ranging from ~ $500$ nm up to single-crystals $6$ mm in diameter. A reduction of grain size shifts the forward transformation temperature downwards, and grain-size effects on transformation temperatures are already observed in specimens with $d$ below ~ $100 \, \mu m$. These effects become more pronounced for $d$ below ~ $20 \, \mu m$. An empirical expression which describes the grain-size effect over the entire range of grain sizes was obtained by processing data from samples with different compositions:

$$M_s(d) = M_s^{SC}(Q,X, \rho_{APB}, \rho_{dis}) - 445 \, ^\circ C \left(\frac{d}{\mu m}\right)^{-0.11} + 268 \, ^\circ C$$

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### References