Materials Physics and Mechanics 46 (2020) 42-49 Received: October 7, 2020

BURST-LIKE SHAPE MEMORY RECOVERY AND CALORIMETRIC EFFECT IN Cu-Al-Ni ALLOY SINGLE CRYSTALS AT CYCLIC TEST

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Abstract. Here we report on compressive stress-strain behavior, ordinary and burst-like shape memory (SM) strain recovery, and associated caloric effects in Cu – 14.02% wt. Al – 4.0% wt. Ni single crystals which have multiphase martensitic structure at room temperature. The effect of repetitive thermo-mechanical cycling on the recovery of the shape memory deformation is investigated. The stress-strain curves of the specimens are smooth in all tests. Immediately after quenching, crystals exhibited burst-like strain recovery accompanied by the jumping of the whole specimen in each deformation-recovery. After several days from quenching, crystals showed weaker jumping which was also reducing with each thermo-mechanical cycle. The average values of the integral thermal effect remained the same from cycle to cycle. Although the starting temperature of burst-like reverse martensitic transformation stochastically varied from cycle to cycle, it showed a general tendency to decrease with an increasing number of cycles until the burst-like effect disappears completely. The heating rate does not significantly affect the position of the DSC peak. Low temperature aging of the specimens resulted in the gradual weakening and disappearance of the burst-like strain recovery. Thus, thermal treatment and loading regimes should be optimized for high-cycle applications of Cu-Al-Ni alloys.
Keywords: shape memory alloys (SMA); strain recovery; martensitic phase transformation; differential scanning calorimetry (DSC)

1. Introduction

High-quality single crystalline shape memory alloys (SMA) outperform conventional polycrystalline materials in actuator applications in terms of precise control of deformation and long fatigue life [1,2].

Thermomechanical and shape memory properties of single crystalline SMAs are strongly anisotropic. For instance, the recoverable shape memory strain differs considerably for different crystallographic directions. Some SMA single crystals, like Ni-Fe-Ga-Co, Cu-Al-Fe-Mn, and Cu-Al-Ni, also exhibit strong anisotropy of shape memory kinetics [3,4]. For certain orientations, these crystals manifest an extraordinarily fast rate of strain recovery. This effect is also referred to as "burst-like strain recovery" [3-7]. In contrast to the shape recovery in conventional SMAs which occurs slowly over a wide temperature range of about 10 K showing relatively low temperature sensitivity, the burst-like strain recovery occurs in a very narrow temperature interval less than a few tenths of a degree [5,6]. The burst-like recovery of shape memory (SM) strain completes almost instantly and is often accompanied by the jumping of the sample. The initial velocity of the sample exceeds up to 30 m/s [3,6].

http://dx.doi.org/10.18720/MPM.4612020_4

Actually, the phenomenon of burst-like martensitic transitions has been known for many years. Machlin and Cohen [8] were possibly the first to report burst martensitic transformations in Fe-Ni and Fe-Ni-C alloys. Later, burst-like martensitic transformations were observed in Au-Cd, Ni-Ti, Fe-Ni-C, Pu-Ga alloys [9]**.** Such transformations occur apparently instantaneously in the time interval of an audible click [9]. The duration of the burst was estimated by Entwistle [10] to be about 10^{-4} to 10^{-3} s. However, direct experimental evidence for that is lacking. Most of the authors report that the burst usually stops before the transformation is complete. In contrast to that, we observed complete burst-like strain recovery in Ni-Fe-Ga-Co [3,6] and Cu-Al-Ni single crystals [11]. The origin of this effect can be ascribed to interphase stresses. A more in-depth analysis of the influence of elastic interphase stresses on the parameters of martensite–austenite transitions in SMA crystals can be found in [11-13].

In recent decades, Cu-based SMAs have emerged as potential material for a variety of applications, such as high damping materials, sensors, and actuators [1]. Although Cu-Al-Ni crystals are well-known SMA materials [12,14], some of their properties like burst-like shape memory strain recovery require more in-depth investigation. Our present knowledge on the effect of burst-like strain recovery is limited only to sporadic observations of the effect in Cu-Al-Ni alloy crystals and estimations of the transformation energy [11].

Up to now, burst-like shape recovery has been observed in Ni-Fe-Ga-Co, Cu-Al-Ni, and Cu-Al-Fe-Mn shape memory alloy crystals [3-6,11], which can restore the original shape almost instantaneously in a very narrow temperature range. The burst-like recovery of SM strain is often accompanied by the jumping of the sample. It is of interest whether this effect is reproducible at multiple cyclic repetitions. We observed a good reproducibility in $Ni_{49}Fe_{18}Ga_{27}Co_6$ crystals, however, multiple cyclic operations were limited by the natural fragility of the crystals. In this study, we focus on burst-like SM recovery at cyclic operation in Cu-Al-Ni crystals and calorimetric effects associated with strain recovery.

Picornell et al. [15,16] were probably among the first researchers who reported anomalous DSC peaks during the burst-like shape recovery. They observed a sharp calorimetric peak during the heating of compressively pre-deformed Cu-Al-Ni single crystals. The peak was ascribed to the γ′- β type transformation of the mechanically formed γ′ martensite to the high temperature β phase. The γ′ martensitic phase disappeared after the first heating run, therefore, in the second cycle, the DSC peak reverted back to its typical form corresponding to a β–β' transformation.

The objective of this article is to investigate new shape memory materials based on Cu-Al-Ni single crystals and their treatment for future applications of burst-like strain recovery.

2. Materials and Methods

Cu – 14.02% wt. Al – 4.0% wt. Ni single crystal were pulled from own melt on a seed orientated along [001] direction by Stepanov growth technique. This growth technology provides high quality and nearly net shape crystals with smooth side surfaces. Cylindrical (Ø5×10 mm^3, mainly for the mechanical test) and prismatic (1.5×2.5×4.5 mm^3 for mechanical and calorimetrical experiments) specimens were cut from 5 mm-diameter crystal rods by spark erosion. The specimens were annealed at 1233 K for 15 min and quenched in water at room temperature. Some experiments were performed on the specimens after additional aging at 455K during 4h. The samples were polished and etched in an aqueous solution of HNO_3 to remove erosion slag and mechanically deformed layers. All specimens were compressed to a full shape memory strain which was over 8% along [001] in each experiment. The compression was performed at a near room temperature (~290-295 K) using an Instron 1342 testing machine at a strain rate of 5×10^{-4} s^{-1}. Transformation temperatures and latent heats of transformations in the undeformed samples after thermal treatment were measured using a Mettler Toledo 822e differential scanning calorimeter with 10 K/min rate of cooling/heating. A heat flux type differential scanning calorimeter (DSC6300, Seiko Instr.) was used for calorimetric measurements of heat flows during the strain recovery in deformed specimens. Details of the calorimetric method can be found in [17].

The rate of shape recovery was measured by a homemade laser interferometer setup with a measurement range of $10^{-7} - 10^{-2}$ m/s [18]. When heated to the transformation temperature, the deformed specimens underwent SM strain recovery which in some cases was accompanied with a shockwave travelling in [001] direction leading to jumping of the whole crystal. The jump was registered by a video camera for estimation of initial speed of the specimens. More than 60 experiments on compression and SM strain recovery were conducted with one specimen in several experimental series.

3. Results and discussion

According to differential scanning calorimetry (DSC) curves shown in Fig. 1, samples quenched at room temperature had both martensitic and austenitic phases. DSC heating and cooling diagrams reveal two main peaks with complex features implying the superposition of several processes. They can be ascribed to multiphase transformations with characteristic (start and finish) temperatures of 245K, 262K, and 281K, 301K at heating and 253K, 248K, and 243K, 233K at cooling, respectively. So martensitic and austenitic phases are present in the initial specimens at room temperature before their deformation by compression. A small difference between the latent heats of the direct and reverse transformations indicates good reversibility of the martensitic transformations. The broad asymmetric shape of the DSC peaks are probably because of multistage martensitic phase transformations.

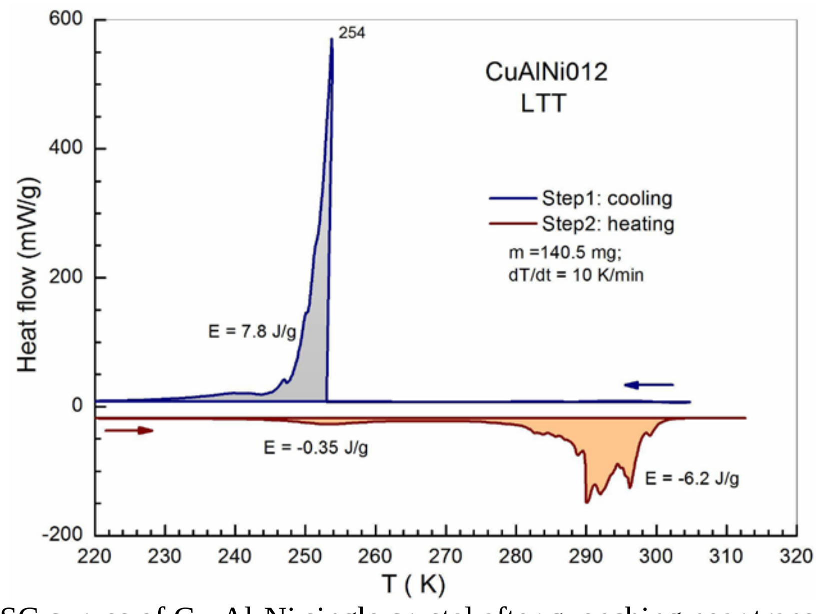

Fig. 1. DSC curves of Cu-Al-Ni single crystal after quenching near transformation temperatures at the first cooling and heating

Figure 2 shows compression (σ–ε) curves for the crystal after quenching in water (a) and quenching followed by aging. Both stress-strain curves look relatively smooth and have no sharp stress drops similar to those observed in Cu–13.5 (13.6) wt.%Al–4.0wt%Ni [11,16] and other crystals with burst-like recovery [3,6,15,19]. The curves show good reproducibility after loading-recovery cycling (over 60 cycles). After unloading, the SM strain is about 8%.

Figure 3 shows interferometer data of the shape recovery rate near the temperature of phase transformation for the sample heated at a constant rate of 2 K/min. It should be noted that the magnitude of the shape recovery rate goes above the upper limit of the instrument range and therefore cannot be measured by the laser interferometer.

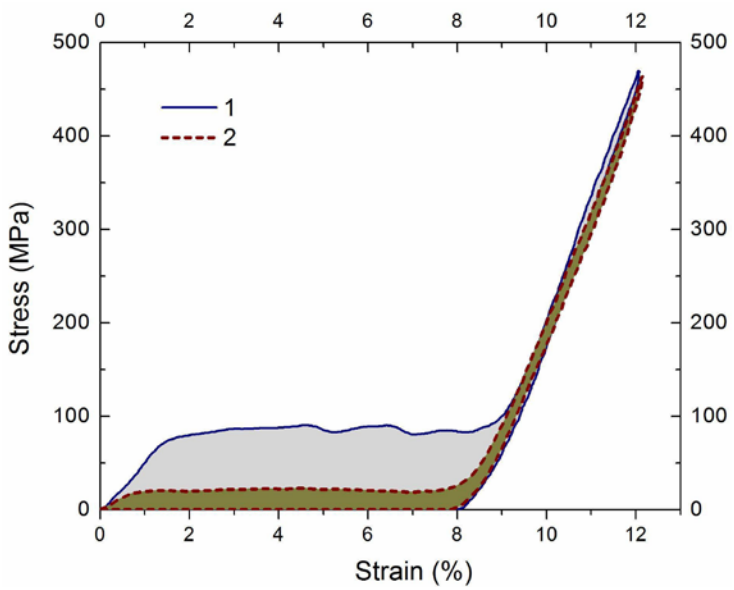

Fig. 2. Stress–strain curves of Cu-Al-Ni single crystalline sample under uniaxial compression along [100] at temperature of 293K; for the sample after quenched (1) and for quenched and aged (2)

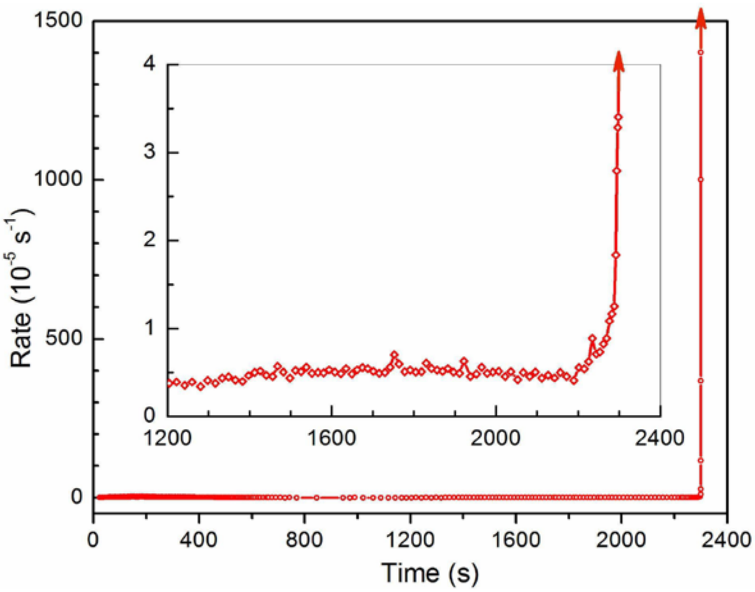

Fig. 3. Rate of strain recovery in deformed Cu-Al-Ni crystal versus time at heating near the temperature of reverse martensitic transformation measured by laser interferometer (heating rate is 2 K/min)

On top of that, burst-like shape recovery is accompanied by jumping of the sample (Fig. 4), which complicates the measurements of strain in the specimens. For that reason, we employed an alternative approach and estimated the burst like shape recovery rate from the initial velocity of the jumping samples. Experimental measurements using a kinetic method [5,6] showed that the start velocity can exceed 20-30 m/s, which can serve as a rough indication of shape recovery rate. Indeed, the real strain recovery rate can be much faster than that value and possibly can approach the speed of a shock wave in solid.

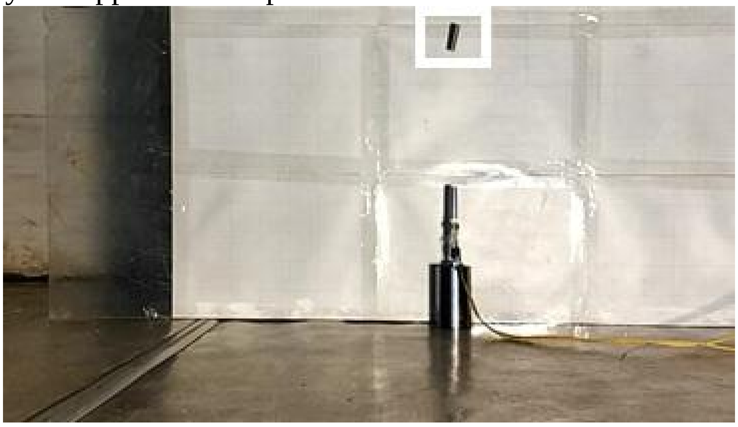

Fig. 4. Video snapshot showing a jump of a 30 g load as a result of burst-like shape memory strain recovery in 1.6g grams Cu-Al-Ni crystal. The initial speed of the crystal is 12 m/s. The launcher consists of a guide tube, an SMA crystal (inside the tube), and a heater

Table 1. Jump express test. Jump strength score: 3 is strong, 2 is medium, 1 is weak jump (or its absent). Heating rate is about ~45 K/min

Number of test	1	2	3	4	5	6	7	8	9	10	11	12	13
Days after quenching	0	0	1	1	1	1	1	1	1	1	5	5	9
Temperature of furnace (T, K)	343	339	337	342	337	340	337	339	341	347	335	342	331
Jump strength (arb. units)	3	3	3	3	3	3	3	3	3	3	2	3	1

The results of the jump test are shown in Table 1 where jump energy was evaluated using a semi-quantitate score from 1 to 3 (1 – the lowest, 3 – the highest). As can be seen from the table, there is a general trend that the jump energy and transformation temperature decrease with time after quenching. The jumps were not observed at temperatures below 330K at the heating rate of 45K/min. Instead only slight trembling or sideways falls of the specimen without jumping were observed.

Figure 5a shows a typical DSC peak for the crystal deformed along [001] during the shape recovery acquired at 0.1 K/min. The peak appears to be very asymmetrical so the maximum of the heat flow practically coincides with the onset of the transformation. It is noteworthy that the curve of DSC heat flow versus temperature (Fig. 5b) forms a loop instead of a peak. This effect can be explained by rapid heat consumption during the burst-like recovery of shape memory deformation which cannot be compensated by the heater. This results in the self-cooling of the sample so that the temperature deviates from the linear progression and drops down by 0.5°C. The reversal of the temperature trend produces a loop on the DSC curve.

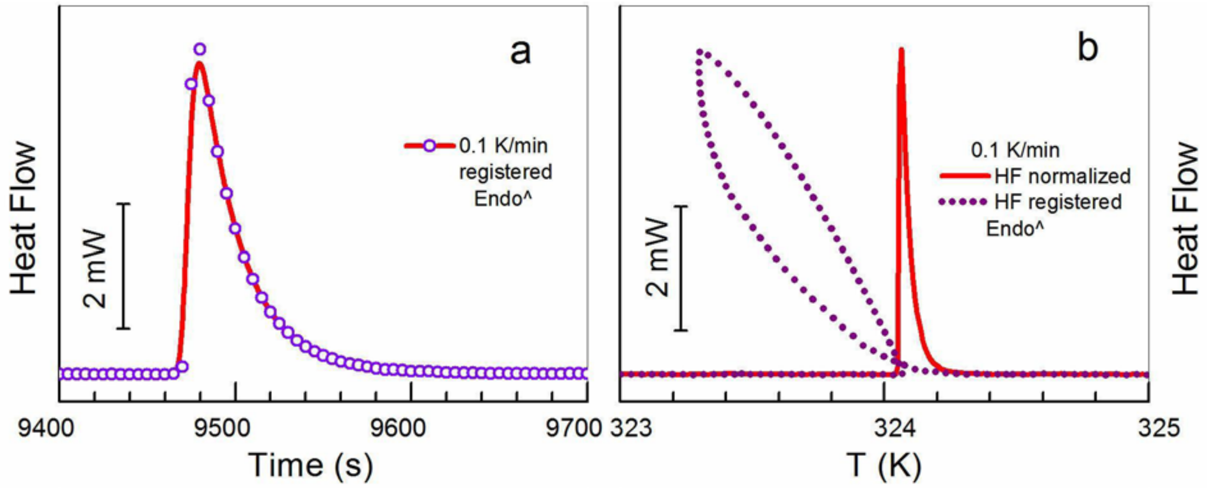

Fig. 5. DSC measurement of heat flow in quenched Cu-Al-Ni crystal versus time (a) and temperature (b) during shape recovery along [001]

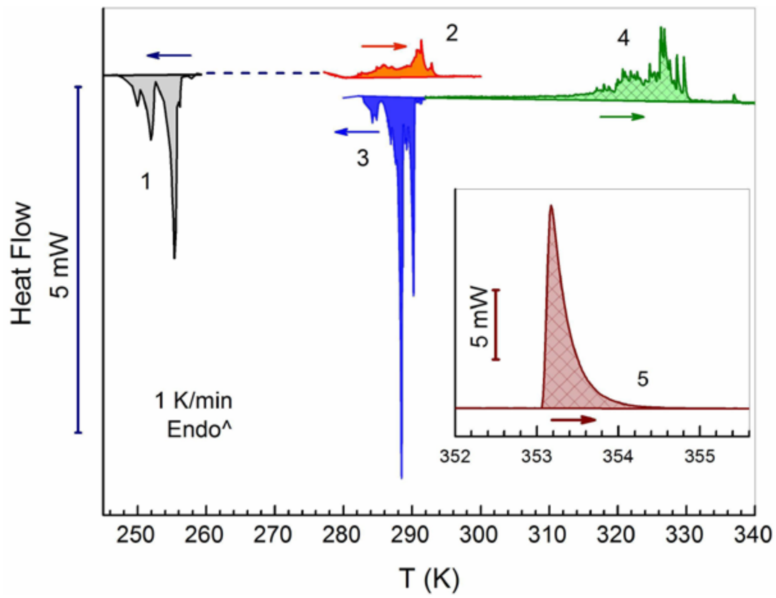

Fig. 6. DSC curves for undeformed Cu-Al-Ni specimens: 1, 2 – cooling and heating of quenched crystal; 3, 4-cooling and heating of quenched and aged crystal. DSC peak of deformed crystals after quenching and aging is shown in the inset (5)

Figure 6 shows DSC curves for the Cu-Al-Ni crystal deformed along [001] direction after quenching (curve a) and after quenching followed by aging (curve b). Aging is known to increase the degree of an order [21]. Also aging increases transformation temperatures by about 30-40 K for pristine crystals and ~25-30 K for deformed specimens. It means that at room temperature martensitic transformation is almost completed, and the crystal is in the austenitic phase. Besides, samples after the thermal treatment were less prone to fast recovery of SM strain. These samples exhibited only weak jumps.

Figure 7a shows DSC curves for the sample compressed along [001] after a different number of deformation-recovery cycles. The maximum of the DSC curve shifts to lower temperatures with an increasing number of cycles. Thus, aging and thermo-mechanical cycling have the opposite effects on the transformation temperature.

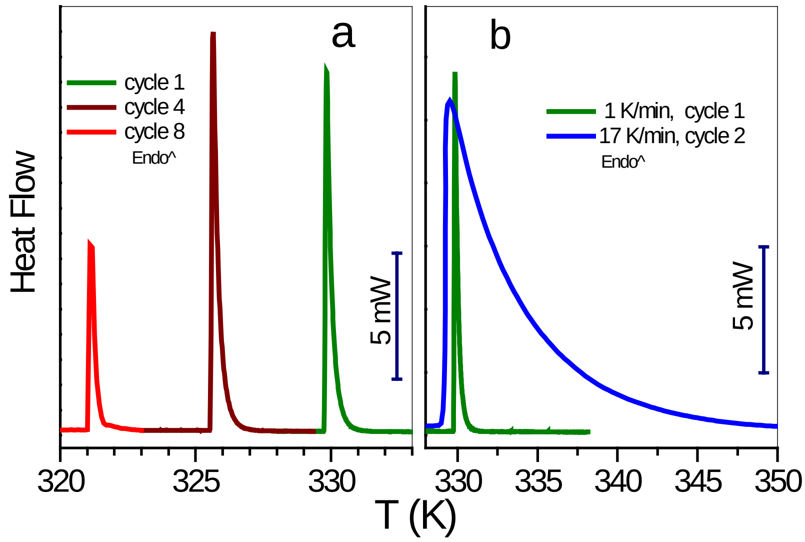

Fig. 7. DSC curves for Cu-Al-Ni crystal deformed along [001].
The shift of transformation temperature at increasing of cycle number (a);
DSC peaks at a heating rate 1K/min and 17 K/min

It is interesting to note that the reverse transformation temperature for the deformed specimen at 1 K/min in cycle 1 and 17 K/min in cycle 2 are the same (Fig. 7b). The effect is similar to that we have recently observed in Ni-Fe-Ga-Co single crystals [22] albeit it is weaker.

4. Summary

We investigated shape memory and associated caloric effects in Cu-Al-Ni crystals. The shape recovery process shows extremely high sensitivity to temperature and completes almost instantly when a critical temperature is reached. DSC study revealed anomalous heat intake during the burst-like shape recovery. The DSC peak position does not show any strong dependence on the heating rate. In contrast, the DSC peak position exhibits a clear shift to lower temperatures with an increasing number of deformation-recovery cycles and time after quenching.

We suggest that the burst-like effect is related to interphase boundary stresses which are typical for multiphase crystals. For that reason, the effect is stronger in quenched crystals and weaker in aged crystals. Relaxation of interphase boundary stresses results in a weaker burst-like effect. The mechanism of relaxation requires further investigation.

Our findings suggest that Cu-Al-Ni crystals and other SMA materials with burst-like shape recovery have the potential as new functional materials and can be used in various technical applications. However, further research and development aimed at the stabilization of the burst-like effect are needed.

Acknowledgments. *The work is supported by Russian Science Foundation [grant number 16-19-00129]. Authors thank Dr. N. Resnina for help with DSC measurements.*

Declaration of Competing Interest. *The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.*

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