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Pseudoelastic cycling in Cu-Al-Be single crystals: Interaction with diffusive phenomena

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Abstract. CuAlBe alloys exhibit martensitic transformations and several properties related to this transformation such as the shape memory effect, pseudoelasticity and the two way shape memory effect. In this work results concerning pseudoelastic cycling of CuAlBe single crystals are presented and discussed. Particularly noticeable is the strong effect of diffusive phenomena on the stress strain curves obtained at test temperatures between 333 K and 373 K. In effect, a stronger stabilization of the martensite is observed during cycling as compared with the stabilization effect upon static conditions, which was found to be negligible at the same test temperatures. Results also indicate that the recovery of the austenitic phase plays a significant role during cycling. The generation of vacancies and the increase in their mobility have been considered in order to explain the observed behavior.

1. Introduction

CuAlBe alloys show a martensitic transformation between an austenitic bcc structure (β) and an 18R martensitic structure [1]. This transformation can be induced either thermally or mechanically. In the latter case, the retransformation takes place after unloading, i.e. the pseudoelastic effect. The effect of pseudoelastic cycling on the martensitic transition will depend on the metallic system and on the thermodynamic coordinates of the mechanical test. As an example, CuAlNi alloys do not show significant effects on the stress strain curves corresponding to the β-18R transition up to 2700 cycles, although dislocations bands formation are detected earlier, after only 460 cycles [2]. CuZnAl alloys, on the other hand, show quite different behaviour. Depending on the alloy composition and working temperature, the evolution of stress-strain curves on cycling will be quite different. At temperatures higher than room temperature, critical stresses to transform decrease upon cycling and original values recover after aging of the β phase at the same temperature [3; 4]. This last effect could be explained taking into consideration two well known diffusion related phenomena in Cu-Zn-Al shape memory alloys: the stabilization of the martensite and the recovery of the β phase [5]. An additional interesting result concerning both mechanisms is that the kinetics of both processes, the stabilization of martensite and the β recovery, do change after cycling. As an example of this, the stabilization can be hardly observed after cycling at 333 K while before cycling, several degrees of stabilization can be measured at the equilibrium concentration of vacancies [5]. Moreover, the changes in the critical stresses to transform for CuZnAl single crystals could be

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modeled by considering the interplay of the mentioned processes and taking into account the time each volume element of the material spends in either phase in a single cycle. In order to get a reasonable fit between the data and the modeling it was necessary to consider an easier stabilization during cycling if compared with the stabilization kinetics measured under static conditions before cycling.

Results concerning pseudoelastic fatigue effects on CuAlBe single crystals have been reported elsewhere [6]. These authors have found a strong increase in the slope of the σ-ε curve corresponding to the stress induced martensitic transformation. This change was explained considering a decrease of the critical stresses activated by diffusion. In this case, authors had identified two competing mechanisms as responsible for the observed behaviour, one related to stabilization of martensite and a reordering of the β, similar to what was considered for CuZnAl crystals.

The β phase in CuAlBe shows a first order transition from BCC to DO_3 which should make it difficult to keep disorder after quenching [7]. Additionally, the changes in the Ms temperatures which are obtained after quenching the β phase have been explained considering the retained vacancies and their evolution to equilibrium [7].These authors considered that the variation in the amount of vacancies induce a change in the concentration of Be with a corresponding change in Ms.

An interesting point here is that the reported experiments concerning pseudoelastic cycling performed by Siredey et al. [6] started with a concentration of vacancies equal or close to the equilibrium one, which leave it open the questions about the physical mechanisms responsible for the variations obtained after cycling. Tidu et al. have reported a change in the deformation of the β phase just after pseudoelastic cycling [8]. This lattice distortion was considered by the authors as a consequence of a structural change of martensite which might take place during pseudoelastic cycling.

The mechanical evolution of CuAlBe single crystals during cycling, although with similarities to those found in CuZnAl single crystals, still presents open questions concerning the origin of the involved phenomena, particularly about those diffusive phenomena which play the main role under dynamic conditions. The present work focuses on those mechanisms which determine the evolution of stress strain curves during pseudoelastic cycling, like the stabilization of the martensite and the recovery of the austenite, under static conditions as well as on the dynamic aspects of the rapid cycling.

2. Experimental methods

The nominal compositions of the used alloys is Cu-11.4 wt % al-0.53 wt% Be. The single crystals of CuAlBe were provided by Nimesis (Metz, France) being cylinders of diameter equal to 1.26 mm and variable lengths between 150 and 200 mm. The single crystals were treated 15 min at 1073 K and quenched in water at room temperature. After that, the crystals were aged during 2 months at 373 K followed by air cooling down to room temperature unless otherwise stated. Samples of 10 mm length were obtained in order to measure martensitic transformation temperatures by electrical resistance methods and samples of 50 mm length to perform mechanical tests. The 4 point method was used to perform the electrical resistance measurements. The surface of the samples prepared for mechanical tests were mechanically and electrolitically polished in a solution of nitric acid in methyl alcohol at a voltage equal to 9 V. Mechanical tests were performed in an Instron electromechanical testing machine model 5567 in a temperature chamber. Optical and transmission electron microscopy observations were performed after pseudoelastic cycling.

3. Experimental results

Fig. 1 shows the electrical resistance vs. temperature for sample cabsc1m1. In order to check the critical transformation stresses and select the test temperature, the Clausius-Clapeyron relationship was obtained for sample cabsc1m3. A slope of 2 MPa/K was obtained for this sample as it is shown in figure 2. Several samples

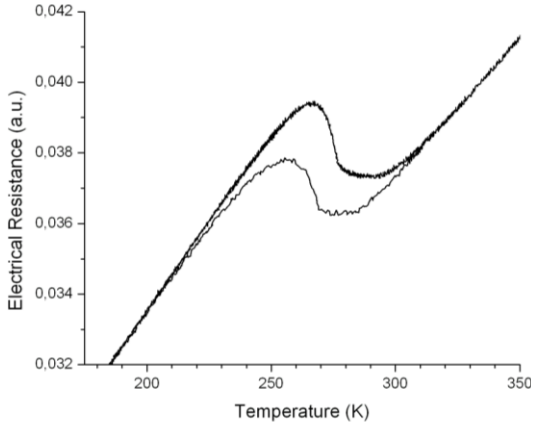


Fig. 1. Electrical resistivity measurement of sample cabsc1m2. Obtained transformation temperatures: M_s=285.8 K, M_f = 227.3 K, A_s=262.5 K, A_f= 314 K. TT of the sample: 15 min at 1123 K, water quench (room temperature) and 2 months at 373 K

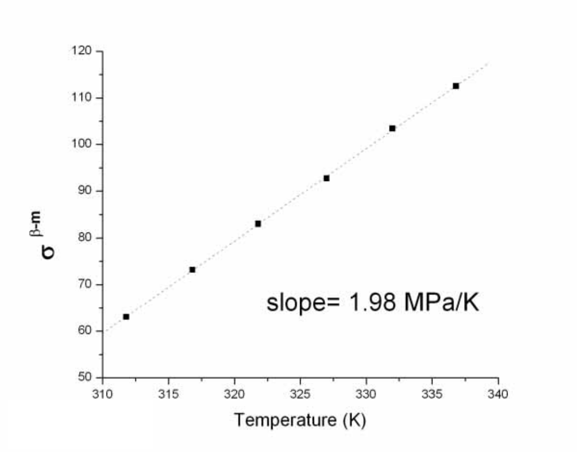


Fig. 2. Critical stress to transform from β to martensite as a function of temperature for sample cabsc1m3. Obtained slope of the Clausius-Clapeyron relationship 1.98 MPa/K.

were pseudoelastically cycled at constant temperature. At each test temperature and before performing the pseudoelastic cycling, experiments were carried out to measure the static stabilization of the martensite. The same method used by Abu Arab et al. for CuZnAl single crystals was used here [9]: the samples were loaded up to a partial transformation of the sample and the obtained deformation was kept constant during 24 h being the sample further transformed and unloaded after this. In this way the decrease in the stress to retransform of that portion of the sample retained in martensite compared to the value obtained before this test was considered as the quantitative amount of the stabilization. This stabilization will be referred from now on as static stabilization in order to distinguish it from a dynamic stabilization effect occurring upon cycling. It should be kept in mind that these stabilization tests are performed under conditions close to the equilibrium amount of vacancies in the material. This type of experiment was performed twice for sample cabsc1m3 at T = 333K and once for the same sample at a test temperature = 373 K. In the first two experiments a stabilization amount of 4 and 1.6 MPa was measured and 6 MPa was obtained at 373 K. The lattest corresponds to 3K considering the Clausius-Clapeyron relationship. Figure 3 shows the result obtained at T= 373 K where it is noticeable that the measured effect is small. An additional stabilization test performed with sample cabsc3m2 at 373 K gave an amount of stabilization corresponding to 2.6 K close to the amount found for sample cabsc1m3 at the same temperature. A decrease in the critical stress to transform of the region which was kept in β phase under load was also observed. The amount of the obtained decrease was detected for those stabilitazion tests performed at temperatures between 333 and 373 K, being approximately equal to the amount of stabilization at the same temperature. A well visible difference between both phenomena has been obtained at 393 K, but this result will not be further discussed here.

Fig 4 shows the main features which characterize pseudoelastic cyling of the tested samples: several σ-ε curves obtained for sample cabsc1m4 at 353 K at a crosshead speed 0.1 mm/min are shown. A reference cycle was obtained deforming the sample up to 10.5 % at 0.1 mm/min and then pseudoelastic cycling was performed at 10 mm/min up to a smaller deformation equal to 8.3 %. Once the rapid cycling was stopped slow cycles were obtained in order to check the recovery of the sample. As part of the sample was not transformed during the rapid cycling, this part of the stress-strain curves gives a reference behavior. Several points are mentioned here:

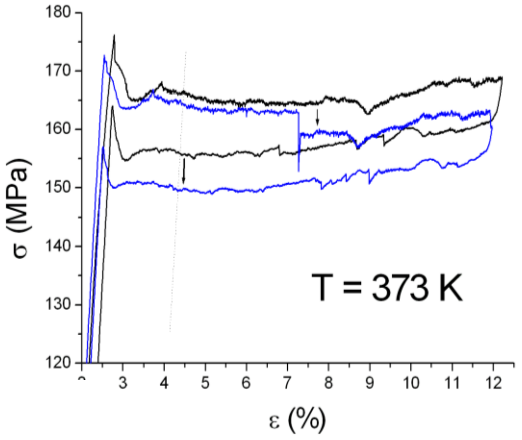


Fig. 3. Static stabilization test performed with sample cabsc1m3 at T = 373 K. The previous cycle is shown in black colour and the stabilization test in blue. Crosshead speed 0.1 mm/min, ε in the x axis obtained from the crosshead speed. Small arrows indicate the stabilization shift = 6 MPa (left) and the decrease of $\sigma^{\beta\text{-}m}$ in the area where β was kept under load= 5 MPa (right)

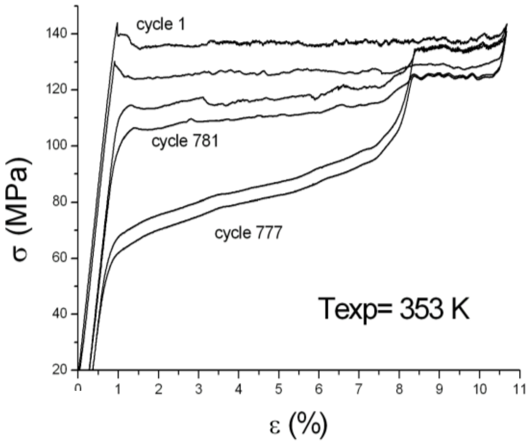
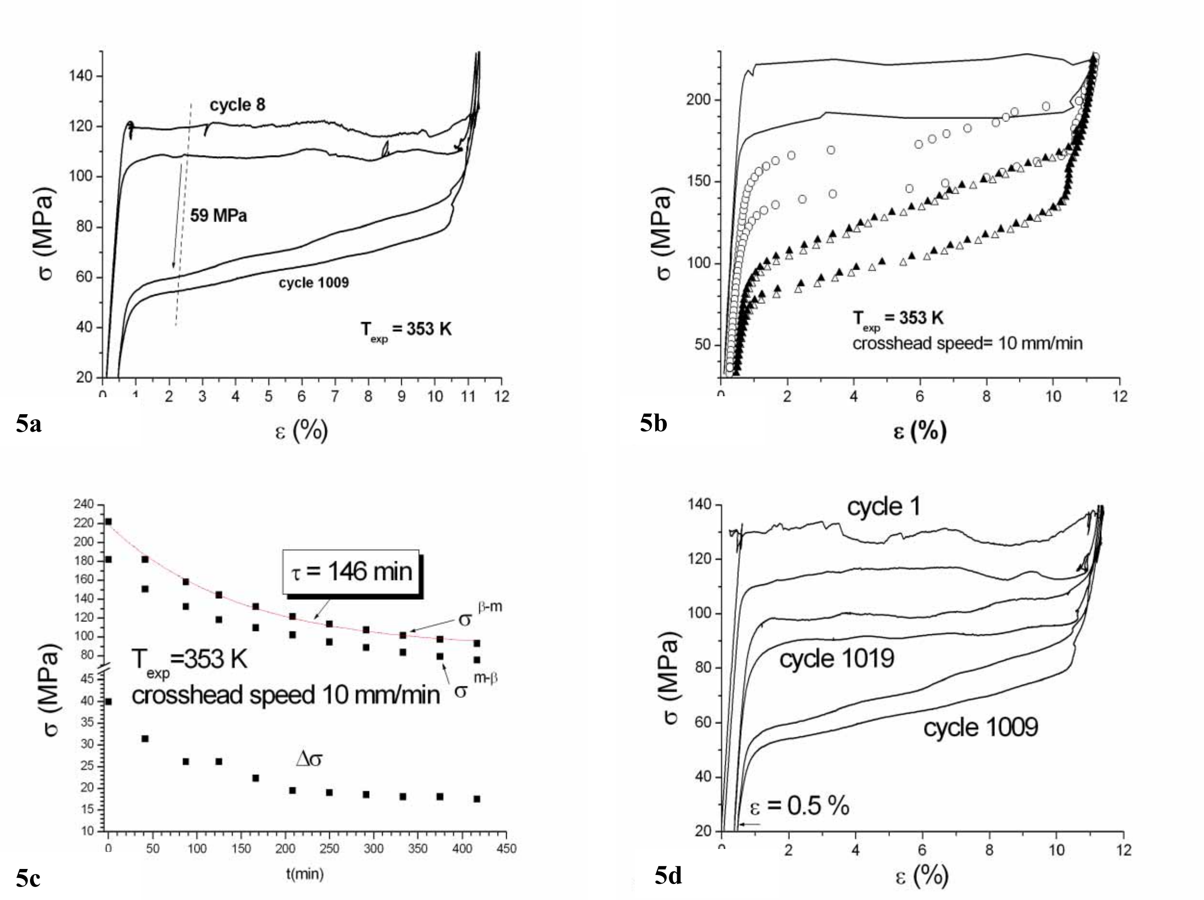


Fig. 4. σ-ε curves obtained for sample cabsc1m4 at T = 353 K. Cycles 1 and 777, previous and after rapid cycling respectively. Crosshead speed 0.1 mm/min, ε in the x axis obtained from the crosshead speed. Cycles 2 to 776 (not shown in fig) performed at 10 mm/min. Cycle 781 obtained after partial recovery of the β phase during 2 days.

a) A decrease of the critical stresses to transform and retransform as a function of number of cycles can be easily observed. These decreases differ for different amounts of deformation and are larger for those parts of the samples which transform at an earlier stage and are negligible for the part of the sample which is the last one to transform. The consequence of this behavior is a strong increase in the slope during the transition stage which changes with the number of cycles N. b) A decrease of the hysteresis down to half of its original value after 777 cycles is well observed. Considering the Clausius Clapeyron relationship, at the test temperature 353 K, the hysteresis corresponds to 5.3 K for cycle 1 and after 777 cycles it decreases down to 2.8 K, c) After stopping the pseudoelastic cycling the critical stresses start to increase in the direction of the values present before the cycling; d) A decrease of the critical stresses to transform in the region kept in austenite is also obtained here and e) A permanent deformation increases with number of cycles and a partial recovery is also observed after stopping the rapid cycling.

A more detailed example concerning the evolution of cycling and recovery of the β phase obtained for sample cab2m1 is presented in fig. 5a. The test temperature in this case is also 353 K and the crosshead speed during cycling 10 mm/min. After 1000 rapid cycles performed at this temperature, the following cycle obtained at 0.1 mm/min shows a strong decrease in the critical stress to transform. This value decreases from 120 MPa down to aprox. 60 MPa for 1 % deformation, which is equivalent to a 30 K increase in Ms temperature. This amount of stabilization of the martensite which is a dynamic effect is at least one order of magnitude larger than the static stabilization obtained at the same temperature, at time intervals even shorter (see Fig.3). The mechanical curves corresponding to a few transformation cycles during the rapid pseudoelastic cycling of the same sample (crooshead speed 10 mm/min) are shown in Fig. 5b. It can be observed here that the cycling behavior leads to an asymptotic behavior. This is also noticed in fig. 5c which shows the critical stresses to transform and the corresponding hysteresis for 1 % of deformation in the pseudoelastic range of the curve. The σ-ε curve obtained 2.5 days after stopping rapid cycling is shown in fig.5d together with cycles obtained before and after rapid



5a 5b 5c 5d

Fig. 5. a) σ-ε curves corresponding to N= 8 and 1009, before and after rapid cycling. Crosshead speed 0.1 mm/min. ε in x axis obtained from extensometer. 1000 cycles in between at 10 mm/min. Dynamic stabilization = 59 MPa (29.5 K) Hysteresis of cycles 8 and 1009 equal to 11.8 MPa and 5.39 respectively.
b) σ-ε curves corresponding to rapid cycles 1(solid line),200 (empty circles) ,900 (full triangles) and 1000 (empty triangles). Crosshead speed 10 mm/min. ε in x axis obtained from an extensometer (10 mm gauge length).
c) Applied stress to transform and retransform obtained from rapid cycles. Sample cabsc2m1, crosshead speed 10 mm/min. t= time spent in martensite for a portion of the sample corresponding to ε = 1 % deformation in the pseudoelastic transformation regime. It is shown the exponential fit for $\sigma^{\beta\text{-}m}$, time constant = 148 min.
d) σ-ε curves corresponding to cycles 1, 1009 after rapid cycling and 1019 after 3879 min of recovery post cycling at the same test temperature obtained for sample cabsc2m1 at 0.1 mm/min crosshead speed. ε in x axis obtained from extensometer .From cycles 9 to 1008 (not shown) crosshead speed= 10 mm/min. Texp = 353 K

cycling. The slope is recovered; however, the recovery of the critical stresses is not complete. The evolution of the critical stresses after stopping rapid cycling is shown in fig.6 as a function of time. The behavior can be well fitted by an exponential growth with a time constant clearly larger than that one obtained for the dynamic stabilization of the martensite (time constants 780 min and 150 min respectively). At last the evolution of the critical stresses during rapid cycling at a crosshead speed 20 mm/min is shown in fig 7 for sample cabsc2m2. The same temperature has been used for this test and the constant time obtained after an exponential fit equal 59 min quite shorter than the value obtained for a smaller speed used for sample cabsc2m1.

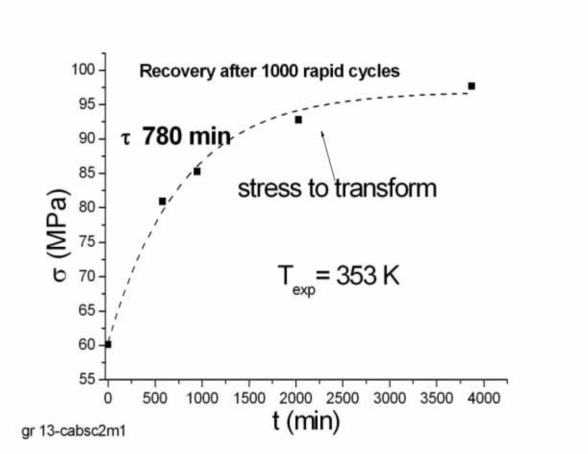


Fig 6. Applied stresses to transform measured as a function of time. Start point corresponds to the end of 1000 rapid cycles. Exponential decay fit is shown together with the obtained constant time. Stresses obtained at aprox. 2% ε in the pseudoelastic transition stage from cycles performed at a crosshead speed = 0.1 mm/min.

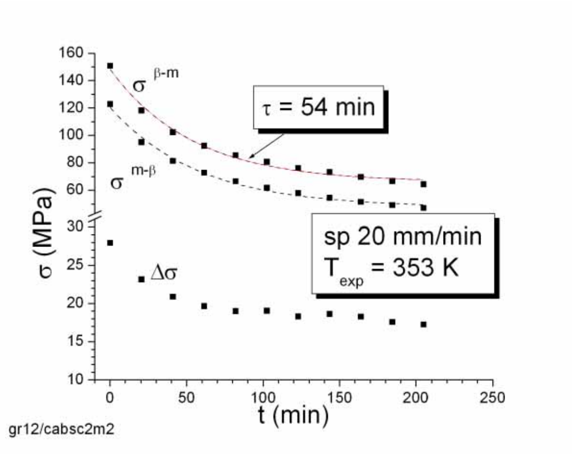


Fig. 7. Applied stress to transform and retransform obtained from rapid cycles. Sample cabsc2m2, crosshead speed 20 mm/min. t= time spent in martensite for a portion of the sample corresponding to ε = 1 % deformation in the pseudoelastic transformation regime. It is shown the exponential fit for $\sigma^{\beta\text{-}m}$, time constant = 54 min

4. Discussion

The obtained experimental results indicate that during pseudoelastic cyling, the critical stresses to transform and retransform, decrease in a inhomogeneous way leading to a well defined pseudoelastic slope which increases with N. This behaviour is similar to a reported one for CuZnAl single crystals tested at temperatures higher than room temperature and also to reported data obtained for CuAlBe single crystals [5, 6]. This behavior was explained considering the stabilization of the stress induced martensite and the recovery of the beta phase once the retransformation takes place. As the time interval which each portion of the sample stays in martensite or in the beta phase is different, the amount of decrease of the critical stresses will also be different giving a slope in the σ-ε curve at the transformation stage. In fact, these concepts allowed to model pseudoelastic cycling in both systems [5, 6].

In the same way as in CuZnAl single crystals an overlapping of two diffusive mechanisms are sufficient to explain the change in slope in the stress strain curves, each one of these, with its proper kinetics. However some differences between both metallic systems can be observed. On one hand the kinetics of the stabilization for CuZnAl single crystals was determined rather easily for the equilibrium concentration of vacancies. This was performed before and after rapid cycling and in fact after cycling it was shown that stabilization of martensite was inhibited due to the presence of defects introduced during rapid cycling. In addition modeling could be applied showing a reasonable fit with experimental results, considering that kinetics of stabilization is enhanced during pseudoelastic cycling if compared with static conditions [5].

One noticeable point concerning CuAlBe single crystal behavior is that the stabilization under static conditions with the equilibrium concentration of vacancies, is a small effect which makes it rather difficult to properly measure the kinetics under static conditions. On the other hand stabilization in these alloys has been clearly obtained if the concentrations of vacancies is large enough, i.e., after quench from high temperatures. Moreover quench thorough Ms has led to a so called hyperstabilization effect which in fact increases Ms in an amount considerably larger than the normal stabilization phenomenon [10-14]. Different mechanisms have been considered responsible for the stabilization in CuAlBe alloys. As an example Dunne et al. consider that pinning of interfaces by vacancies is responsible for normal stabilization phenomena and a DO_3 order somehow retarded by the action of Be atoms would be responsible for the hyperstabilization phenomenon [13]. Kustov et al. consider that the hyperstabilization effect is probably a mechanical effect, and in fact can be enhanced by pre-strain [10, 11].

The experiments presented so far do not allow to precisely assessing the physical mechanism behind the dynamic stabilization, moreover considering that the initial amount of vacancies should be close to the equilibrium concentration, differing from the start conditions mentioned above. Tidu et al., have shown that CuAlBe single crystals with the equilibrium concentration of vacancies, and pseudoelastically cycled, show in the β phase a change in the deformation state corresponding to a tendency to form an othorrombic cell [8]. This change should be inherited from the martensite which is indeed altered due to cycling. The authors discuss several alternatives concerning the origin of the measured distortion and mainly suggest that the martensite during cycling evolves in the direction of a phase similar to the (β'_X) reported by Duval et al. for Cu-Al alloys close to the Cu_3Al composition [15]. However it is still unknown which structure should be the final one after the stabilization of the martensite. An interesting point here is that a permanent deformation is also detected macroscopically in the stress-strain curves after cycling in all the samples here tested, and in fact partially recovers after aging. This effect is likely related to the experimental finding by Tidu et al. This remanent deformation increases during to cycling and slowly decreases simultaneously with the recovery of the β phase. We can state here that the recovery of this effect after cycling perfectly fits with a exponential decay which at T=353 K shows a time constant close to 1600 min. It cannot be disregarded that formation of martensite and retransformation after cycling play some role in this. However this effect has been measured in all the cycled samples at stresses significantly lower than the critical stress to retransform. Tidu et at. do not consider dislocations as the cause of the distortion they found due to the small amount of dislocations which are retained after cycling and the absence of broadening of X ray peaks. They do not find retained martensite in their used samples. Our experimental observations with transmission electron microscopy although not presented in this manuscript have shown a small amount of dislocations after 1000 pseudoelastic cycling. However this number of cycles is enough to make it visible the strong evolution of the tensile-strain curves including the shift in the remained deformation and its partial recovery.

A last point we would like to emphasize is the noticeable difference in the kinetics constants if static and dynamic stabilization are compared. This effect is visible in CuZnAl alloys but results indicate a stronger effect in CuAlBe alloys. Siredey et al. have observed this phenomenom although they used a different method to determine the static stabilization effect. The decrease in the stress to transform to martensite obtained during the static stabilization tests for the part of the samples kept in β phase under load might also have an influence on the dynamic behavior, however this effect seems to be rather small to have a strong effect. Tidu et al. explain the strong stabilization as a consequence of the structural change of martensite which is not complete in each cycle and an inherited disorder in the β phase. However it is still an open question why this does not occur under static conditions. We consider here two options which need to be further analysed: the creation of vacancies during cycling and the movement of vacancies due to the interface movement. The creation of vacancies during fatigue has been reported both in materials where no martensitic transitions take place and also after pseudoelastic fatigue at low temperatures in CuZnAl singles crystals [16-18]. Cingolani et al suggest the creation of vacancies to explain shifts in Ms after a few pseudoelastic cycles obtained under conditions apparently free of extra vacancies [19]. The other possible way to rationalize the obtained results is to consider that the movement of the β-18R interface enhances the movement of vacancies. This would be facilitated by the fact that concentration of vacancies differ in β and martensite leading to a non equilibrium condition for each part of the material during most of the rapid cycling test. A result which reinforces this possibility is the fact that two samples of the same single crystal cycled at the same temperature at different crosshead rates showed different constant times after an exponential fit of the decrease of the critical stresses. (see fig. 5 c and fig. 7). The constant time strongly decreases for a higher crosshead speed (or cycling frequency).

Acknowledgments

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References

[1] R.Romero, A.Somoza, M.A.Jurado, Ll.Mañosa, A.Planes, Acta Metall.Mater.**45**, 2101 (1997)
[2] R. Gastien, C.E. Corbellani, M. Álvarez Villar, M. Sade, F.C. Lovey, Mater.Sci.Eng., **349**, 191 (2003)
[3] J.Malarría, M.Sade, F.C. Lovey, Mat.Science and Eng.A **308**, 88 (2001)
[4] A. Yawny, J. Malarría, F.C. Lovey, M. Sade, J. Physique IV **7**, Colloque, C5-531 (1997)
[5] A.Yawny, F.C. Lovey, M. Sade, Mat. Science and Eng. A. **290**, 108 (2000)
[6] N. Siredey, A. Eberhardt, Mater.Sci.Eng.A. **290**, 171 (2000)
[7] L. Mañosa, M. Jurado, A. Gonzalez-Comas, E. Obradó, A. Planes, J. Zarestky, C. Stassis, R. Romero, A. Somoza, M. Morin, Acta Mater **46**,.1045 (1998)
[8] A. Tidu, A. Eberhardt, B. Bolle, F. Moreau, J.J. Heizmann, J. Appl. Cryst. **34**, 722 (2001)
[9] A. Abu Arab, M. Ahlers, Acta Metall. **36**, 2627 (1988)
[10] S. Kustov, J. Pons, E. Cesari, M.Morin, Scripta Mater. **46**, 817 (2002)
[11] S. Kustov, J. Pons,E. Cesari, J. Van Humbeeck, M. Morin, Mater. Sci. Eng. A **378**, 283 (2004)
[12] C.H. Gonzalez, C.J.de Araujo, N.F. Quadros, G. Guenin, M. Morin, Mater.Sci.Eng. A **378**, 253 (2004)
[13] D. Dunne, M. Morin, C. Gonzalez, G. Guenin, Mater.Sci.Eng. A **378**, 257-262 (2004)
[14] D. Dunne, K. Ireland, C. Gonzalez, M. Morin, G. Guenin, Mater.Sci.Eng.A **438-440**, 339 (2006)
[15] P. Duval., P. Hayman, R. Acad. Sci.**267**, 388 (1968)
[16] J. Malarría, M. Sade, F.C. Lovey, Z.Metallkd. **87,** 953 (1996)
[17] J. Polák, Scripta Metall..**4**, 761 (1970)
[18] D. Segers, J. Van Humbeck, L.Delaey, M.Dorikens,L.Dorikens-Vanpraet, Appl.Phys. A **36**, 179 (1985)
[19] E. Cingolani, R. Stalmans, J. Van Humbeeck, M. Ahlers, Mater.Sci.Eng.A **268**, 109 (1999)