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Influence of Grain Size on Shape Memory and Internal Friction in $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ Alloy

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Shape-memory alloys belong to the functional materials, which exhibit shape memory, superelasticity and high damping-capacity phenomena. Cu–Al–Mn shape-memory alloys remain of particular interest as they show good machinability and are much cheaper than nitinol. In addition, their functional performance is quite attractive as well. The present paper is dedicated to the changes in shape memory and internal friction induced by the grain-size reduction in low-temperature cast $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy.

Key words: martensitic transformation, grain size, shape memory, internal friction, Cu–Al–Mn alloys.

Стопи з пам'яттю форми належать до функціональних матеріалів, які виявляють пам'ять форми, надпружність і високу здатність до демпфування. Стопи Cu–Al–Mn з пам'яттю форми залишаються популярними серед дослідників, оскільки вони демонструють добру оброблюваність і набагато дешевші за нітинол. Крім того, їхні функціональні характеристики також достатньо привабливі. Дана стаття стосується змін пам'яті форми та внутрішнього тертя, спричинених зменшенням розміру зерен у низькотемпературному литому стопі $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$.

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Ключові слова: мартенситне перетворення, розмір зерна, пам'ять форми, внутрішнє тертя, стопи Cu–Al–Mn.

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1. INTRODUCTION

Cu-based shape memory alloys are those that belong to the group of industrial shape memory alloys. The reason for their attractiveness in a sense of application is not only the thermoelastic character of the martensitic transformation that takes place in them ensuring reversibility at shape memory behaviour, but their relative cheapness and simplicity in preparation as well. In fact, intensive research of these alloys started from the cornerstone work on Cu–Al alloys by Kurdyumov and Khandros in 1949, where they have confirmed the existence of the thermoelastic phase equilibrium predicted previously by Kurdyumov himself [1]. Since then, researchers all over the world focused their efforts on studies of crystal structure, crystallography, thermodynamics and kinetics of the martensitic transformations in Cu-based alloys in particular and Warlimont and Delaey elegantly summarized these research results in their monograph in 1974 [2]. Surely, shape memory, superelasticity, high damping capacity behaviour associated with the martensitic transformation was also studied for these alloys as well. One might find important details in the work of Tadaki [3] or in one of the more recent general reviews on a subject (see [4], for example).

Cu–Al–Mn shape memory alloys still attract much attention as they show enhanced plasticity due to the existence of β -austenitic phase that possess $L2_1$ semi-ordered structure undergoing martensite transformation according to Kainuma *et al.* [5, 6] contrary to the brittleness of $B2$ or $D0_3$ Cu–Al–Ni and Cu–Zn–Al shape memory alloy systems [3, 7]. Specifically, Cu–Al–Mn alloys exhibit attractive damping capacity [8], shape memory [6, 9] and superelasticity [10]. The latter is becoming even more popular due to the possibility to produce high quality wire. One of the important issues is the grain size as its reduction improves ductility and might be critical for Cu–Al–Ni and Cu–Zn–Al alloys [3, 7] and proved to be beneficial for Cu–Al–Mn alloys [8, 10]. The present paper is dedicated to the uncovered peculiarities of the grain-size reduction influence onto shape memory and internal friction demonstrated on cast low temperature Cu–Al–Mn shape memory alloy.

2. EXPERIMENTAL

Cu–13% wt. (25.86 at.%) Al–5% wt. (4.88 at.%) Mn alloy composition was chosen because of the expectation of martensitic transfor-

mation and associated shape memory well below room temperature. It was induction melted and cast into room temperature ceramic mould and into a mould cooled down to 140 K. After casting, specimens were annealed at 1173 K for 30 minutes and quenched into water. X-ray diffraction has been recorded using Dron-3M diffractometer in radiation $\text{CuK}\alpha$. Rietveld refinement of the x-ray diffraction pattern obtained was carried out with the help of Maud 2.9993 build 532 software [11] with goodness of fit $R_{\text{wp}} = 7.3\%$ at $R_{\text{exp}} = 2.9\%$. Microstructures were studied using Zeiss Axiovert 40 optical microscope in polarized light. Shape memory behaviour and internal friction changes together with elastic modulus temperature dependencies were obtained in 3 point bending on $22 \times 2 \times (0.4-0.5)$ mm plate like specimens (setup with 20 mm distance between nodes; oscillating frequency 1 Hz; heating-cooling rate 5 K/min) using Netzsch 242 Dynamic Mechanical Analyzer (DMA) and Proteus software.

3. RESULTS AND DISCUSSION

Figure 1 represents the result of Rietveld refinement of the x-ray diffraction pattern of $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy cast at 140 K, annealed and quenched (casting into room temperature mould shows similar pattern—not shown).

It can be seen that, at room temperature, the major phase is $L2_1$ -austenite with volume fraction of 95% and lattice parameter $a = 5.8744 \text{ \AA}$, while remaining 5% of volume fraction belongs to the γ'_1 -

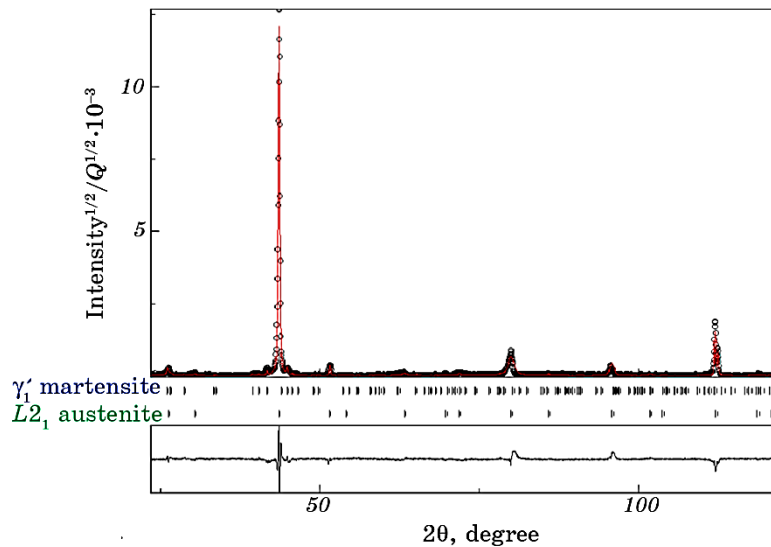


Fig. 1. Results of Rietveld refinement of x-ray diffraction of cast at 140 K, annealed, and quenched specimen of $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy.

orthorhombic martensite ($Pnmm$ space group) with lattice parameters $a = 4.465_5 \text{ \AA}$, $b = 5.320_4 \text{ \AA}$, $c = 4.333_2 \text{ \AA}$.

Optical microscopy studies revealed that after casting of $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy into room temperature ceramic mould the microstructure consists of large grains (average about $200 \mu\text{m}$) that demonstrate some kind of growth texture (Fig. 2, *a*).

Casting into a mould cooled down to 140 K results in finer grains that are $20\text{--}50 \mu\text{m}$ in size (Fig. 2, *b*). Therefore, there is a clear evidence of grain size reduction in the latter case that is due to the increase in cooling rate upon crystallization.

To measure shape memory with a help of DMA, the experiment was set in order to apply static load well above the temperature range of the martensitic transformation (loaded after heating up to 440 K). Then loaded samples under the same static bending stress of 40 MPa were cooled down to 113 K and subsequently heated up back to 440 K and the deflection in 3-point bending versus temperature was observed for them. The results of such measurements for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy cast into room temperature ceramic mould and into a mould cooled down to 140 K are shown in Fig. 3.

It can be seen that forward (M_s , M_f) and reverse (A_s , A_f) martensitic transformation temperatures that correspond to accumulation of martensitic deformation on cooling and shape recovery on heating are sim-

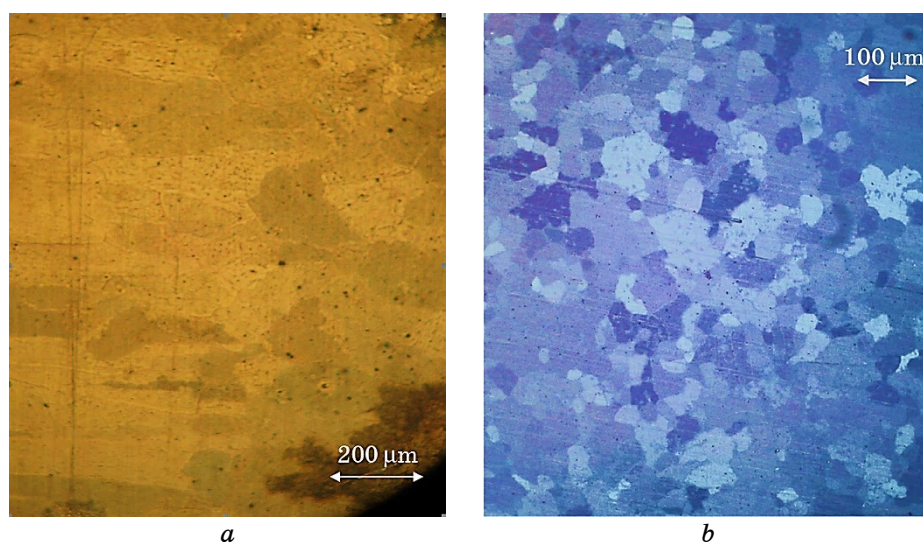


Fig. 2. Microstructures of the $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy: cast into room temperature ceramic mould (*a*), cast into a mould cooled down to 140 K (*b*), after casting specimens were annealed at 1173 K for 30 minutes and quenched into water (optical microscopy; polarized light).

ilar but not identical for large grain size of about 200 μm (casting into room temperature ceramic mould; Fig. 2, *a*) and smaller grain size of 20–50 μm (casting into a mould cooled down to 140 K; Fig. 2, *b*). To be exact, in the case of large grain size, forward martensitic transformation starts and finishes ($M_s=200$ K, $M_f=185$ K) at about 10 K higher comparing with smaller grain size ($M_s=190$ K, $M_f=175$ K), while reverse martensitic transformation is almost the same ($A_s=245$ K, $A_f=255$ K), if one defines these temperatures as onset points with an inflection in between. It can be also seen that, in both cases, the shape recovery is complete but the reversible deformation amount is different. In the present case of 3-point bending, the deformation was calculated according to the following formula $\varepsilon = (4h(dL)/(l^2 + (dL)^2)) \times 100$, where h is plate thickness, dL is deflection and l is distance between nodes (all in mm). So, in the case of large grain size (about 200 μm , Fig. 2, *a*) accumulated and restored martensitic deformation was $\varepsilon_R = 0.2\%$, while, upon the grain size reduction (20–50 μm , Fig. 2, *b*), it undergone 2-fold increase ($\varepsilon_R = 0.4\%$).

In order to determine elastic modulus and internal friction (loss factor), the dynamic load of oscillating force was applied (stress 40 MPa) resulting in 20 μm amplitude ($(8-10) \times 10^{-3}$). Proteus software calculates elastic modulus as $|E| = E' + iE''$, where E' is storage modulus and E'' is loss modulus. Loss factor is obtained as $\text{tg}\delta = E''/E' \approx Q^{-1} = (1/2\pi)(\Delta W/W)$, where ΔW is the energy (generally converted into heat) absorbed after loading and unloading and W is the applied energy

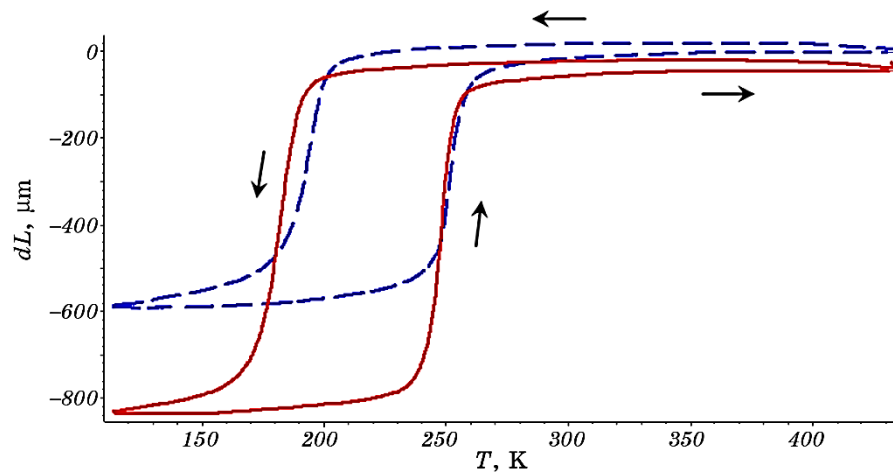


Fig. 3. Deflection in 3 point bending (dL) vs. temperature measured in Netzsch 242 DMA under static stress 40 MPa for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy cast into room temperature ceramic mould (200 μm grain size, plate thickness $h = 0.4$ mm; dashed line) and into a mould cooled down to 140 K (20–50 μm grain size, plate thickness $h = 0.5$ mm; solid line).

during loading. In Figure 4, the elastic modulus *vs.* temperature behaviour has been shown for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy upon almost 10-fold grain-size decrease.

It can be seen that martensitic transformation temperatures according to elastic-modulus changes with temperature shown in Fig. 4 correspond well with those obtained for shape memory behaviour shown in Fig. 3. It should be noticed that the absolute values of modulus are quite different for different grain sizes. As elastic modulus is a structure insensitive property and depends primarily on the interatomic interaction, this difference can only be explained in terms of high elastic anisotropy ratio $A = 2C_{44}/(C_{11} - C_{12}) \approx 13$ for Cu–Al-based alloys [12]. In this sense, large grains that show almost columnar microstructure (Fig. 2, *a*) might be the reason for higher directional stiffness along the measured plate, once for smaller grain size we have average distribution of directions and because of that elastic modulus values in austenite are very much like the ones measured on small grain polycrystalline wires in [8]. Contrary to the results in [8], the value of elastic modulus in martensite is smaller comparing to austenite although it is growing with cooling from the minimum observed during forward martensitic transformation. Subsequent heating back to 440 K results in passing through a minimum associated with reverse martensitic transformation, which is deeper comparing with a forward one implying that lattice softening during reverse martensitic transformation is more significant for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy.

As for internal friction (loss factor $\text{tg}\delta$ or damping) measured simul-

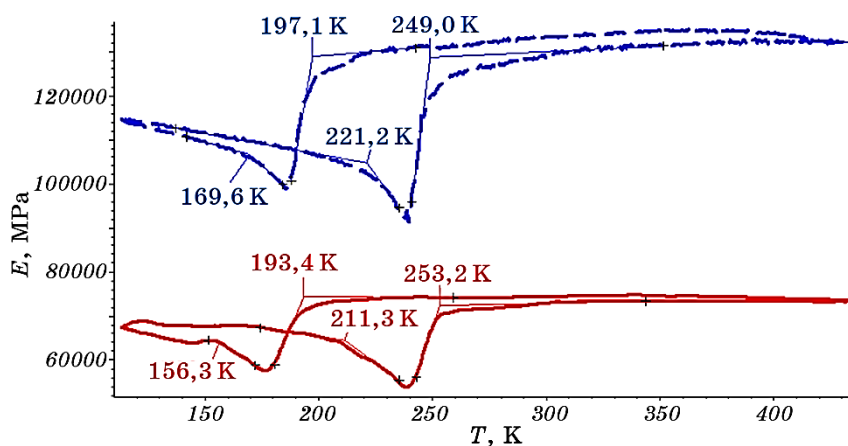


Fig. 4. Elastic modulus *vs.* temperature behaviour (oscillating frequency 1 Hz, oscillating amplitude 20 μm ($(8-10) \times 10^{-3}$), heating-cooling rate 5 K/min) for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy with 200 μm grain size (dashed line) and 20–50 μm grain size (solid line). Martensitic transformation temperatures calculated as onsets with the help of Proteus software are also shown.

taneously in these DMA experiments, its behaviour *vs.* temperature is shown for large and smaller grain sizes in Fig. 5.

It can be seen (Figure 5) that for the large and smaller grain size $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy specimens, two internal friction peaks correspond to elastic modulus minima (Fig. 4) and temperature intervals of martensitic deformation accumulation on cooling and its recovery on heating (Fig. 3). According to [13], these internal friction peaks contain two contributions, namely, ‘transient’ and ‘non-transient’. The latter is related to phase transformation mechanism. They all lay over so-called ‘intrinsic’ one that exists in austenite, two-phase austenite/martensite mixture during the transformation and in martensite. Authors of [13] relate ‘intrinsic’ contribution in martensitic state to the mobility of intervariant boundaries in thermoelastic martensite.

It seems evident that in the case of the large grain size (Fig. 5, dashed line) internal friction decreases after the peak on cooling to the value that was initially observed in high temperature austenitic region. Further heating leads to the increase in internal friction only in the temperature interval of the reverse martensitic transformation and it ends up in high temperature region once again at low internal friction value. It has to be noted that complete shape recovery in $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy (Fig. 3) means that the character of the martensitic transformation is definitely thermoelastic. At the same time, it is becoming obvious that intervariant boundaries for thermoelastic martensite formed in large grains are immobile. Yet, almost 10-fold decrease in grain size for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy results in very high internal friction in the martensite state (Fig. 5, solid line), as $\text{tg}\delta$

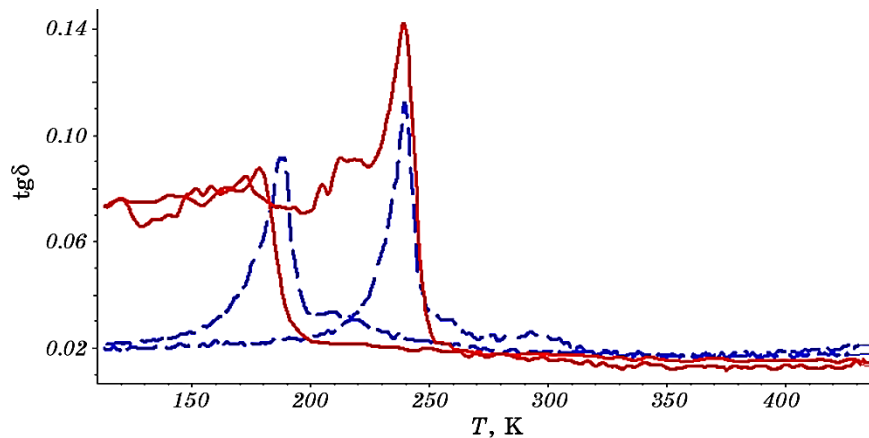


Fig. 5. Loss factor $\text{tg}\delta$ *vs.* temperature behaviour (oscillating frequency 1 Hz, oscillating amplitude $20\ \mu\text{m}$ ($(8-10)\times 10^{-3}$), heating-cooling rate 5 K/min) for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy with $200\ \mu\text{m}$ grain size (dashed line) and $20-50\ \mu\text{m}$ grain size (solid line).

grows to the peak value of 0.09 and does not decrease much in martensite in 0.07–0.08 range on cooling. Subsequent heating results in the increase of $\text{tg}\delta$ above 0.14 at the peak and decrease to the austenitic value in high temperature range. It has to be also noted that the internal friction peak during reverse martensitic transformation on heating is higher comparing with forward one on cooling (Fig. 5). It corresponds well with deeper minimum in elastic modulus during reverse martensitic transformation shown in Fig. 4 because lattice softening definitely helps the mobility of interfaces in general. Anyway, it can be supposed that the decrease in grain size leads to the mobility of the intervariant boundaries in thermoelastic martensite through changes in martensite crystal morphology from spear like to thin plate. The latter morphology might also be responsible for the increase in accumulated and recovered martensitic deformation at shape memory (Fig. 3). To find a proof of that, additional investigation will be required.

4. SUMMARY

It can be concluded that $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy upon quenching from 1173 K undergoes thermoelastic martensitic transformation from $L2_1$ austenitic phase into γ'_1 -orthorhombic martensite. Thermoelastic martensitic transformation in $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy is accompanied by complete shape recovery, while minima in elastic modulus coincide with internal friction peaks in the temperature intervals of martensite deformation accumulation and its recovery during forward and reverse martensitic transformation correspondingly. Higher internal friction peak during reverse martensitic transformation associated with lower elastic modulus minimum comparing to forward martensitic transformation. It means that higher interface mobility is ensured by the more significant lattice softening within the reverse martensitic-transformation temperature range. The large grain size for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy lead to the formation of the martensite state that shows no sign of the intervariant boundary mobility in thermoelastic martensite because the internal friction in this case is as low as it is in the austenitic state. It is possible to decrease austenite grain size with the help of high crystallization rate through casting into low temperature mould. Resulting 10-fold decrease in grain size ensures high mobility of intervariant boundaries in thermoelastic martensite for $\text{Cu}_{69.26}\text{Al}_{25.86}\text{Mn}_{4.88}$ alloy, which in its own turn results in high internal friction in martensite state. The possibility to regulate shape memory and internal friction through the grain size manipulation uncovered in present work might become very useful in application of cast or 3D-printed Cu-based shape memory alloys.

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