Scripta Materialia 124 (2016) 155–159

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

Stress-assisted atomic diffusion in metastable austenite $D0_3$ phase of Cu-Al-Be shape memory alloys

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ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form 24 June 2016
Accepted 24 June 2016
Available online 19 July 2016

Keywords:
Shape memory alloys (SMA)
Cu-Al-Be
Stress-assisted diffusion
Internal friction
Relaxation

ABSTRACT

Cu-Al-based shape memory alloys are firm candidates to be used up to 473 K. The main limiting aspect is the activation of diffusion processes in the metastable austenite phase, which drive the alloy decomposition. In the present work the study of short-distance diffusion processes has been approached by internal friction. A relaxation peak has been found in the metastable β ($D0_3$) phase of a Cu-Al-Be shape memory alloy, around 500 K (at 1 Hz), with an activation energy of $E_a = 1.38 \pm 0.05$ eV. An atomic mechanism of elastic dipoles Antisite-Vacancy reorientation, involving stress-assisted short distance Cu-atoms diffusion, has been proposed.

Shape memory alloys (SMA) constitute an important family of smart materials due to their capacity to work simultaneously as sensors and actuators thanks to a reversible martensitic transformation (MT). The MT, which can be thermally induced by cooling or stress-assisted by the application of a stress, is characterized by an atomic shearing of the lattice planes from a high-temperature high-symmetry phase called austenite to a low-temperature low-symmetry phase called martensite. This transformation gives place to the shape memory effect (SM) and the superelasticity (SE) property, which make them highly interesting as functional materials (for a general overview, see text books [1–3]).

Ternary alloys based on the Cu–Al binary system are being developed as an alternative to the conventional Ti–Ni alloys, which are the most commercially widespread SMA. Indeed, Cu-Al-based ternary SMA are undergoing a revival due to their excellent behaviour at micro and nano-scale [4–9], which offers a competitive advantage over the Ti-Ni alloys, to work as sensors and actuators in micro electro-mechanical systems (MEMS). In addition Ti-Ni SMA have only a limited martensitic start (Ms) temperature range from 200 K to 350 K [3,10], whereas Cu-Al-based SMA exhibit a broader transformation range from low temperature, 77 K [11–13] up to 473 K [14,15], as well as a good superelastic behaviour in different systems such as Cu-Al-Mn [13,16], Cu-Al-Be [17,18] and Cu-Al-Ni [15,19,20].

However, the austenite β phase in Cu–Al-based alloys is only stable at high temperature and it must be quenched in order to obtain the β phase frozen in metastable condition, which undergoes the MT by further cooling. Then, in order to guarantee a reproducible and reliable behaviour during the working conditions in practical applications, the thermal stability of the metastable β phase is a key parameter that must be quantitatively evaluated, because the diffusive processes produce the precipitation of stable phases [21], which inhibit the MT. Nevertheless, although the activation energy for Al diffusion in the α solid solution phase, in Cu–Al system, has already been reported [22–24], there is little information concerning the diffusion of Cu and Al in the β phase [25,26] and the available data are not in good agreement. On one hand, Romig [25] determined a mean value of 1.83 eV for the self-diffusion activation energy in β phase of Cu-Al, in the 1073–1223 K temperature range. However, in this work [25] the diffusion couples were annealed in disordered β phase, while the concentration profiles and the distances between markers were measured, after quenching, so in martensite phase which is known to produce severe distortions on the sample. This fact makes such measurements not reliable enough. On the other hand, the activation energy for the Al diffusion determined from the data by Asundi and West [26] is 1.2 eV, in the 673–823 K range, which is an unrealistic low value. The lack of precise information on these activation energies, especially at low temperatures in metastable β phase, stems from the natural tendency of Cu–Al alloys to decompose into stable phases below the eutectoid temperature (≈838 K), and also from the difficulties to perform tracer diffusion experiments due to the lack of suitable isotopes [15]. Consequently a good understanding of

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http://dx.doi.org/10.1016/j.scriptamat.2016.06.034

the fundamentals of these diffusive processes is required to improve the materials' performances, and the activation energy for diffusion is the crucial parameter to describe properly such processes. The aim of the present work is to offer a quantitative answer to this open crucial question.

To reach this goal, a non-conventional approach is considered to investigate diffusive processes at low temperatures, by using internal friction (IF) measurements (see the review [27]) as the appropriate tool to study such phenomena in the metastable β phase. Indeed, short distance diffusion processes associated to a Zener relaxation were reported as precursor of long distance diffusion processes for important systems such as Al-Li [28] or Ti-Al [29], giving access to the activation energy of the mobile atomic specie.

However, the metastable β phase of the Cu–Al system cannot be accessed at low temperature because the MT is taking place, during quenching, at rather high temperatures, between 800 K and 700 K [30]. Fortunately, a way of overcoming this problem is the addition of a third element to decrease the MT temperatures. In particular Be strongly decreases the martensite start temperature (Ms) according to the expression Ms(°C) = 1245–71%Al-893%Be (wt.%), reported by Belkahla et al. [11]. Thus, a small Be amount significantly decreases the MT temperatures enabling the study by IF of the diffusive processes in the frozen metastable β phase.

Then, a single crystal of a Cu75.40%-Al22.80%-Be1.80% alloy (at.% analysed via inductive coupled plasma (ICP)) has been considered as model alloy for the present study. A long single crystal was grown by Bridgman method, in the form of a wire of 1.6 mm diameter, with the [001] direction oriented along the cylinder axis, from which one piece 50 mm long was cut. The sample was annealed at 1023 K in argon atmosphere during 1800 s and then quenched into boiling water at 373 K according to the optimized thermal treatments reported in a previous work [31]. IF and dynamic modulus measurements were carried out in an inverted torsion pendulum working in sub-resonant mode [32], in the 300–600 K temperature range, at different frequencies between 10^{-3} and 10 Hz, with an oscillation amplitude of $\varepsilon_m = 2 \times 10^{-5}$ and using a heating rate of 1 K/min.

Fig. 1a shows the IF spectrum (at 1 Hz) and dynamic modulus variation measurements corresponding to the first heating of the sample after the thermal treatment. The IF spectrum shows a peak at 400 K, which corresponds to the reverse martensitic transformation as evidenced by the associated hardening in the dynamic modulus. This result fully agrees with a previous work, where the MT was characterized via calorimetry [31]. Apart from that, a second IF peak, named Pz, appears at 500 K superimposed to a high-temperature background (HTB). The HTB appears typically in IF measurements as the low-temperature side of another peak, or simply as a Maxwell behaviour linked to different thermally activated processes [27,33]; in both cases it can be fitted to an exponential function, but its study is not the subject of the present work. The Pz peak has been studied as a function of the oscillation frequency (f), and Fig. 1b shows clearly that Pz shifts towards higher temperatures as the frequency increases. This behaviour indicates that Pz is associated to a thermally activated relaxation process, allowing us to determine its activation energy (E_a) from an Arrhenius diagram. Fig. 2a shows the Arrhenius diagram obtained by plotting $\mathrm{Ln}(2\pi f)$ versus $1/T_P$, being T_P the temperature of the Pz peak maximum at each frequency f; then, from the least square fitting [27,33], the activation energy of $E_a = 1.38 \pm 0.05$ eV and the characteristic relaxation time of $\tau_0 = (3.02 \pm 0.09) \times 10^{-15}$ s were determined.

In order to analyse in depth the microscopic origin of the relaxation process responsible for the Pz peak, the experimental peak has been compared with the theoretical one expected from a Debye relaxation due to a single-time relaxation process (Fig. 2b). First, we have fitted the HTB to an exponential function and then subtracted it from the experimental spectrum, to isolate the peak, as presented in Fig. 2b. Finally to evaluate the broadening of the peak, we compare it with the theoretical expression of a slightly broadened Debye peak, assuming a Gaussian

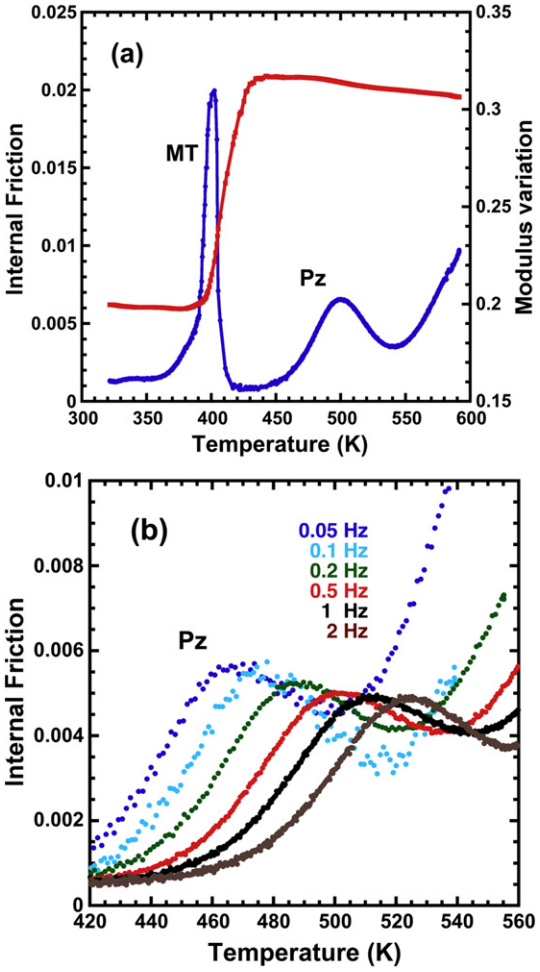

Fig. 1. a) Internal friction spectrum (blue dots and line) and dynamic modulus curve (red square and line) for the Cu-Al-Be SMA, during the first heating run after quenching. Internal friction peak labelled MT is linked to the reverse martensitic transformation and the peak labelled Pz is a relaxation peak. b) Series of internal friction spectra showing the Pz peak at different frequencies from 2 Hz to 0.05 Hz, evidencing the shift of the peak to lower temperature when decreasing the frequency.

distribution [33]:

$$IF = \tan\phi = \tan\phi_{\max} \cdot \cosh^{-1}\left[\frac{E_a}{r \cdot k_B} \cdot \left(\frac{1}{T} - \frac{1}{T_p}\right)\right] \quad (1)$$

In the above expression (1), ϕ is the experimentally measured phase angle (loss angle) between strain and stress, $\tan\phi_{\max}$ is the maximum height of the peak and k_B holds for the Boltzman constant. The parameter r is the broadening factor of the distribution, which for the best fitting becomes $r = 1.12$, indicating that the Pz peak fits quite well with a Debye peak ($r = 1$), with only a minor deviation due to the uncertainty from the HTB function. Consequently the Pz peak corresponds closely to a single-time relaxation process, because it is practically a Debye peak, and can be identified as a Zener peak due to point defects mobility in the metastable β phase of the Cu-Al-Be system. Since the Zener relaxation is interpreted in terms of changes in short-range order produced by a stress-assisted reorientation of a pair of solute atoms, its activation energy is associated to the diffusion enthalpy of one of the alloy constituents [27].

Let us analyse the possible atomistic model that could explain this relaxation. A point defect or a pair of point defects in a crystal lattice produce a local elastic distortion, which is called elastic dipole and is characterized by a second-rank tensor [27], being able to interact with the applied stress. In absence of any applied stress, all p-oriented elastic

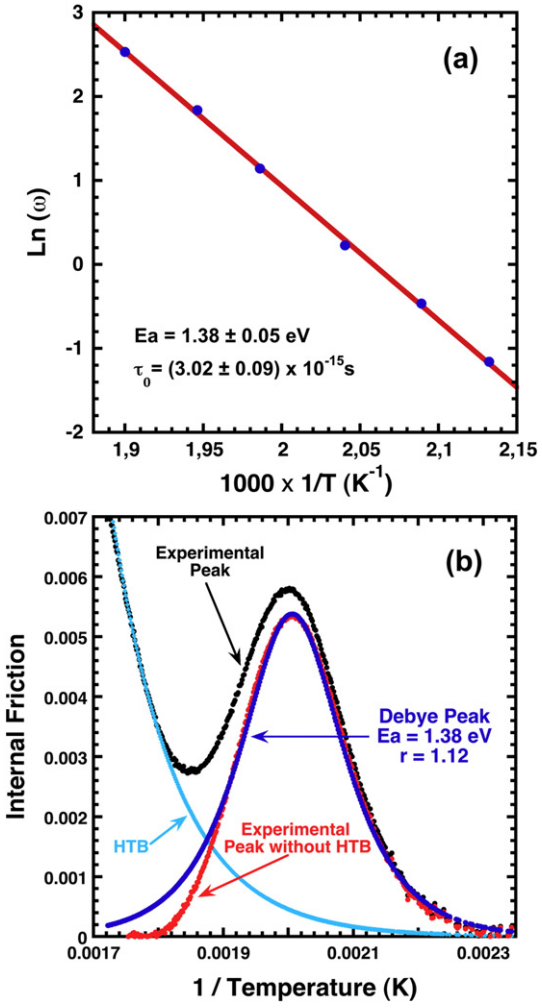

Fig. 2. a) Arrhenius diagram for the temperature of the Pz peak maximum as a function of frequency, for the peaks of Fig. 1b. From the slope of the line the activation energy E_a is determined. b) Experimental peak before (black dots) and after (red dots) subtraction the high-temperature background HTB (cyan diamonds), and comparison with the theoretical Debye peak fitting (blue dots) with a broadening factor $r = 1.12$.

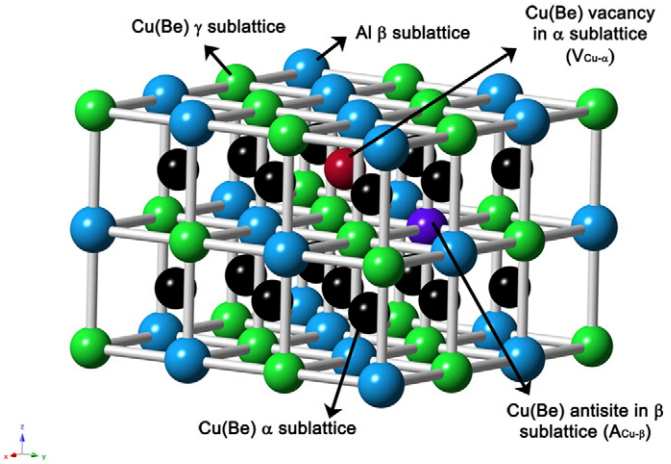

Fig. 3. Atomic $D0_3$ lattice of the metastable β-phase of Cu-Al-Be SMA, where the three sublattices α (black), β (blue) and γ (green) are indicated. The antisite defect in the β-sublattice is indicated as a violet sphere and the vacancy in the α-sublattice is indicated as a red sphere.

dipoles of a defect have the same energy in the crystal lattice; however, if a stress field able to produce a reorientation of some of the p-oriented elastic dipoles is applied, the degeneration of the p-levels of energy is broken and some preferential orientation decreases the local energy of this configuration with respect to others. Then, an anelastic relaxation towards the new local atomic configuration of the defect with minimal energy will be produced, giving rise to an IF peak. However, some symmetry restrictions exist for anelastic relaxation observation, since the symmetry of the defect must be lower than the symmetry of the crystal. In bcc crystals, only defects with trigonal symmetry are able to produce an observable anelastic relaxation in the nearest neighbour (nn) configuration and only defects with tetragonal symmetry are able to produce relaxations in the next nearest neighbour (nnn) configuration [27]. The β phase in a Cu-Al-Be alloy is a cubic phase with $D0_3$ order [34], a lattice parameter $a = 5.825$ Å and an *Fm*-3 m space group [35]. This structure is composed of 3 sublattices α (Cu, Be), β (Al) and γ (Cu, Be) as shown in Fig. 3; indeed Be atoms would be either in α or γ sublattices, being β sublattice reserved for Al atoms in $D0_3$ intermetallics. In the present case a torsion pendulum was used to study a single crystal cylinder oriented in such a way that the [001] direction was along the cylinder axis, this means that it is not possible to observe the anelastic relaxation produced by trigonal defects with [111] dipole orientation, because the shear stress will not produce any splitting of the free-energy levels. Consequently, tetragonal defects must be responsible for the observed relaxation. Moreover, in the $D0_3$ structure the atoms of different sublattices are not energetically equivalent and the energy of defect formation depends on the sublattice. Therefore, some extra considerations should be taken into account. On one hand, in similar intermetallics with $D0_3$ order, such as Fe_3Al or Fe_3Si, the vacancy concentration is higher on the α sublattice, because its vacancy formation enthalpy is lower than in the other sublattices [36,37]. On the other hand, Al constitutional vacancies are not observed on the β sublattice, because the antisite defects present a lower formation enthalpy than Al vacancies [36,37].

Taking this into account, the following relaxation mechanism for the austenite phase with $D0_3$ structure is proposed. In our Cu75.40%-Al22.80%-Be1.80% (at.%) alloy the lack of Al, compared with the stoichiometric one (25%), must be compensated by Cu(Be) antisite atoms on the β sublattice instead of Al vacancies; Such an antisite atom is represented by a violet sphere in Fig. 3. Now let us consider a Cu(Be) vacancy V_{Cu} on the α sublattice, represented by a red sphere, close to the antisite atom position in β sublattice, as drawn in Fig. 3. The Cu(Be)-β antisite plus the Cu(Be)-α vacancy (V_{Cu}) constitute an elastic dipole in the [111] direction in its rest position (Fig. 4a). If a shearing stress is applied parallel to the {001} plane, the elastic dipole will rotate by exchanging a Cu(Be)-γ atom with the V_{Cu}. Depending on the local stress field the elastic dipole will be oriented on the [100] direction (Fig. 4b) or on the [010] direction (Fig. 4d). When the stress is withdrawn, the vacancy will tend to return to its rest position in the β sublattice (Figs. 4c and a). Then, during a complete oscillation cycle the dipole Antisite-Vacancy will rotate from [100] to [010] passing through the intermediate position, which is also the initial and final positions for zero stress, as described in Fig. 4e. For a particular temperature the jump of the vacancy (and the rotation of the dipole) will take place in resonance with the applied stress, given place to a relaxation process and an internal friction peak. A short video-animation of the dipole reorientation is included as Supplementary material.

It may be concluded that the IF relaxation peak observed at around 500 K (1 Hz) in the metastable β phase of the Cu-Al-Be system, has been identified as a Zener relaxation peak produced by the rotation of dipoles Antisite(β)-Vacancy(α-γ). Both kind of atoms, Cu and Be, share the sublattices α and γ, and we may ask what is the atomic species jumping during the relaxation process. Indeed, the Pz peak is practically a Debye peak (single-time relaxation) and therefore only one kind of atom, Cu or Be, could be responsible for the relaxation, otherwise two peaks or a much broader peak would be expected. The answer to this question deserves discussion. The maximum height of the Pz peak (as a relative measure of its strength) will be proportional to the mole

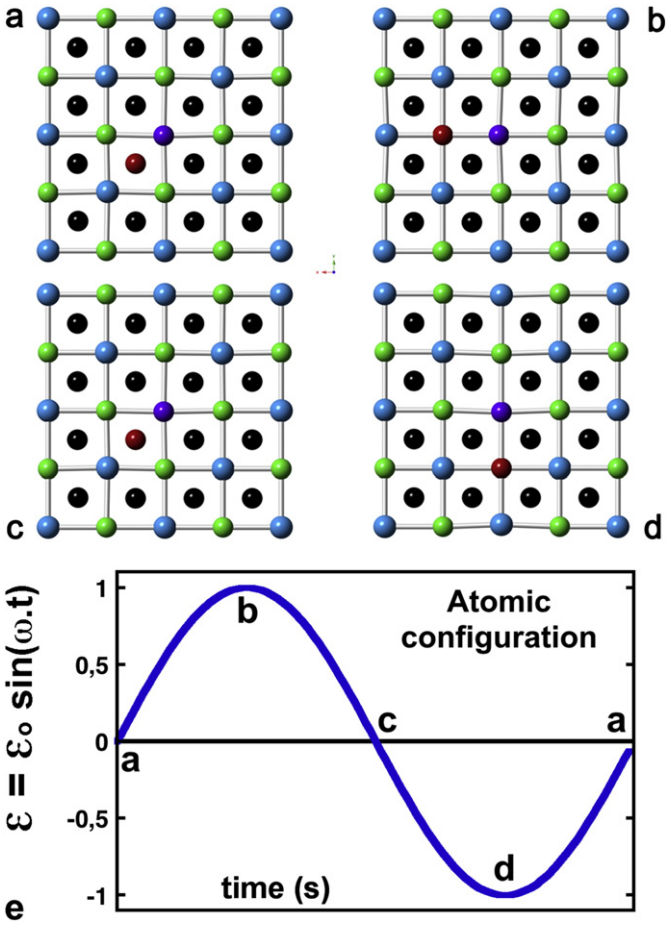

Fig. 4. Atomic lattice view parallel to the (001) plane. a) Initial configuration of the elastic dipole, Antisite-Vacancy (violet-red) on the [111] direction, in absence of stress. b) Stress-assisted reorientation of the dipole on the [001] direction when the positive oscillating stress is applied. c) Recovery to the rest position when the oscillating stress returns to zero. d) Stress-assisted dipole reorientation on the [0 − 10] direction for the negative oscillating demi-cycle. e) Correlation between the oscillating strain and the corresponding atomic configuration above described.

fraction of elastic dipoles, Antisite(β)-Vacancy(α-γ), and the mole fraction of Antisite-β is determined by the deviation of the Al concentration with respect the $D0_3$ stoichiometry. Then, for a given Al concentration and a given temperature T (vacancy concentration) the height of the Pz peak will be proportional to the mole fraction of jumping atoms in nearest-neighbour position of the dipole vacancy. So, if Be atoms were responsible for the relaxation, the height of Pz must increase with Be concentration. To verify this point, we have produced a similar single crystal from another alloy with the same Al concentration but richer in Be, Cu74.66%-Al22.6%-Be2.74% (at%). In this alloy we have also observed the Pz peak but with a much smaller strength than the one of the alloy presented in Fig. 1, as illustrated in the Supplementary material. On the contrary, it seems that a high amount of Be prevents the apparition of the relaxation, probably due to the formation of more stable triple-defects Be(γ-α)-Antisite(β)-Vacancy(α-γ). In any case, we can exclude Be atoms as the jumping species and consequently the Pz relaxation must be associated to the exchange of Cu atoms with the dipole vacancy. This means that the measured activation energy for the Pz peak, $E_a = 1.38$ eV, can be attributed to the Cu self-diffusion in the metastable austenite $D0_3$ β phase. As expected, this activation energy for self-diffusion is much lower than the one in the FCC Cu lattice, which is 2.07 eV [38]. Indeed, Al atoms produce an expansion of the FCC lattice in Cu-Al alloys, and consequently the activation energy for the elementary vacancy diffusion mechanism decreases till $E = 1.72$ eV [23]. In addition BCC lattice is less compact than the FCC, and the activation energy for diffusion is expected to be around 20% lower in BCC than in FCC lattice [38]. Then, the measured value of $E_a = 1.38$ eV, agrees with the expected percent change. Finally, we have to comment that, the obtained value for self-diffusion in $D0_3$ phase of Cu-Al-Be alloys ranges as an intermediate value of those previously reported [25,26] for β phase of Cu-Al alloys.

The above conclusion has widespread repercussions on the technology of Cu-Al-based shape memory alloys, because it can be applied to different ternary systems. Indeed, the proposed mechanism can be precursor of long-range diffusion processes, and therefore the determined activation energy $E_a = 1.38$ eV is for Cu diffusion in the metastable austenite β phase, controlling the first stages of precipitation of the stable phases in which the alloy can decompose by further heating. As commented before this is the key parameter for any further modelization of the stability of Cu-Al-based shape memory alloys in order to improve their reliability for practical applications.

This work was supported by the European H2020 Project REACT, Grant N° 640241, and the Spanish Ministry MINECO projects, MAT2012-36421 and CONSOLIDER-INGENIO 2010 CSD2009-00013, as well as by the Consolidated Research Group IT-1090-16 from the Education Department and the project ELKARTEK ACTIMAT, KK-2015/0000094, from the Industry Department of the Basque Government.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scriptamat.2016.06.034.

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