



Diffusive phenomena and pseudoelasticity in Cu–Al–Be single crystals



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ABSTRACT

Cu–Al–Be single crystals show pseudoelasticity and the shape memory effect in a well-defined composition range. The β_3 -18R martensitic transition is the origin of these phenomena. The transformation temperatures and the critical stresses to induce the martensitic transition are affected by diffusive phenomena taking place both in the parent phase and in martensite. Pseudoelastic cycles were used to obtain quantitative data concerning the effect of diffusive phenomena like stabilization of martensite, ordering of the parent phase under load and recovery of this phase on the critical stresses to transform. Information was then obtained on changes in the relative phase stability. A model is presented to explain those changes taking place in the parent phase aged under load and in the martensitic 18R structure. Experimental data on the kinetics of diffusive phenomena is also presented and analyzed.

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1. Introduction

The Cu–Al–Be system belongs to the group of shape memory alloys (SMA) which are in turn included in the group of the so called Smart Materials. Two main properties characterize SMA: the one way shape memory effect and the pseudoelasticity [1]. The first one concerns to the shape recovery when deformation in the martensite is followed by heating to the austenite. On the other hand, pseudoelasticity implies the development of a large deformation under a mechanical stress and the recovery of the original shape after unloading [2]. The physical mechanism behind these properties lies on the existence of a martensitic transformation between metastable structures [3]. As an example, the pseudoelastic effect in Cu–Al–Be alloys occurs for a well-defined range of compositions [4,5]. In this particular shape memory alloy, it is associated with a transition between a metastable $L2_1$ type structure and a slightly monoclinic one. The former can be obtained by quenching the bcc phase from high temperatures and is referred to as the parent phase or austenite (as an extension from the steel field). At high temperatures the disordered ternary alloy is bcc (or A2), while at lower temperatures first and second neighboring atoms order forming a $L2_1$ structure [6]. This ordered phase is denoted here as β_3 to distinguish it from the non-ordered

high temperature bcc phase, usually denoted as β . The monoclinic structure of the martensite can be described by a stacking of 18 compact planes in the conventional cell and is referred to as 18R [5]. Four critical temperatures are usually considered to characterize the load free transformation: M_S , M_F , A_S and A_F . The first two indicate the start and end of the forward β_3 to 18R martensitic transition upon cooling while the latter are associated with the reverse transformation to austenite upon heating [1]. The addition of Be strongly affects the transition temperatures (130 K/at.% of Be), enabling the selection of composition according to the required M_S [5].

Alternatively, the transformation can be stress induced in a reversible way above A_F . Tension loading of a β_3 phase single crystal results in a stress induced transformation to the 18R martensite upon reaching a critical stress. This transformation proceeds at an almost constant stress, developing deformations of up to 10%. In spite of a stress hysteresis during the reverse transition, the material recovers its shape on unloading. The resulting complete stress–strain curve constitutes a pseudoelastic cycle. The critical stress at which the austenite begins to transform to martensite is determined by the difference between the temperature T at which the material is loaded and the M_S temperature. Typically, a linear dependence of the critical stress with this temperature difference ($T-M_S$) is observed, which resembles the Clausius–Clapeyron relationship.

The shape memory and pseudoelastic properties have stimulated strong efforts to develop applications of these systems [7]. One idea is related to the use of these alloys to dissipate energy

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in structures subjected to dynamic events like earthquakes by using the inherent energy dissipation of the hysteresis associated with a pseudoelastic cycle [8]. In all these cases, a reasonable stability of functional parameters is desirable and strong research efforts are devoted to the characterization and improvement of material performance. It is well known that Cu-based SMA are prone to detrimental effects associated with the occurrence of atomic diffusion-related processes. Of particular relevance is the stabilization of the martensitic phase [9]. This effect is related to the change in free energy of the martensite due to a change of the atomic order with the consequent modification of the relative stability between the phases involved [10,11]. This, in turn results in a decrease of the critical stress to revert the stress induced transformation or, equivalently, in the increase of the critical temperature for the reverse transformation to the parent phase [12]. It is remarked here that the stabilization of martensite has been observed in Cu-based alloys around room temperature. Due to the diffusionless character of the transitions involved, the austenitic structure obtained from a previously stabilized martensite inherits the change of the atomic configuration produced in the martensite. Therefore, variations of the degree of order in the parent phase have to be considered. The reverse transformation of the martensite can also become more difficult by other mechanism like the interaction with linear defects (dislocations, dislocation arrays) introduced either by plastic deformation or by pseudoelastic cycling [13]. The result is the presence of retained martensite at temperatures where austenite should be the stable phase. The characterization of the extent of the stabilization effects in Cu–Al–Be alloys is of fundamental importance due to the potential use of this system in applications which require stability in martensitic transformation temperatures [14–19].

Reported experiments in Cu–Zn–Al have shown that critical stresses can also be modified if the parent phase is kept under a constant load. This reversible effect suggested that changes in the atomic order of the austenite might take place upon applying mechanical stresses [20]. Both mentioned phenomena, i.e., stabilization of martensite and changes in critical transformation stresses due to applied stresses, have been reported and deeply analyzed in Cu–Zn–Al alloys [10,20,21]. However, several works suggest that the behavior of Cu–Al–Be shape memory alloys differ from Cu–Zn–Al in some matters. Among them, it has been shown that 18R martensitic single crystals in the Cu–Al–Be system show a slight structural distortion when tensile stressed. This distortion takes place in a reversible way, and disappears with no hysteresis when the material is unloaded. Additionally, the mentioned distortion takes place at non-constant stresses which depend linearly on temperature [22]. Other differences between both metallic systems are associated to the mobility of vacancies, the mechanical behavior of the 18R martensitic phase and the dynamic properties related to pseudoelastic fatigue [19,22–25].

The dynamic behavior is particularly interesting in Cu–Al–Be single crystals. Different authors have shown that during pseudoelastic cycling, stresses to transform decrease in an inhomogeneous way suggesting a stabilization of the martensite during cycling. Moreover, every time the material retransforms to the β_3 phase, a reversion of effects occurs. This was referred to as β_3 recovery [24,25]. Therefore, the strong change in mechanical behavior during cycling will depend on the time intervals that each part of the material spends in the parent phase and in martensite, which in fact differ for the different portions of a specimen. A similar result has been also found in Cu–Zn–Al single crystals [21]. The magnitude of the effect depends on the specific system considered and, in fact, dynamic stabilization of martensite is stronger in Cu–Al–Be alloys [25].

It is clear then, that the knowledge of those mechanisms which alter critical stresses under quasistatic conditions is mandatory in

order to get a full comprehension of dynamic phenomena. In the present manuscript the attention will be focused on diffusive phenomena which take place at a concentration of vacancies as close to the equilibrium value as possible and influence the critical stresses to induce the martensitic transformation. Cu–Al–Be single crystals are to be used for this research and a wide test temperature range will be considered. Concerning the mentioned temperature range used in the present manuscript, it must be taken into account that the 18R martensite, if tensile stressed, transforms to another martensitic structure, known as 6R. This transition takes place for tensile crystallographic orientations close to $\langle 100 \rangle_{\beta_3}$, at a critical stress which has a slight negative dependence on temperature [26]. The present work analyzes diffusive phenomena both in the β_3 austenitic structure and in the 18R structure in the whole temperature range where this martensite forms under tensile stresses, avoiding the overlapping with the 18R–6R phase transition. A phase transformation diagram which clarifies the stress–temperature behavior of Cu–Al–Be single crystals of the same orientation as used here, has been recently published [26].

2. Materials and methods

Cu–Al–Be single crystals were provided by Prof. V. Torra (University of Catalonia), as 1.3 mm diameter wires of approximately 200 mm length. The nominal composition of the alloy was Cu–11.40 wt.% Al–0.53 wt.% Be (22.63 at.% Al, 3.15 at.% Be). From these crystals, specimens with 60 mm length were obtained. They were thermally treated as follows: heated up to 850 °C (1123 K), maintained at this temperature for 15 min, quenched in water at 100 °C (373 K), kept at this temperature for 60 min and finally cooled in air down to room temperature. In this way the resulting vacancy concentration is close to the equilibrium value at room temperature [22,27]. The surface of the samples was mechanically polished with fine grinding paper. Then, seven steps of electropolishing were applied in a solution of nitric acid in methanol at 9 V separated by rest periods to allow the flow down of the oxide layer. The tensile axis of the specimens in the austenitic phase was determined by X-rays using the Laue reflection method. They were all the same, being at 8° of $[100]$ towards $[110]$, (i.e., near $[710]$). Martensitic transformations were stress induced under tensile load in an Instron 5567 testing machine equipped with an Instron 3119-005 temperature chamber. Tensile tests were performed at a cross-head speed of 0.1 mm/min to disregard any thermal effect originated in the latent heat associated to the martensitic transition. An extensometer MTS 632.13F-20 with a gage length of 10 mm was used except when explicitly mentioned. The terms ϵ_e or ϵ_c will be used to indicate that the plotted deformation was obtained from the use of the extensometer or from the crosshead movement, respectively. In all experiments, test temperatures were higher than A_f , which was previously measured by electrical resistivity ($A_f=303$ K).

The main experiment consisted in partially transforming the sample up to a well-defined deformation, keeping the sample at this state during different time intervals and completing the pseudoelastic cycle. In this way different parts of the specimen were kept either in martensite or in the β_3 phase under load. When the pseudoelastic cycle is completed, the shift in the critical stress to transform the region previously kept in austenite gives information on changes of atomic order in the parent phase under load. In addition, the shift of the retransformation stress of the region previously kept in martensite enables to measure the amount of stabilization of the 18R phase. The samples which have been used are listed in Table 1, where the first letter identifies the crystal to which the sample belongs

Table 1

Samples used in the present work. First letter identifies the single crystal. The number following it identifies the specimen. σ^{β_3-18R} indicates the critical transformation stress at the reference cycle, $\Delta\sigma^{\beta_3-18R}$ indicates the amount of stabilization after holding the crosshead for 1440 min (unless specifically stated) at the mentioned test temperature. The shift in critical transformation temperatures can be obtained from the last column, considering the slope of the Clausius–Clapeyron relationship (2 MPa/K).

Sample	Test temperature [K]	σ^{β_3-18R} [MPa]	$\Delta\sigma^{\beta_3-18R}$ [MPa]
A1	333	103	2
A1	373	166	6
B2	353	125	3
B3	353	143	2
C1	373	147	5 (after 1880 min)
D1	393	189	8
D2	353	122	1
D2	393	196	11

and the number identifies the sample. Test temperatures are shown in the table, as well as the critical applied stress (σ^{β_3-18R}) to transform at the specific test temperature. The recovery of the parent phase was measured by following the evolution of consecutive pseudoelastic cycles. More details will be given in what follows when considered necessary.

3. Experimental results

3.1. Ageing in martensite or in β_3 under load

Fig. 1 shows the typical behavior at test temperatures equal to or lower than 100 °C (373 K), after partially transforming a specimen to a strain of 5% and leaving it at constant deformation under stress for 1440 min (thick blue line). Point P in the figure indicates the deformation at which loading was interrupted. After this time, the pseudoelastic cycle was completed. The initial or reference cycle (thin black line) was also plotted for comparison. The test temperature in Fig. 1 was 100 °C (373 K).

It is noticed that although some stress fluctuations are observed during the martensitic transformation, which might be considered as an imperfect plateau, the stress variations seen during the β_3 -18R transition follow the same pattern at the first and second transition. This is well detected at the whole transformation stage and can be rationalized if the transformation of the sample follows the same sequence in both consecutive transitions. The small deformation speed surely contributes to this behavior. A small decrease of approximately 2 MPa in the critical stress to transform to 18R is also observed in the second cycle when compared to the reference one. A slight stabilization effect can explain this small shift according to results obtained under dynamic conditions [25]. Additionally, a similar effect was found by Cingolani et al. [19]. These authors suggested a creation of vacancies as a possible mechanism to explain the observed shift in the critical transformation stress. This effect vanishes after ageing the austenite during a certain time interval.

It can be observed that further transforming the sample at the second pseudoelastic cycle, requires a lower critical stress for the part of the specimen kept in the parent phase, but showing similar stress features as in the reference cycle. The retransformation occurs at a stress lower than that obtained in the reference cycle. The whole sample retransforms at a similar stress level, indicating

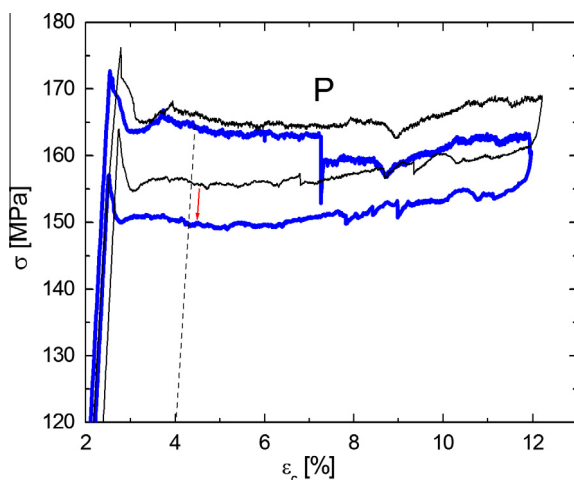


Fig. 1. Stress–strain curves obtained for sample A1 at 100 °C (373 K). Reference cycle (thin black line) and second cycle (thick blue line). The second cycle was interrupted keeping fixed the crosshead of the testing machine at point P. Deformation was obtained from the crosshead movement at the present test. The red arrow at ε_c approximately equal to 4% indicates the amount of stabilization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that two phenomena took place: the stabilization of martensite in the region already transformed to the 18R structure and a mechanism occurring in the region kept under load in the β_3 structure. The sample portions affected by these two phenomena retransform without obeying the order of appearance observed in the reference cycle, as the stress features are detected to occur in an altered sequence. The magnitude of the martensite stabilization is usually measured as the shift of the critical stress to retransform to the parent phase ($\Delta\sigma^{18R-\beta_3}$) [10]. This is highlighted in Fig. 1 by a small arrow at ε_c approximately equal to 4%, which shows the amount of stabilization. This is measured following a straight line (dashed line in Fig. 1) parallel to the elastic slope of the austenitic structure. In the present case, both the decrease in critical stress to retransform taking place in the stabilized region and the corresponding one to the region kept in austenite under load have the same magnitude. These values are rather small but well measurable. Positive values for $\Delta\sigma^{18R-\beta_3}$ are used, since the sign of the stress shift is clear in all the mentioned cases. The small shift shown by the transformation stress in the second cycle, in comparison with the reference one, does not alter the main features of the measured decrease in the critical stress to retransform to austenite. The observed decrease in stress values to retransform can be expressed as a critical temperature change (ΔT) using the Clausius–Clapeyron relationship, with a slope of 2 MPa/K, considering the tensile axis orientation [22]. Additional pseudoelastic curves after different time intervals in β_3 phase under no load enabled to observe a tendency to the recovery of the critical stresses. The shift ($\Delta\sigma^{18R-\beta_3}$) of the critical retransformation stresses changes with test temperature as can be seen in Table 1.

The just described results indicate the convenience to search a temperature at which the magnitude of the observed phenomena could be differentiated and thus better assessed in further experiments. From recent works [22,26], 120 °C (393 K) seems to be the highest reasonable test temperature to avoid overlapping between the β_3 -18R and the 18R-6R transitions, which takes place at 125 °C (398 K) for the Cu–Al–Be composition used in this manuscript. The following experiments were then performed at 120 °C (393 K).

Fig. 2a shows the result of an experiment where different time intervals are involved when the pseudoelastic cycle is interrupted and aged at intermediate deformations. A complete β_3 -18R pseudoelastic cycle considered as an initial or reference cycle is plotted (thin black line). The following cycle is performed interrupting the transformation at fixed amounts of deformation (thick blue line). These amounts of deformation will be referred to as ε_1 and ε_2 . These values, obtained with the extensometer, correspond to 39% and 71% of transformation of the 10 mm under analysis. The sample was kept an interval t_1 at ε_1 and t_2 at ε_2 , keeping fixed the crosshead of the testing machine. Finally the sample was deformed up to 100% of transformation and immediately retransformed to the parent phase down to zero stress. The pseudoelastic cycle shows then three well distinguished regions, denoted as A, B and C. Zone A represents that part of the sample which was kept in the martensitic state a time $t = t_1 + t_2$. Zone C corresponds to the part of the sample kept in the β_3 structure under load during the same time interval, and region B corresponds to the part aged in β_3 under load for a time t_1 and afterwards in martensite for a time t_2 . Concerning the test presented in Fig. 2a, $t_1 = 1254$ min and $t_2 = 208$ min, and so the first transformed region was then kept in martensite approximately for 1462 min. In fact, a short additional interval has to be added when considering the time elapsed to perform the corresponding segments of the cycle. This correction will be performed in each case.

The pseudoelastic cycle aged at intermediate deformations clearly shows now two distinct features: keeping the material in the martensitic state leads to a stabilization of the martensite while that part of the specimen kept under load at the parent phase

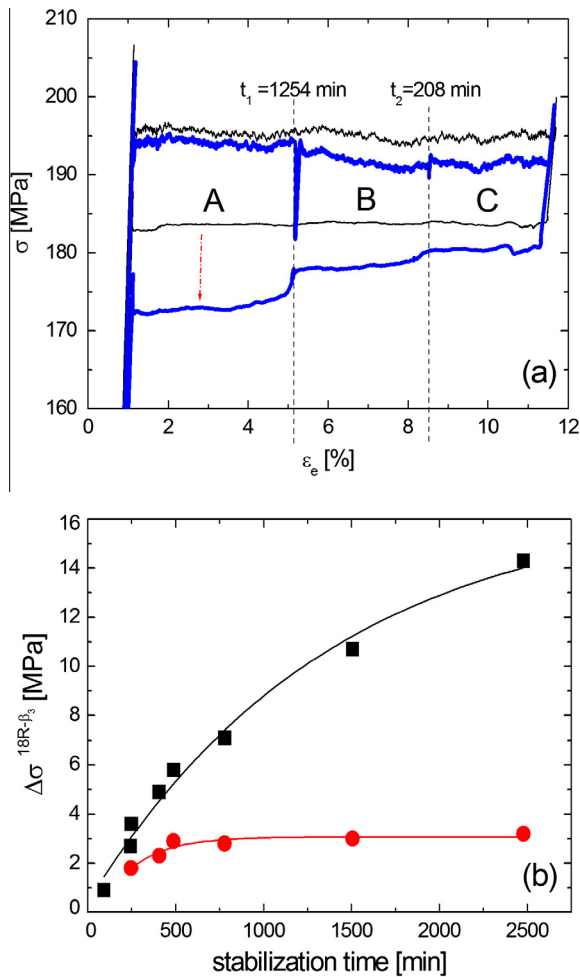


Fig. 2. Results of the stabilization test. (a) Stress–strain curves obtained for stabilization tests performed at $T = 393$ K. Sample D2 was used. A reference cycle is shown (thin black line) and the thick blue line shows the interrupted cycle. Crosshead is fixed at $\varepsilon_e = 5\%$ and 8.3% during $t_1 = 1254$ min and $t_2 = 208$ min, respectively. Regions A, B and C are indicated and commented in the text. Shifts of the critical retransformation stress corresponding to the stabilized parts of the samples and to those regions aged in the austenitic phase are visible. (b) The absolute values of stress decreases obtained from several tests are plotted. However all the shifts are negative as mentioned in the text. Squares and the associated exponential fit correspond to stabilization of martensite. Circles and associated exponential curve correspond to aging of β_3 under load. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shows a decrease of both critical transformation stresses, to transform and to retransform. A significant point is that at this test temperature, both phenomena show well distinguished magnitudes. The amount of martensite stabilization of region A reaches 11 MPa, approximately 5 K according to the Clausius–Clapeyron relationship, after 1462 min. A red arrow (dotted line) shows the magnitude of the stabilization amount in region A (see Fig. 2a). The decrease of the critical stresses in region C, after ageing β_3 during the same time interval, equals to 3 MPa. A slight difference is obtained between decreases in the critical stress to transform and the corresponding one to retransform in region C. For the sake of comparison we will consider in what follows the shift $\Delta\sigma^{18R-\beta_3}$. In case of zone B both phenomena take place sequentially, i.e., stabilization takes place after the decrease in critical stresses due to ageing in austenite under load. The amount of stabilization in zone B reaches 3 MPa. Five additional tests were performed to obtain data on the amount of $\Delta\sigma^{18R-\beta_3}$ for different time intervals of aging, either in the martensitic state or in β_3 under load. The mentioned

features are again well detected in these additional tests, which allow obtaining further data on the stress variations.

The stress shifts observed at the different conditions are plotted as a function of the corrected ageing time in Fig. 2b. Data obtained from zones B (overlapped phenomena) are introduced considering that stabilization takes place after the critical stress decreases due to ageing of the austenite under load. It is noticed from this figure that both the magnitude of the stress shift and the corresponding kinetics clearly differ if the stabilization of martensite and the ageing of the β_3 phase under load are considered. The measured decrease of $\Delta\sigma^{18R-\beta_3}$ due to ageing the austenite at 120°C (393 K) and constant load is rather small when compared with the decrease due to stabilization for time intervals larger than 1000 min. However, the effect is easily measurable and in fact an evolution with time can be well determined. A fit of the data using an exponential function gives a time constant equal to 1200 min for the kinetics of stabilization at 120°C (393 K). Additionally, a time constant equal to 270 min and an asymptotic value approximately equal to 3.1 MPa were obtained in the case of keeping the β_3 phase under load.

It is interesting to notice that the characterized phenomena are also observable at lower temperatures. However a significant point, like the difference of magnitude of the critical stresses to retransform obtained by stabilization or by keeping the material in β_3 under load, is clearly detected only at a temperature of 120°C (393 K). The difference in kinetics of both phenomena is also noticeable at this temperature. Moreover the complete recovery to the reference state can be clearly observed at this test temperature, as it is commented below.

3.2. Recovery of β_3 in a load free state

After completing the stabilization tests, the recovery of the β_3 phase was analyzed by performing additional cycles. As an example, the results of the recovery stage corresponding to the test presented in Fig. 2a are presented in Fig. 3. To help the eye, the σ – ε curve corresponding to the stabilization test is also shown in the

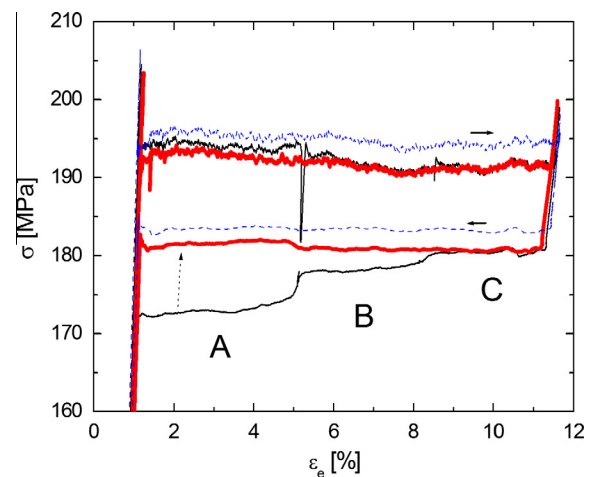


Fig. 3. Stress–strain curves obtained after the stabilization test of Fig. 2a. The unloading curve obtained after the interrupted test is also shown as a thin black line. The σ – ε cycle immediately obtained after the interrupted test is plotted as a thick red line. A small arrow indicates the recovery of the β_3 phase in region A. The retransformation of the interrupted test and of the following cycle exactly overlap in region C. The dashed blue line corresponds to the transformation obtained 717 min after the interrupted test which thoroughly overlaps the reference cycle (not shown here), indicating complete recovery. Small arrows to the right and left are shown just above the transformation and retransformation in the last mentioned cycle to indicate the direction for travelling the pseudoelastic cycle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

same figure (thin black line). Regions A, B and C are shown following the same criteria as in Fig. 2a. The first complete pseudoelastic cycle after the aged one is plotted in Fig. 3 as a thick red line. It becomes evident that the stresses tend to recover the values of the reference cycles. The amount of recovery R can be determined by the measurement of the ratio between the increase of the retransformation stress ($\Delta\sigma_r$) and the measured stress decrease during ageing in the interrupted test: $R [\%] = 100 \times (\Delta\sigma_r / \Delta\sigma^{18R-\beta_3})$. A small arrow parallel to the elastic slope indicates the recovery of part A obtained at the first subsequent pseudoelastic cycle (after 6 min ageing in austenite). The decrease of the critical stress to retransform is also taken here as a positive value, so $R > 0$.

The obtained cycle (thick red line in Fig. 3) shows that the kinetics of recovery of the β_3 phase is clearly different in the region previously stabilized in martensite, where approximately $R = 70\%$ is obtained, while in the portion kept in austenite under load no recovery is observed. This is noticed if region C is observed in the graph. Both retransformation curves in this region, the corresponding to the stabilization test and to the following cycle in the recovery stage, nearly overlap, leading to $R = 0$ for this short time of recovery. This interesting finding indicates that the recovery of the austenitic structure is related to a different route if it is obtained from a stabilized martensite or from the same austenitic structure under load. A further cycle, obtained after 717 min in β_3 at the unloaded condition, shows a complete recovery of this structure and the stress–strain curve overlaps the initial (reference) cycle. In Fig. 3, due to the overlapping of the completed recovered behavior and the reference state, only one of the corresponding curves is plotted by a dashed blue line. Small arrows to the right for the transformation and to the left for the retransformation are shown just above this σ – ε cycle to call the attention on the well-defined reference cycle. The complete recovery of the austenite within the resolution of the present experiments has been obtained in additional tests performed at the same test temperature, after previous ageing under load during different time intervals. This fact is a relevant point and clearly indicates the following: (i) no precipitation phenomena takes place at this temperature in the considered time intervals, (ii) a well-defined reference state does exist which supports the hypothesis concerning the equilibrium amount of vacancies at the start of the tests, and (iii) both phenomena, the one taking place in martensite and the mechanism occurring in the parent phase under load are diffusive and reversible.

The rapid recovery of β_3 when previously stabilized in martensite, compelled to obtain data after shorter time intervals. In order to do this, an additional experiment was carried out where, after stabilization during 2468 min, short cycles were performed by unloading down to a stress slightly lower than $\sigma^{18R-\beta_3}$ and then stress inducing a small amount of martensite. In this way data for the recovery after shorter time intervals can be obtained. The recovery R after martensite stabilization is plotted in Fig. 4. An exponential fit gives a time constant equal to 40 min.

4. Discussion

4.1. Analysis of the experimental results

The results obtained so far give information of diffusive phenomena taking place in the Cu–Al–Be system at a low concentration of vacancies. A direct consequence of the diffusive phenomena taking place both in martensite and in austenite is related with a shift in martensitic transformation temperatures. The low concentration of vacancies, which can be considered close to the equilibrium one, enables to disregard effects from the evolution of concentration of vacancies on the critical stresses which have been reported in the literature [23,27,28]. In the mentioned references, the authors have shown that after quenching Cu–Al–

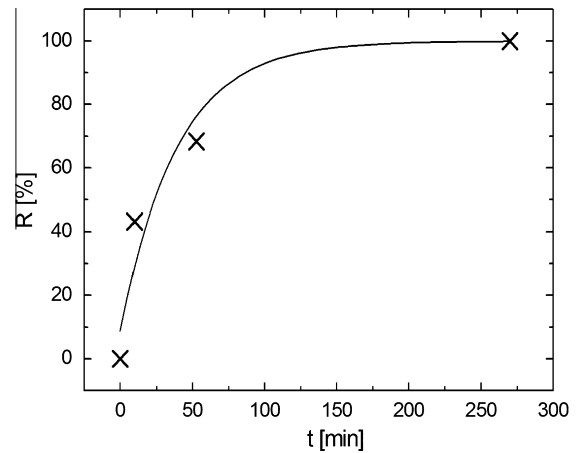


Fig. 4. Ratio of recovery R (increase of critical stresses to retransform/decrease of stresses to retransform at interrupted tests) vs. the ageing time of β_3 , for the sample previously stabilized in martensite 2468 min. Data was obtained from sample D2. A time constant equal to 40 min is obtained.

Be alloys, a shift in M_s is measured and the kinetics of this evolution follows a similar curve vs. time as the change in concentration of vacancies measured by positron annihilation. This fact, in addition to measurements by neutron diffraction which did not detect further changes in the degree of order, led those authors to consider that variations in M_s after the quench are not due to a change of quenched disorder of the bcc structure. In fact, in the mentioned papers, the authors considered that the change in concentration of vacancies might be associated with a variation of Be concentration, which would originate a shift in the martensitic transformation temperatures. This change of transformation temperature is not a recoverable process since the concentration of vacancies evolves in an irreversible way as far as thermodynamic coordinates, like temperature, do not change. Shifts in critical stresses to induce the martensitic transformation obtained in the present work after aging treatments under load, cannot then be explained by changes in the concentration of vacancies since this concentration is very small and a recovery of the critical transformation stresses is obtained after ageing at the same temperature.

A result which might in fact be related with the presence of vacancies is the slight serrated morphology of the stress strain curve during the β_3 –18R transformation, which has been observed in all the tests performed at the reference condition and different test temperatures. This phenomenon, which is not observed after a sufficient number of cycles or during retransformation from 18R to the β_3 structure, even during the start of cycling, has been shown to exist by Gonzalez et al. [16] in single crystals. These authors show in their reported experiments a considerably stronger effect, which they explain by an interaction between the β_3 –18R interface and vacancies which introduce some kind of pinning during transformation. The strong effect in magnitude they report, as compared to the serration in the curves observed in the present work, can be understood by the difference in thermal treatments which leave in their samples a higher concentration of vacancies.

The present results show the existence of three well defined diffusive phenomena in the Cu–Al–Be system, one in the martensitic phase and the other two taking place in the β_3 structure. Stabilization of martensite takes place after keeping the material in this phase. The stabilization of martensite in Cu based alloys has been analyzed by a large amount of authors and leads to an increase of the critical temperatures or the equivalent decrease in $\sigma^{18R-\beta_3}$. As an example, Dunne et al. [15] analyzed the effect of different thermal treatments on Cu–Al–Be alloys, in a polycrystalline state and also in single crystals. It is noticeable that two different stabilization effects have been reported, a normal stabilization

effect (NSE) and a hyper stabilization effect (HSE), which shifts A_5 to a considerably higher temperature range. The HSE needs a rapid quench through M_5 and different mechanisms have been suggested to explain it. As an example, in reference [15] the authors consider that Be has a retarding effect on the ordering during the quench. A different approach has been considered to explain the NSE, which has been explained in the same work by a pinning effect caused by vacancies. In the mentioned paper however normal stabilization is obtained also after quenching, leaving a high amount of vacancies.

In the present paper, it is shown that martensitic stabilization takes place at temperatures quite close to room temperature with a concentration of vacancies close or equal to the equilibrium one. The effect is rather small although clearly measurable after keeping the sample in the stress induced martensitic state at temperatures equal or above 333 K. The decrease of $\sigma^{18R-\beta_3}$ enabled to obtain a quantitative information on the magnitude of stabilization which reached amounts of 5 K after ageing times of 1440 min and 7 K after 2468 min at 393 K. Notwithstanding, Fig. 2b shows that this is not the asymptotic stabilization value attainable at the highest temperature. Although the diffusive character of this process is clear, no model exists till the moment which could explain the type of atomic movements that take place in the martensite. An interesting point is that pseudoelastic cycling through the β_3 -18R transformation leads to a strong dynamic stabilization also, if the original concentration of vacancies is close to the equilibrium value [24,25,29]. Tidu et al. measured by X-ray analysis a recoverable strain change after pseudoelastic cycling, leading to an orthorhombic distortion of the parent structure. Considering that the evolution of stress–strain curves during this type of cycling at temperatures higher than room temperature can be well explained by a sequence of martensite stabilization and austenite recovery, the distortion they measured can be considered as a structural change taking place during martensitic stabilization, which is inherited by the austenitic structure after retransformation. In fact, they measured the strain tensor after cycling, showing that a distortion takes place which enlarges the lattice in the $[100]_{\beta}$ direction, parallel to the tensile one, distorting the cubic cell. This effect is obtained by the authors after keeping a sample in martensite under stress during 24 h at 348 K, obtaining nearly the same lattice distortion as after performing 50 pseudoelastic cycles. Tidu et al. consider that diffusion in martensite takes place towards a structure named β'_x observed in Cu–Al near Cu_3Al composition [29], a long period superlattice formed by the introduction of anti-phase boundaries. This is not demonstrated up to now and the knowledge of the atomic movements able to explain this mechanism in martensite is still required. Additionally, the final structure the martensite might reach if diffusion allows a minimization of its free energy, is also unknown. On the other hand, a structural distortion taking place during stabilization of martensite indicates that an atomic reordering, not known in detail, could explain this phenomenon. As a complementary data, the measured orthorhombic distortion measured by Tidu et al. decreases after ageing 60 min at 403 K from $\Delta\varepsilon (\times 10^{-2}) = 0.651$ down to $\Delta\varepsilon (\times 10^{-2}) = 0.103$, indicating a clearly recoverable behavior. The results in the present work indicate that a complete recovery after stabilization can also be obtained at a temperature even smaller (i.e., 393 K).

The same type of experiment, which enabled to analyze the presence of martensitic stabilization in case of using interrupted pseudoelastic cycles, gives also information on the diffusive mechanism taking place in β_3 when it is kept under load. Results shown in the present work clearly indicate that the critical stresses to induce martensite decrease when β_3 was previously aged under stress. The amount of this decrease is of the same order of magnitude as the decrease due to stabilization of martensite, if the test temperature is below 373 K. At higher temperatures, decreases

due to stabilization of martensite become larger. However, the observed effect in the region aged in austenite under stress is noticeable. Additionally, after unloading the β_3 structure, the initial (reference) critical stress is recovered after a certain time interval. This strongly suggests that the effect is also diffusive. This phenomenon, not deeply analyzed up to the moment in Cu–Al–Be alloys, has in fact been reported for Cu–Zn–Al single crystals [10,20,21]. It has been found that the application of an external constant stress during the ageing of β_3 phase in Cu–Zn–Al single crystals decreases reversibly the stability of the parent phase with respect to the martensite. It has been also shown that it is due to the reordering of Zn and Al atom pairs, due to their larger atomic sizes [20].

Finally, after either stabilization of martensite or ageing under load in β_3 , a recovery of the parent phase takes place if the material is unloaded and left enough time in this structure. Each of the mentioned phenomena has its own kinetics. In fact, it is noticeable that recovery of the austenite, previously transformed and stabilized in martensite, starts immediately after unloading the sample, while some time is required to detect a recovery in the β_3 previously aged under load. A relevant point which was shown here is the existence of a well-defined reference cycle. This has been clearly determined after recovery of the β_3 phase, which leads to a precise overlapping of the stress–strain curves between the recovered cycle and the initial one. From the analysis of reported results in the literature, it follows that a further comprehension of the mechanisms responsible for the mentioned effects is necessary. In the following section of this discussion, a model is presented to rationalize each of the observed phenomena that take place when ageing.

4.2. Development of a mean field model

In order to rationalize the obtained results a mean field model is presented. It will allow to calculate the free energy variations that are produced in the austenite and in the martensite by specific atom interchanges. To this end, expressions to calculate the enthalpy and entropy of arbitrary atom configurations have to be proposed. This will be done next.

Long-range order in Cu-based alloys can be described by subdividing the high temperature bcc lattice into four interpenetrating fcc sublattices, denoted by the index $J = I$ to IV , (see Fig. 5).

In the simplest approximation the occupation probability P_A^J of an atom A on sublattice J is independent of the site in the J -sublattice. The degree of order does not depend on the heat treatment in Cu–Al–Be [23]. Only the vacancy concentration can be altered, that in turn manifests in variations of the transformation temperatures. It is assumed that the crystals, have a perfect long-range ordering

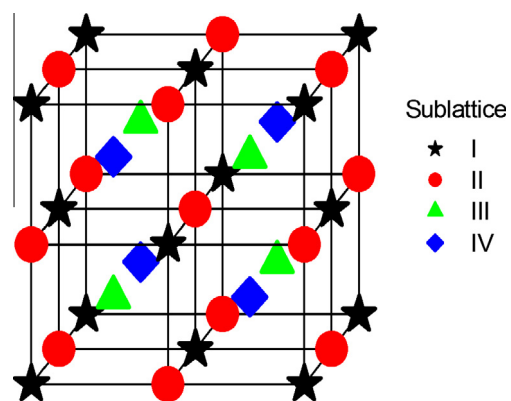


Fig. 5. A cube of $2 \times 2 \times 2$ bcc cells in which the four fcc sublattices are defined. The cell parameter of each fcc is twice the size of the one of bcc.

prior to the martensitic transformation and that they possess the equilibrium vacancy concentration. This is an approximation, because at the finite temperature at which the experiments are performed, some equilibrium disorder exists. Furthermore, diffusion is necessary to reach this state, but if it becomes too sluggish, the equilibrium state may not be reached. The assumption of a perfect order permits to relate the occupation probabilities and order parameters to the concentration C_A in atomic fraction of element A. The following equations hold

$$\begin{aligned} P_{\text{Cu}}^I + P_{\text{Al}}^I + P_{\text{Be}}^I &= 1 \\ P_A^I + P_A^{II} + P_A^{III} + P_A^{IV} &= 4C_A \end{aligned} \quad (1)$$

For a quantitative description of the ordering phenomena, it has been found necessary to have reliable pair interchange energies (PIE), extending to nearest and next nearest neighbors [6]. They are defined as the difference between the interaction energies $V_{AA}^{(i)}$ and $V_{BB}^{(i)}$ of A–A and B–B pairs, respectively, compared to $V_{AB}^{(i)}$ between A and B pairs in i -th neighbor position. The PIE for the β_3 phase are denoted as $W_{AB}^{(i)}$ and are given by $W_{AB}^{(i)} = -2V_{AB}^{(i)} + V_{AA}^{(i)} + V_{BB}^{(i)}$. They are positive when ordering is favorable. The energy of the lattice can be obtained by multiplying the pair site occupation probabilities by the corresponding PIE, then summing over all pairs and finally normalizing per atom. After doing these calculations, two contributions can be clearly distinguished, a constant value which depends only on the concentration of the alloy, and another one which is a function of $N_{AB}^{(i)}$, the number of A–B atom pairs in i -th neighbor position. Only the latter term has to be considered, together with the corresponding entropy, when analyzing phenomena that alter the degree of order. The contribution to the energy in the austenite is then given by

$$\begin{aligned} E_{\text{AUS}} = -\frac{1}{4N} & \left[N_{\text{CuAl}}^{(1)} W_{\text{CuAl}}^{(1)} + N_{\text{CuBe}}^{(1)} W_{\text{CuBe}}^{(1)} + N_{\text{AlBe}}^{(1)} W_{\text{AlBe}}^{(1)} + N_{\text{CuAl}}^{(2)} W_{\text{CuAl}}^{(2)} \right. \\ & \left. + N_{\text{CuBe}}^{(2)} W_{\text{CuBe}}^{(2)} + N_{\text{AlBe}}^{(2)} W_{\text{AlBe}}^{(2)} \right] \end{aligned} \quad (2)$$

being N the total number of atoms. A similar expression holds for the martensite. In this case the $W_{AB}^{(i)}$ must be replaced by $m_{AB}^{(i)}$, the pair interchange energies that correspond to the martensite, and the number of atom pairs has to be recalculated, because the number of neighbors is different. The pair interchange energies of the β_3 phase have been assessed recently using the model presented here [6], being

$$\begin{aligned} W_{\text{CuAl}}^{(1)} &= 1210 \text{ K} & W_{\text{CuAl}}^{(2)} &= 900 \text{ K} \\ W_{\text{CuBe}}^{(1)} &= 635 \text{ K} & W_{\text{CuBe}}^{(2)} &= 125 \text{ K} \\ W_{\text{AlBe}}^{(1)} &= -85 \text{ K} & W_{\text{AlBe}}^{(2)} &= 330 \text{ K} \end{aligned} \quad (3)$$

To have the pair interchange energies in units of J/mol, the previous values have to be multiplied by the Boltzmann constant. On the other hand, the PIE of the martensite, necessary to do the evaluation of the relative stability of the phases, are not available in the literature and must be deduced.

It has been proposed that the PIE are a function of the distance between the atoms [30]. As the two structures are related by a martensitic transformation, it is possible to express these distances in units of the lattice constant a_β of the austenite. Then, first and second neighbors in the β_3 phase are in positions 0.866 and 1, respectively, whereas in the martensite they fall at 0.891 and 1.260. So, a rough estimate of the PIE in the martensite can be made. To this end, the first neighbor values of the martensite were linearly interpolated using the PIE of the austenite. Whereas, the second neighbors values of the martensite were obtained using the relation

$$4W_{\text{AB}}^{(1)} + 3W_{\text{AB}}^{(2)} = 6m_{\text{AB}}^{(1)} + 3m_{\text{AB}}^{(2)} \quad (4)$$

proposed in [30]. These calculations result in

$$\begin{aligned} m_{\text{CuAl}}^{(1)} &= 1150 \text{ K} & m_{\text{CuAl}}^{(2)} &= 215 \text{ K} \\ m_{\text{CuBe}}^{(1)} &= 540 \text{ K} & m_{\text{CuBe}}^{(2)} &= -110 \text{ K} \\ m_{\text{AlBe}}^{(1)} &= -10 \text{ K} & m_{\text{AlBe}}^{(2)} &= 235 \text{ K} \end{aligned} \quad (5)$$

Similar to what was done in [20], a computer program was used to count the number of first and second neighbor pairs of each kind (CuAl, CuBe and AlBe) in the β_3 phase and in the martensite, and the configurational part of the energy was calculated as explained previously. To obtain the free energy variation that will allow the analysis of the relative stability of the phases, the corresponding changes in configurational entropy had to be calculated. This has been performed using the entropy expressions from the cluster variation method. For the β_3 phase the basic cluster was an irregular tetrahedron as presented in [6]. In the case of the martensite, the tetrahedron approximation of the fcc lattice was applied for each of the sublattices, following [31].

4.3. Simulation of atom interchanges and calculation of free energies

Once the variation of the free energy can be calculated, the task is to find out atom interchanges between neighboring atoms that alter the relative phase stability according to what was determined from the experiments. In Cu–Al–Be the atom sizes decrease from Al (1.43 Å) to Cu (1.28 Å) to Be (1.12 Å), and as a first approximation only the rearrangements between Cu and Be atoms will be considered. In this way, the thicker Al atoms are assumed to stay at their initial sites. A computer program was used to simulate the real distribution in the initial ordered state, in a sample of $60 \times 60 \times 60 \beta_3$ phase unit cells, i.e., 3.456×10^6 atoms. This configuration constitutes the reference state. Then, particular atom interchanges were postulated, a certain number of jumps were performed and the resulting free energy change of both phases was evaluated. In this way, it was possible to detect the effect of the different interchanges as also of possible interferences between them.

4.3.1. Martensite stabilization

In Cu–Zn–Al alloys the martensite stabilizes by reducing its free energy through the interchange of neighboring Cu and Zn atoms. In the case of Cu–Al–Be, the equivalent first neighboring CuBe pair interchange has demonstrated to be also effective in stabilizing the martensite. This is exemplified in Fig. 6. The initial ordered state of the β_3 phase is shown in Fig. 6a. The configuration after the atom interchange that favors the stability of the martensite is schematized in Fig. 6b. The change of the free energy of the phases as a function of the number of first neighbor CuBe interchanges is shown in Fig. 6c. The minimum is reached when sublattice IV is nearly free of Be atoms. This arrangement approaches a distribution that would correspond to DO_3 order in the austenite. In this state, the stabilization is enormous, exceeding 800 MPa.

Notwithstanding, it has to be noted that this configuration has to be reached by atom diffusion through a vacancy mechanism, but respecting the ordered structure. This means that not all the jump alternatives are possible, hindering the kinetics of the process and limiting the final energy gain that the system could obtain.

4.3.2. Ageing β_3 under load

In this case it is necessary to find out an atom configuration that, being stable in the β_3 phase, becomes unstable when the stress is applied. It can be associated with an increase of the elastic internal energy, which favors the atom redistribution to relieve the stressed configuration, changing the relative stability of the phases and decreasing the transformation stress. One such configuration is shown in Fig. 7a. It consists of a Cu atom in sublattice III (open magenta circle), surrounded by four coplanar Al atoms in second

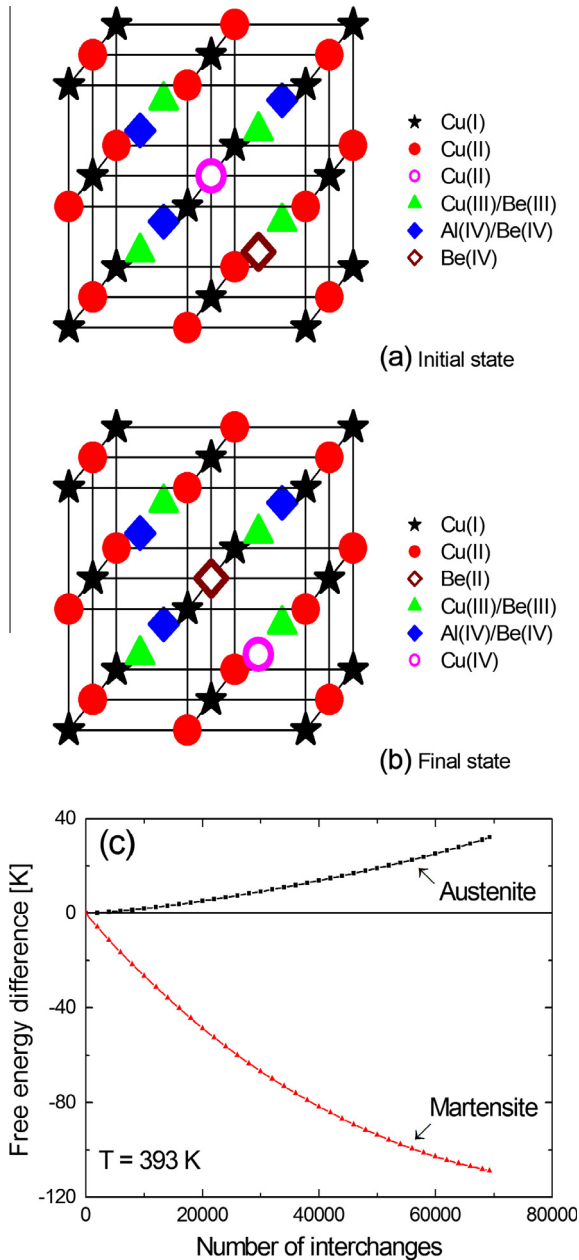


Fig. 6. (a) The initial atom configuration corresponding to $L2_1$ order. (b) The distribution that results after an interchange of a Cu from sublattice II with a Be from sublattice IV. (c) Evolution of the free energy as a function of the first neighbor CuBe atom pair interchanges.

neighboring positions in sublattice IV. They are in one of the $\{100\}$ β_3 planes, that whose normal is nearest to the tensile axis. On applying the stress, the Al atoms will tend to get closer to the Cu atom, creating a compressed region. It is possible then to think that it would be convenient for the system to locate a Be instead of the Cu atom to relieve the compressive stresses. This process is schematized in Fig. 7b, after the interchange of a Cu from sublattice III with a Be from sublattice IV. It has been found that many interchanges of this kind are possible, i.e., there are abundant sets of Cu atoms surrounded by four Al and with a Be in second neighbor position near to the tensile axis. In Fig. 7c is shown the behavior of the free energy of the phases. It can be seen that the interchanges are possible, because they do not increase the energy of the β_3 phase in an exaggerated manner. The shift of the transformation stress which is predicted by ageing the austenite under

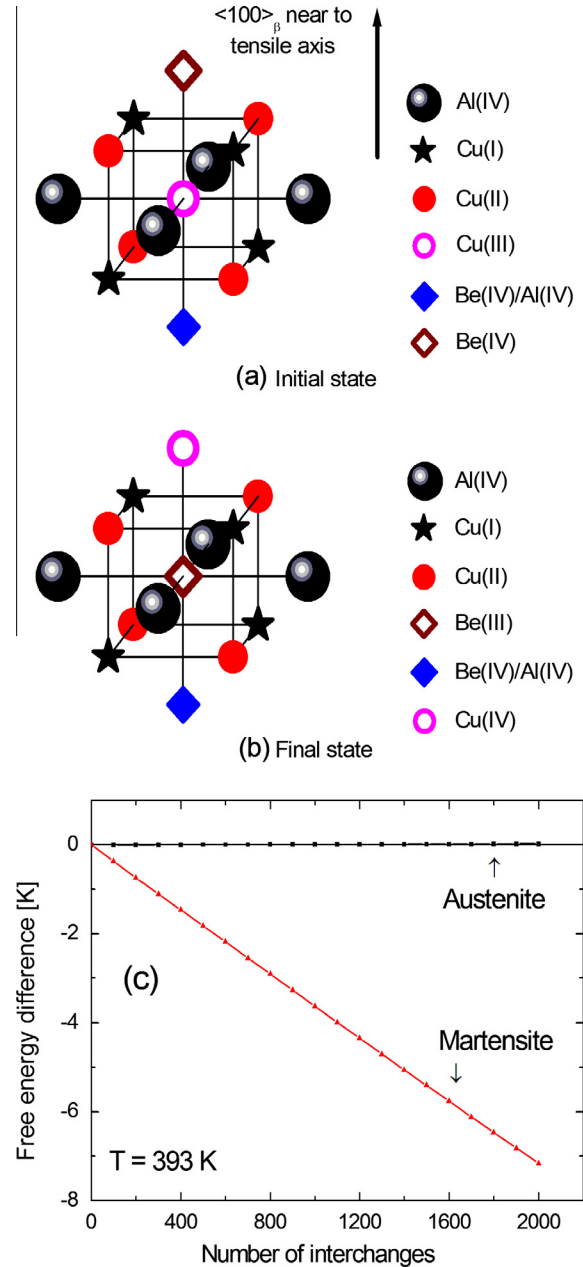


Fig. 7. (a) Specific arrangement of four Al surrounding a Cu atom in a $\{100\}$ β_3 plane. When a tensile load is applied to the sample along a direction near to the plane normal, the distance between the Cu and each Al is reduced and elastic energy is increased. (b) The interchange of the compressed Cu atom in (a) with a Be in second neighbor position relaxes the stressed configuration. (c) Evolution of the free energy as a function of the second neighbor CuBe atom pair interchanges.

load exceeds the measured values. Again, kinetic arguments have to be applied to limit the number of atom interchanges that are performed. According to the values in Fig. 7c, 300 interchanges are enough to reproduce the measurements.

4.3.3. On the recovery of the β_3 phase

Finally, it has been shown that either after retransformation from the stabilized martensite to β_3 or by unloading the β_3 previously kept under load, a recovery mechanism takes place. This recovery leads to a state which, within the resolution of the present experiments, does not differ from the reference state of the austenitic structure. However, experimental results have been presented showing different kinetics of recovery of the β_3 structure

depending on the previous state of the material: stabilized martensite or austenite under load. The latter shows a slower kinetics that can be rationalized considering the proposed model for atomic pair interchanges: stabilization of martensite is explained by pair interchange between first neighbors, while a pair interchange between second neighbors is required to explain the free energy decrease after keeping the austenite under load. The reverse mechanism will require then more time to recover the original order if the austenite has to recover from second neighbor interchanges.

5. Conclusions

Diffusive mechanisms occurring under load were analyzed in Cu–Al–Be single crystals at a concentration of vacancies close to the equilibrium one. The main conclusions are:

- (i) Stabilization of tensile induced martensite was detected for a large range of temperatures.
- (ii) A decrease of critical stresses to induce martensite was obtained after keeping the austenite under load.
- (iii) Both effects show a similar magnitude for temperatures smaller than 373 K but clearly differ from each other at 393 K.
- (iv) The decrease of critical stresses is due to diffusive and reversible phenomena. It can be explained by the free energy variation of the involved structures, when considering the interchange between Cu and Be atoms.
- (v) First neighbor interchanges of atoms enabled to rationalize the stabilization of martensite, while second neighbor interchanges explain the effect of keeping the austenite under load.
- (vi) The proposed model also allowed rationalizing different kinetics for the recovery of the austenite.

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