On the influence of austenitization on the morphology of α-phase in tempered Cu–Zn–Al shape memory alloys

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Abstract

The paper reports some austenitization effects on the α-phase morphology in a tempered martensitic Cu–21.57 Zn–7 Al (wt.%) shape memory alloy (SMA). By means of differential scanning calorimetry, X-ray diffraction and optical and electron microscopy, it has been shown that the effects of the stress-state induced in austenite persist even after martensitic transformation and tempering at 773 K. The two analyzed austenitization states, hot-pressed and homogenized, respectively, aimed to reproduce two steps of an industrial technologic flow for SMA manufacturing. Basically, austenitic hot-working diminished the size of disoriented α-phase precipitates while austenitic homogenization enabled the formation of a Widmanstätten structure with oriented long α-phase needles, among which those corresponding to α(1 1 1) intersect at about 70° and those corresponding to α(2 0 0) at 90°.

Keywords: Constrained recovery; Training-cycling tests in bending; Bainite formation; Stabilized phases; α-Phase preferred formation

1. Introduction

Cu–Zn–Al-type shape memory alloys (SMAs), with critical temperatures \( M_s = 73–373 \text{ K} \), typically contain Cu-(19–30)Zn-(4–8)Al (wt.%) and small additions of some grain-refining elements, such as B, Zr, Mn, Ti, Co, etc. [1,2]. Within the above compositional range, up to three equilibrium phases, namely \( \alpha \), \( \beta \) and \( \gamma \) [3–6], as well as up to three martensitic phases, designated as \( \alpha' \), \( \beta' \) and \( \gamma' \) [7], are normally expected to occur. The equilibrium phases \( \alpha \) and \( \gamma \) are generally avoided basically because they do not transform martensitically and impede martensitic transformation being too soft and too hard, respectively. Therefore the only phase useful for the SM behavior is \( \beta \) (bcc) with electron concentration \( n_e/n_0 = 1.48 \) [8] and stability range near the eutectoid composition in the ternary system [9]. Since it undergoes either a thermally or a stress-induced martensitic transformation it is termed “austenite” [10]. During cooling, prior to martensitic transformation, austenite may experience up to two ordering reactions \( A2 \rightarrow B2 \rightarrow L2_1 \), providing no high cooling rates are applied [11]. Among the above three martensites the most common one is \( \beta' \) which is thermally or stress-induced from ordered \( \beta_2(B2) \) or \( \beta_3(L2_1) \) austenites, as \( \beta'_2(9R) \) or as \( \beta'_3(18R) \), respectively [12].

The optimal functioning of the applications made from ordinary Cu–Zn–Al-type SMAs should comprise only the fully reversible martensitic transformations \( \beta_2(9R) \leftrightarrow \beta'_2(9R) \) or \( \beta_3(18R) \leftrightarrow \beta'_3(18R) \). However various previous works reported that, owing to some diffusion-controlled phenomena, either intermediate or equilibrium phases can precipitate during martensite ageing. For instance, \( \alpha \)-phase was observed with a textured shape in commercial Cu–Zn–Al-type springs before training [13] and with a specific orientation [14] and morphology [15] in tempered martensitic alloys. On the other hand, at higher Zn contents, the precipitation of \( \gamma \)-phase was observed in stabilized martensite [16] especially after prolonged ageing [17] being favored by the formation of vacancies clusters [18] or by the formation of stabilized stress-induced martensite [19]. In alloys with less than 7 wt. % Al, during martensite ageing above 473 K lath martensite with higher Al content was formed that eventually decomposed by eutectoid reaction into \( \alpha + \gamma \) [20]. If the Al content was up to 5 wt. %, during isothermal ageing of martensitic alloys in the range 453–573 K, the formation of transitory \( \alpha_1 \) bainite \( (9R) \) was reported that became disordered \( (3R) \) and finally transformed into equilibrium \( \alpha \)-phase [21].

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Being considered as a product of competitive mechanism of eutectoid decomposition that nucleates after an incubation time and requires diffusion for its growth [22], α₁ bainite was observed after isothermal transformation, firstly in Cu–Zn alloys [23] and subsequently in Cu–Zn–Al [24]. For Cu–Zn–Al alloys, the mechanism [25] and morphology [26] of bainite transformation during isothermal ageing were studied both in free-state and under applied stress [27]. Since it has a diffusionless nucleation and a diffusion-controlled growth, even if its formation is accompanied by a geometry change designated as reverse shape memory effect [28], bainitic transformation is irreversible, in contrast to martensitic transformation.

Besides high temperature decomposition, martensite can be subjected to low temperature stabilization [29] accompanied by the change of long range atomic order [30] which prevents the reverse martensitic transformation thus causing the degradation of the shape memory effect [31].

The present paper aims to report the shape memory behavior of a martensitic Cu–Zn–Al SMA with 7 wt.% Al and to reveal the role of tempering in the properties adjustment by means of structural changes. Special emphasis is laid on the influence of austenitization on the morphology of α-phase precipitated during tempering in the martensitic alloy under study. Two austenitic conditions that reproduce two consecutive steps of an industrial technologic flow are considered and the interaction between β₂ austenite (B₂, \(a = 0.294 \text{ nm}\)) [32], β₂martensite (M9R, \(a = 0.441 \text{ nm}; b = 0.268 \text{ nm}, c = 1.92 \text{ nm}\) and \(\beta = 88.4^\circ\)) [33], α₁ bainite (9R, \(a = 0.452 \text{ nm}; b = 0.264 \text{ nm}\) and \(c = 1.918 \text{ nm}\)) [21] and θ-phase (fcc, \(a = 0.375 \text{ nm}\)) [32] during tempering and subsequent water cooling is analyzed.

2. Experimental details

A Cu–21.57 Zn–7 Al (wt.% SMA was cast, hot pressed (40% thickness reduction) and heat treated according to Fig. 1. Thus, lamellar specimens for constrained recovery [34] tensile tests and for training-cycling tests in bending [15] as well as square specimens for X-ray diffraction studies were cut under adequate cooling to the final dimensions 1.5 mm × 2.2 mm with active length 80 mm, 0.5 mm × 4 mm × 50 mm and 2 mm × 20 mm × 20 mm, respectively. X-ray diffraction (XRD) specimens were ground, polished and etched in the same way as metallographic specimens. Etching was performed during 1 min with a solution (20 g-K₂S₂O₅, 5.5 ml-Na₂S₂O₃, 50 ml-distilled water) which was neutralized with water, acetone and ethanol. Thin foils for transmission electron microscopy (TEM) were prepared by twin-jet electropolishing in an electrolyte solution consisting of 75 vol.% methyl alcohol and 25 vol.% nitric acid.

Constrained recovery tensile tests were performed on a Heckert FPZ 100/1 tensile testing machine by electrical resistive heating of elongated specimens, according to a previously described procedure [35].

Training-cycling tests in bending were carried out on an experimental device called deflectometer [36] the functioning principle of which was previously detailed [37]. Essentially the specimens in martensitic state were bent by three different loads of 0.24, 0.44, 2.94 N. With the loads fastened at their free end, the specimens were subjected to heating–cooling cycles during which they lifted the loads by shape memory effect (SME) and lowered them due to the softening induced by direct martensitic transformation. The device is equipped with limit stops that automatically commute between the heating and cooling modes and with sensors that enable recording the variation of the displacement of specimen’s free end as a function of temperature with a precision of 0.5 mm and 1 K, respectively.

XRD experiments were performed on a Dron 2,0 diffractometer with Cobalt anode, with particular care in order to avoid texturing effects. The Miller indices of the diffraction maxima were ascribed with a precision of ±0.1°, by simulating

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Fig. 1. Schematic thermogram illustrating the heat treatments applied to the experimental alloy.

Fig. 2. Stress variations with time during four constrained recovery tensile tests performed on a specimen \(A_0\) initially loaded up to 250 MPa which developed the same maximum stress during heating at four decreasing strains maintained constant.
the corresponding diffractograms for the phases mentioned in the previous section, by means of the POWDER CELL program [38]. The error for determining the relative intensity on the recorded diffractograms has been 1.5%.

Differential scanning calorimetry (DSC) measurements were conducted on a 2920 Modulated DSC TA INSTRUMENTS unit, with a temperature variation rate of 10 K/min and isothermal maintaining for 3 min at the end of each ramp.

Metallographic observations were performed on a LEICA optical line comprising Aristomet light microscope and Orthomat E exponometer.

TEM observations were made with a JEM 2000FX transmission electron microscope operating at 200 kV, using a double tilt sample holder.

3. Results

3.1. Constrained recovery tensile tests

Constrained recovery SME involves the development of rather elevate recovery forces due to the external constrainst that prevent the SM element to restore its hot shape. Fig. 2 summarizes the results of an experiment comprising several constrained recovery tensile tests, performed on a specimen \( A_0 \) loaded to 250 MPa that reached the same maximum stress of 250 MPa during heating at different strains maintained constant. The specimen was initially loaded up to 250 MPa that corresponds to a strain of 2.38%. While this strain was maintained constant, the specimen was heated. At the beginning of the resistive heating, \( a_1b_1 \), thermal expansion occurred that lowered the stress but constrained recovery SME subsequently was produced that raised stress back to its initial level, \( b_1c_1 \). Heating stopped at 250 MPa and the specimen was cooled in air to room temperature (RT), \( c_1d_1 \). Then strain was reduced to 2.13%, \( d_1b_2 \), which also decreased stress correspondingly and a new heating was applied during which stress increased back to 250 MPa. After three gradual unloadings, stress reached 0 MPa at a permanent strain of 1.54% where a total stress of 250 MPa was developed, as well, on heating.

When analyzing the variation of the stress developed by constrained recovery SME, on the portions \( b_1c_1 \), as a function of the constant strain where the tests were performed, it appears that recovery stress decreased with the applied strain, according to a third order polynomial relationship.

3.2. Training-cycling tests in bending

Three specimens \( A_0 \) were trained in bending under three loads applied at their respective free ends. After five heating–cooling cycles, the variation of free end displacement as a function of temperature became cyclic, closed loops being obtained in all three cases. The corresponding displacement–temperature vari-

![Fig. 3. Variation of the free end displacement as a function of temperature for specimens \( A_0 \) subjected to training in bending under three different loads, from the beginning (1st cycle) to the end (5th cycle) of training.](image)

![Fig. 4. Simplified X-ray diffractograms of the heat treated specimens according to Fig.1, emphasizing tempering effects: (a) hot forged specimens \( A_0, A_{13-15} \); (b) homogenized specimens \( B_0, B_{13-15} \).](image)
Fig. 5. DSC charts recorded during heating up to 873 K, indicating three known phase-transitions, designated with A, B and C, respectively and possibly bainite formation above 600 K: (a) specimen $A_0$; (b) specimen $B_0$.

Fig. 6. DSC charts recorded during a cooling-heating cycle between 423 and 193 K indicating a reversible martensitic transformation: (a) specimen $A_0$; (b) specimen $B_0$.

Table 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Calculated parameters for Co Kα radiation</th>
<th>Specimen (measured values of 2θ (°))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$h$ $k$ $l$</td>
<td>$d$ (nm)</td>
</tr>
<tr>
<td>$\beta'_2$</td>
<td>$-1$ $-1$ $1$</td>
<td>0.2278</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>0 $-1$ $-5$</td>
<td>0.2197</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1 $1$ $1$</td>
<td>0.2125</td>
</tr>
<tr>
<td>$\beta'_2$</td>
<td>1 $1$ $4$</td>
<td>0.2078</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1 $1$ $0$</td>
<td>0.2056</td>
</tr>
<tr>
<td>$\beta'_2$</td>
<td>0 $-1$ $-6$</td>
<td>0.2054</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>2 $0$ $0$</td>
<td>0.1849</td>
</tr>
</tbody>
</table>

After removing the load, this trained specimen was further subjected to heating–cooling cycles during which it developed two-way shape memory effect (TWSME). Since it was no longer constrained by the load, the specimen’s free end increased its stroke but the two limit stops confined the displacement to 5 mm. During TWSME cycling, the same decreasing tendencies of both $A'_s$ critical temperature and transformation hysteresis (proportional to the surface area between heating and cooling curves) decreased as well. At the specimen trained in bending under an applied load of 2.94 N, the displacement of its free end reached 4.73 mm, which represents the largest value of the three above cases.

Table 1 provides analytical and experimental data used for indexing the diffraction maxima from Fig. 4.
erally noticed from the 100th to the 1000th TWSME cycle. Thus, $A'_e$ decreased from 410 to 405 K while transformation hysteresis decreased with 43%.

3.3. XRD observations

The X-ray simplified diffractograms of the eight specimens defined in Fig. 1 are illustrated in Fig. 4 in such a way as to reveal both homogenization and tempering effects. The calculated values of Miller indices, interplanar spacings and $2\theta$ angles, as well as measured values of $2\theta$, in the significant region 40–60°, are summarized in Table 1, for the recorded maxima.

The two austenitization states, hot pressed air cooled $A_0$ and homogenized water quenched $B_0$ have different structures due to both $\alpha_H^{-}\beta_1$-phase and $\alpha_H^\prime\beta_2$ austenite expected to occur in specimen $A_0$ which has a multivariant martensitic structure. In hot pressed specimens $\alpha_H^{-}\beta_1$-phase persists, even after tempering and air-cooling, with crystallites that contain the close packed planes (1 1 1) and (2 0 0) oriented parallel to the specimen’s surface. The ratio between the relative intensities, corresponding to the two orientations, $\alpha(2 0 0)/\alpha(1 1 1)$ increased with tempering temperature up to a maximum value of 0.41 [14], value which remained unchanged after water cooling [15].

3.4. Tempering effects

Fig. 5 shows the DSC charts recorded for specimens $A_0$ and $B_0$ during heating up to 873 K. In both charts three transformations occurred which in this case, according to literature, have been ascribed to: A—endothermic reverse martensitic transformation; B—exothermic precipitation of $\alpha$-phase and C—endothermic order–disorder transition of austenite [39]. In spite of the different treatments applied to $A_0$ and $B_0$ which have different structure, the three transformations occurred at approximately the same temperatures. In addition to the three transitions, a fourth flat endothermic peak located above 600 K has been illustrated in Fig. 5. It is presumed that this peak, which was previously observed on the DTA thermograms as well [40], could correspond to bainite formation.

In order to reveal tempering effects on the martensitic transformation, each of the eight specimens were heated at a temperature where, according to Fig. 5, martensite reversion should be complete and then subjected to a cooling–heating cycle. The reverse martensitic transformation (designated as A in Fig. 5) has been ascertained by means of the DSC charts shown in Fig. 6, recorded during a cooling–heating cycle between 423 and 193 K.

A much more significant difference between hot pressed and homogenized specimens is noticeable in Fig. 7 that shows the...
DSC charts of the specimens tempered at 573 K. In Fig. 7(a) a reversible martensitic transformation was obviously produced in specimen $A_{13}$ with smaller hysteresis but larger enthalpy as compared to $A_0$, which shows that a part of the initial stress state caused by forging was relieved. On the other hand, in Fig. 7(b) specimen $B_{13}$ did not show any sign of transformation, during a cooling–heating cycle between 423 and 193 K.

The significant difference between the behaviors of specimens $A_{13}$ and $B_{13}$ is also reflected by the aspect of the respective optical micrographs in Fig. 8. In Fig. 8(a) the structure of speci-
imen A13 is obviously martensitic. In Fig. 8(b), since water cooling was performed below 623 K and the plate-like transformation product reveals internal striations [23] which seem to be irregularly distributed and have the appearance of microtwins [41] the structure of specimen B13 could be fairly bainitic rather than martensitic.

The expected presences of martensite in specimen A13 and of bainite in specimen B13 are confirmed by the TEM images shown in Fig. 9. According to data found in literature, the stacking faults [42] and selected-area diffraction (SAD) pattern [17] from Fig. 9(a) and (c), respectively, correspond to β2 martensite, while the plate-shaped product and its SAD pattern, from Fig. 9(b) and (d), respectively, could be ascribed to α1 bainite [24].

According to Fig. 5, α-phase precipitation is initiated at around 673 K and completed at 773 K therefore the specimens tempered at these two temperatures could bring some evidence about the course of this exothermic transformation.

The DSC charts of specimens A14 and B14, tempered at 673 K showed that no transformation occurred during a cooling–heating cycle between 423 and 193 K. However, specimen A14 contains austenite but, due to the large amount of α-phase that was observed, β2 should be depleted in copper and therefore its critical temperatures would be too low.

The micrographs of specimens A14 and B14, (Fig. 10) reveal the occurrence of α-phase but the two figures are very different. Considering that hot pressed specimen A0 had higher stresses in initial state, it is reasonable that A14 shows shorter α-phase rods (needles) a large part of them being agglomerated along grain boundaries that acted as stress concentrators, Fig. 10(a). On the other hand, Fig. 10(b) shows that the former bainitic plates became much finer, preserved their V-formation but the largest part of them turned to α-phase needles. For this reason bainite was not detected in Fig. 4(b) at the specimen tempered at 673 K. This behavior is consistent with the TTT-diagram of the alloy under study that shows an inflection point at 673 K where the shortest holding periods are required for α-phase precipitation [43].

The DSC charts of the specimens tempered at 773 K, during a cooling–heating cycle between 353 and 133 K, are shown in Fig. 11. Since incomplete exothermic peaks followed by clear endothermic peaks are noticeable on both charts it is assumed that a partial direct martensitic transformation occurs on cooling and martensite reversion is produced on heating, at cryogenic temperatures. Here again, specimen A15 with larger amount of austenite has larger transformation enthalpy as compared to specimen. Owing to the increase of the amount of precipitated Cu-rich α-phase, austenite became richer in zinc and aluminum and for this reason its martensitic transformation temperatures were shifted to very low values.
During the first heating, the critical temperature is reached, stress firstly decreases due to thermal expansion, until $A'_t$ critical temperature is reached, and then increases again, causing the occurrence of constrained recovery SME. Since no stress drops were recorded at the end of each of the four heating stages, it is obvious that heating was interrupted between $A'_t$ and $A'_f$ critical temperatures. After the first cooling under stress, $c_1d_1$, it is assumed that no thermally induced martensite variants are formed at RT, since direct martensitic transformation starts at 305 K, according to Fig. 6(a). Therefore at the end of the first constrained recovery tensile test, only austenite and stress-induced martensite would be obtained. During the subsequent tests, the reversion of stress-induced martensite occurred at the beginning of heating, causing stress to increase.

Assuming the transitory formation of $\alpha_1$ bainite as a precursor of $\alpha$-phase precipitation, since the latter was already present in hot pressed specimens after austenitization, no $\alpha_1$ formation is expected with increasing tempering temperature. Accordingly, none of the bainite peaks were indexed in Table 1 for the diffraughtograms of hot pressed specimens On the other hand, in the diffractograms of $B_0$ homogenized specimens only two martensite variants could be detected, in Fig. 4(b). With increasing tempering temperature, it is assumed that firstly a large part of martensite remained untransformed and then a small part of it turned to bainite. Among various possible $\alpha_1$ peaks only (1 1 3) was assumed to belong to bainite at the specimen tempered at 573 K, Fig. 5(b). This assumption has been confirmed by optical microscopy, Fig. 8(b) and TEM, Fig. 9(b) and (d). Further increase of tempering temperature enabled the transformation of bainite to $\alpha$-phase, with the two above orientations, while a small part of martensite remained untransformed until 773 K where it finally turned to austenite.

The transformation enthalpies are at least double at hot pressed specimen $A_0$ as compared to homogenized $B_0$ in accordance with Fig. 4, where the former presents austenite that takes part to the direct and reverse martensitic transformation, while in the latter no retained austenite was detectable. Since $A_0$ should have higher dislocation densities induced by hot pressing, it is expectable that the direct martensitic transformation on cooling occurs at lower temperatures in Fig. 6(a) than in Fig. 6(b) [44]. This decrease of the critical transformation temperature could also be ascribed to the presence of $\alpha$-phase in specimen $A_0$, which depletes the austenitic matrix in copper thus increasing its zinc content.

This behavior shown in Fig. 7 agrees with the presence of austenite in the diffractogram corresponding to $A_{13}$ in Fig. 4(a) and to its absence in the corresponding diffractogram of $B_{13}$ from Fig. 4(b). Since specimen $A_{13}$ contains austenite, it is this phase that transforms to martensite on cooling. On the other hand, Fig. 5 has shown that during heating the presumed formation of bainite could start at 573 K being enhanced by the 300 s holding. According to the TTT diagrams, the isothermal transformation for 300 s at 573 K of a Cu–21.5 Zn–7 Al (wt.% ) SMA is too short as to allow $\alpha$-phase precipitation [43] therefore this transformation can fairly be excluded in the alloy under study at 573 K. The reason for which bainite could be detected in specimen $B_{13}$ and not in specimen $A_{13}$ could be related to the pre-existence of $\alpha$-phase in the latter. Moreover, since the presumed bainite peak is flatter in Fig. 5(a) than in Fig. 5(b) one can expect that a smaller amount of transformation product would be obtained in specimen $A_{13}$ than in $B_{13}$. [44]
5. Conclusions

The Cu–21.57 Zn–7 Al (wt.%) SMA under study, in hot pressed air cooled state, developed both tensile constrained recovery SME and TWSME, after being trained in bending, in spite of the pre-existence of α-phase. The stress developed by tensile constrained recovery decreased with increasing permanent strain according to a third order polynomial fit. The maximum stress reached 250 MPa for a permanent strain of 1.54%. After being trained by repeatedly lifting a 2.94 N load, the specimen obtained a critical temperature with 5 K, from 410 to 405 K and the corresponding transformation hysteresis with 43%.

Bainite formation, predicted by DSC, was assumed by XRD and confirmed by optical microscopy and TEM only in homogenized specimen B13 tempered at 573 K. Due to the pre-existence of α-phase in specimen A13, the bainite amount is expected to be too low, therefore non-distinguishable, and for higher tempering temperature it is suggested that transitory bainite turned to equilibrium α-phase.

The stress-state induced in austenite proved to influence the tempering behavior of the martensitic Cu–Zn–Al SMA under study, even after heat treatments performed at temperatures as high as 773 K. The internal stresses caused by hot-pressing and air-cooling lowered the critical transformation temperatures of martensite, prevented bainite formation, favored α-phase precipitation both along austenite grain boundaries, mostly after 673 K-tempering, and inside them, as short disoriented rods, after 773 K-tempering. Tempering enabled the preferred formation of α-phase according (1 1 1) and (2 0 0) orientations characterized by intersections at about 70° and 90°, respectively.

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