

I. TKALCEC\*<sup>#</sup>, D. MARI\*, R. SCHALLER\*

## MECHANICAL SPECTROSCOPY OF ORDERED BINARY Au-Cu

### SPJEKTROSKOPIA MECHANICZNA UPORZĄDKOWANEGO STOPU Au-Cu

We have studied a binary Au-Cu single crystal by mechanical spectroscopy. Upon very slow cooling from high temperatures, additional relaxation peaks arise at lower frequencies in isothermal spectra after the disappearing of the Zener peak below 665 K due to ordering. A high transient peak is visible at 660 K and it progressively disappears on cooling until 625 K. Another high peak is clearly visible upon following heating until 660 K. Above that temperature it decreases in parallel with the increase of the Zener peak. If the ordered structure is obtained by slowly heating the sample that has been quenched from the disordered state, no low-frequency peak is visible in the isothermal spectra, only a much lower background, which further decreases in parallel with the reappearance of the Zener peak. The low frequency relaxations are possibly due to the movement of antiphase boundaries and twin interfaces in the ordered structures.

*Keywords:* Internal friction, gold alloys, order-disorder phase transition, Zener relaxation.

Przy użyciu spektroskopii mechanicznej badano monokryształ Au-Cu. Podczas bardzo powolnego chłodzenia z wysokich temperatur, w skutek uporządkowania pojawiają się dodatkowe piki relaksacyjne przy niższych częstotliwościach w widmach izotermicznych po zniknięciu piku Zenera poniżej 665 K. Wysoki pik przejścia widoczny jest w 660 K i stopniowo znika podczas chłodzenia aż do 625 K. Kolejny wysoki pik jest wyraźnie widoczny podczas ogrzewania do 660 K. Powyżej tej temperatury pik ten zmniejsza się ze wzrostem piku Zenera. Jeśli uporządkowaną strukturę uzyskuje się przez powolne ogrzewanie próbki, która wcześniej została schłodzona w stanie nieuporządkowanym, to żaden pik o niskiej częstotliwości nie jest widoczny w widmie izotermicznym, a tylko obserwuje się o wiele niższe tło, które jeszcze bardziej zmniejsza się aż do ponownego pojawienia się piku Zenera. Relaksacje przy niskiej częstotliwości prawdopodobnie są spowodowane ruchem granic antyfazowych i bliźniaczych w strukturach uporządkowanych.

## 1. Introduction

The AuCu system is one of the best examples of stress-induced diffusion causing a relaxation peak in the mechanical spectroscopy, commonly referred to as Zener relaxation or Zener peak. This peak is present when the atoms form a random solid solution ( $\alpha$ -phase) at high temperature and it fades out [1] upon alloy ordering to AuCuII and AuCuI phases at even low temperatures. AuCuI (tetragonal  $L1_0$  structure) is stable at low temperatures, and AuCuII (with nearly periodic antiphase boundaries) is stable between about 655 K and 688 K [2]. The mechanism and the kinetics of ordering have been studied by several authors using various techniques and it has been shown that the resulting microstructure depends on the thermal history [3,4]. In this work, we examine the low frequency internal friction in ordered structures formed either upon successive cooling steps from the disordered state or successive heating steps of the sample quenched from high temperature.

## 2. Experiments

Single crystal of binary Au-Cu alloy was obtained by the Bridgman technique in a graphite crucible after induction melting of 4N-pure gold and copper. The specimen was cylindrical,  $\varnothing 2 \text{ mm} \times 20 \text{ mm}$ .

Measurements of internal friction and of dynamic modulus were performed in an inverted torsion pendulum as a function of temperature and as a function of frequency, respectively. Temperature spectra were obtained in forced mode at a frequency of 0.5 Hz during heating or cooling at the rate of 2 K/min under vacuum. Frequency spectra in the range 0.001 Hz - 5 Hz were obtained during a stepwise isothermal process with a step of 5 K after 90 min annealing at each temperature. The strain amplitude was  $5 \times 10^{-5}$ . One surface of the annealed and quenched sample was polished and the microstructure obtained upon ordering was observed by an optical microscope.

\* ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, INSTITUTE OF CONDENSED MATTER PHYSICS, STATION 3, CH-1015 LAUSANNE, SWITZERLAND

<sup>#</sup> Corresponding author: iva.tkalcec@epfl.ch

### 3. Results

The temperature spectra of internal friction and dynamic modulus obtained on heating and cooling of a binary AuCu single crystal are presented in Fig. 1. A strong hysteresis is observed between 620 K and 690 K. Only the high temperature flank of the Zener peak is visible on cooling. Below 645 K, internal friction quickly decreases, coinciding with a rapid increase of the dynamic modulus. Upon heating, the internal friction remains relatively low until 685 K when it suddenly increases, accompanied by a dynamic modulus decrease. At higher temperatures, only a very low background is observed.

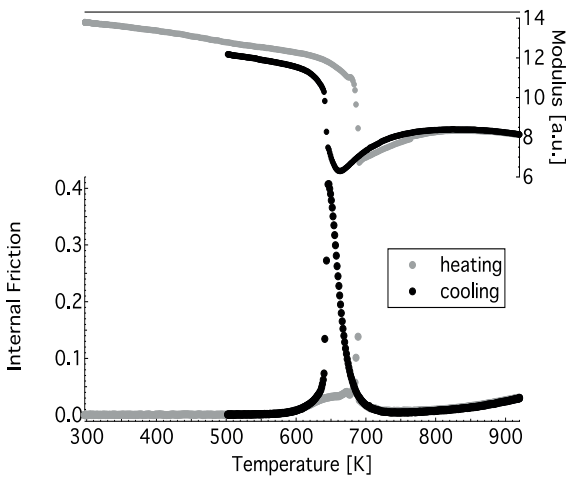


Fig. 1. Internal friction and dynamic modulus temperature spectra for a binary AuCu single crystal.

The sample was annealed for 15 min at 923 K and then quenched in water to preserve the disordered microstructure at room temperature and create an ordered structure on a subsequent heating. Isothermal spectra were then obtained during successive stepwise heating runs starting from 593 K with a step of 5 K. For clarity, Fig. 2 displays only the curves obtained from every second measurement. At low frequencies, only a background is observed. The Zener peak at 614 K is very low, and it gradually increases in the subsequent isothermal spectra. The background only shifts to higher frequencies until 644 K. Above that temperature it starts to decrease gradually. The decrease is abrupt above 686 K. In the last curve at 696 K, the Zener peak has a maximum at a frequency higher than the pendulum limit, and only its low frequency flank is visible in the figure.

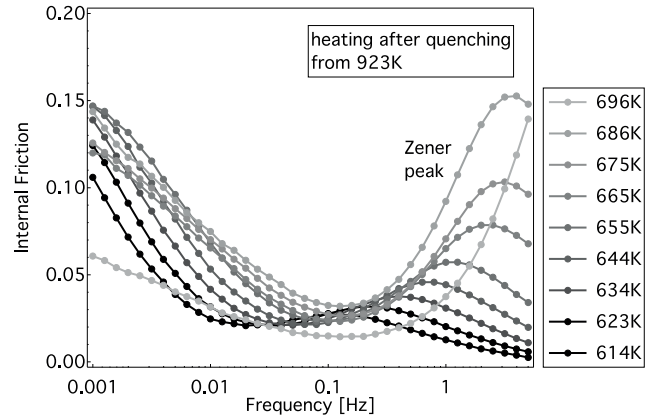


Fig. 2. Isothermal internal friction spectra of a binary AuCu single crystal. The spectra are obtained after successive heating steps of the sample that has been previously heated to 923 K for 15 min and then quenched. Only a background is observed in the low frequency region. This background starts to decrease above 644 K in parallel with the increase of the Zener peak

Figure 3 presents the isothermal spectra obtained during successive stepwise cooling steps from 707 K with a step of 5 K. Some spectra are omitted for clarity. At 665 K, the height of the Zener peak strongly decreases and a new relaxation peak (P1) is visible at about 0.016 Hz. The P1 peak is a transient peak, its height strongly decreases with further cooling.

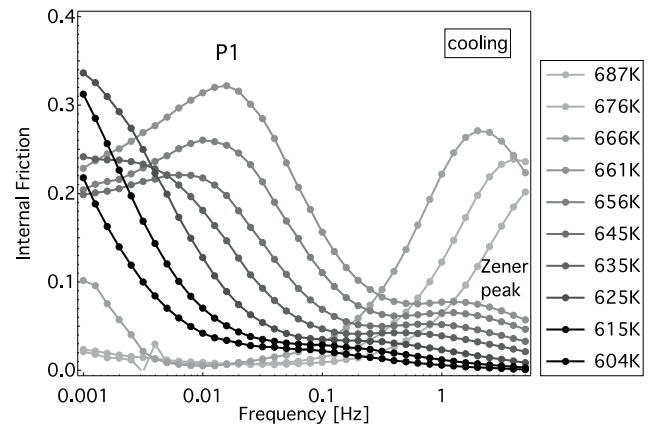


Fig. 3. Isothermal internal friction spectra of binary AuCu single crystal obtained upon successive stepwise cooling steps. After the strong decrease of the Zener peak, a high transient peak is visible at 660 K and it progressively disappears until 625 K

After the final temperature of 594 K reached in cooling (not shown), new isothermal spectra were obtained during successive heating steps in a step of 5 K. For clarity, not all spectra are presented in Fig. 4. A low frequency peak, P2, is clearly visible. Its height is very high (0.35) and almost stable upon successive heating steps until 666 K when the peak starts to decrease in parallel with the increase of the Zener peak at higher frequencies.

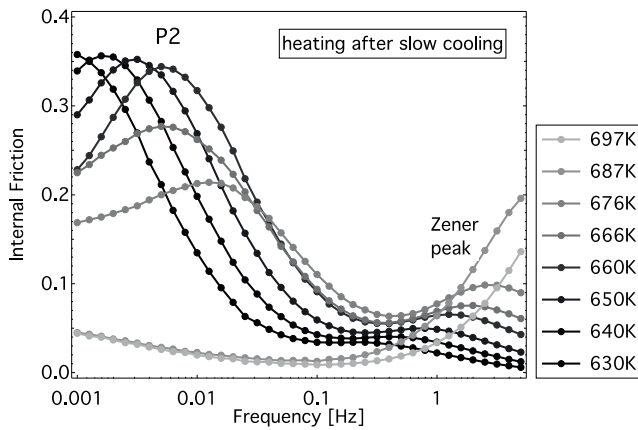


Fig. 4. Isothermal internal friction spectra of binary AuCu single crystal obtained after successive heating steps of a sample that has been previously stepwise cooled from a disordered state. A low-frequency peak is observed until 660 K above which it starts to decrease and it completely disappears above 687 K

The sample microstructure as observed by optical microscope on a polished surface after ordering under different conditions is presented in Fig. 5.

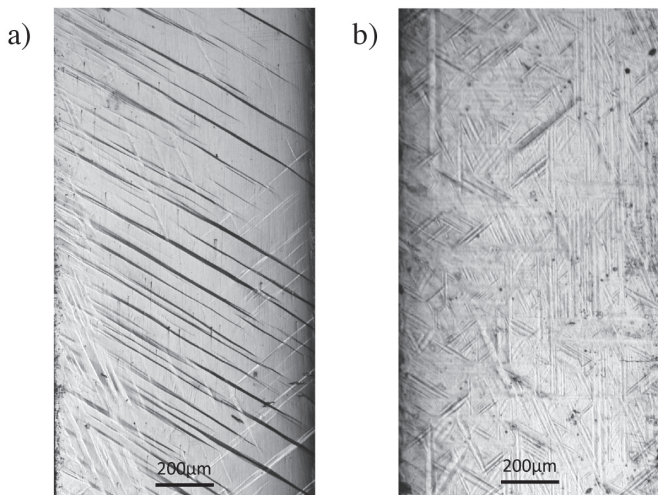


Fig. 5. a) Variants visible on a polished surface after ordering at 598 K of the sample that has been previously heated to 923 K for 15 min and then quenched. b) Twinned structure visible on a polished surface after ordering upon successive stepwise cooling from 707 K

#### 4. Discussion

A grain boundary peak is regularly observed in gold alloys [5] adjacent to the Zener peak. It occurs at higher temperatures in temperature spectra or at higher frequencies in isothermal spectra. No such peak is observed in Fig. 1, confirming the monocrystalline nature of our sample.

De Morton and Leak [6] have reported the height of the Zener peak of 0.8 at 652 K for oscillations at 1 Hz for a polycrystalline sample. In our measurements, the maximum value of internal friction due to the Zener relaxation is found to be 0.407 (Fig. 1). As, in our case, the specimen is a single crystal, and the intensity of the Zener relaxation depends on the orientation, it is not surprising to find a lower peak height.

It is not possible to calculate precisely the activation energy for the Zener peak in a disordered structure using our measurements. The value obtained using three measurements during cooling is found to be  $E_a = (2.09 \pm 0.05)$  eV with the limit relaxation time  $\tau_0 = (1.1 \pm 0.9) \times 10^{-17}$  s. Using the master-curve technique [5], the activation energy of the peak P2 is found to be  $E_a = (2.03 \pm 0.01)$  eV with the limit relaxation time  $\tau_0 = (9 \pm 5) \times 10^{-15}$  s. The longer relaxation time for the peak P2 compared to the Zener peak leads to the conclusion of the higher dimensionality of the defect responsible for such peak.

Upon slow cooling from the disordered state, a AuCuII structure may be formed first remaining stable in a 30 K range. It is characterized by a high density of antiphase boundaries, nearly periodic every five unit cells. The peak P1 observed upon slow cooling only between 661 and 635 K in Fig. 3 could be attributed to the movement of antiphase boundaries in the AuCuII ordered structure.

The fully AuCuI ordered alloy contains many fine-scale ordered  $L1_0$  variants having their  $c$  axis randomly oriented along one of the three possible directions [3]. The formation of a finely twinned structure reduces the internal stresses due to the formation of the tetragonal AuCuI. The twin interfaces could be responsible for the peak P2. The slow cooling produces a very high density of twin boundaries (Fig. 5b), giving rise to a high peak P2. The ordering upon heating after quenching produces apparently a much coarser structure (Fig. 5a), resulting in a much lower background that is possibly the right flank of a smaller peak that appears at even lower frequencies.

#### 5. Conclusions

A low frequency mechanical spectroscopy has been measured in an ordered binary Au-Cu sample at the first time. New relaxation phenomena are observed for the ordered structures. If an ordered structure is obtained by slow cooling, it is characterized by relaxation peaks. First, an intermediate relaxation peak is observed between 661 K and 635 K and it is possibly due to the antiphase boundaries in AuCuII. Upon further cooling leading to the formation of AuCuI, another peak is observed at even lower frequencies. It could be due to the twin interfaces in the AuCuI structure. This peak is absent if the ordered AuCuI structure is obtained upon heating after quenching from disordered state at high temperature, only a much lower background can be observed. The microstructure of ordered AuCu clearly depends on the thermal history of the sample.

#### Acknowledgements

Varinor, Branch of Richemont International SA is acknowledged for financial support.

#### REFERENCES

- [1] J. Hennig, D. Mari, R. Schaller, Order-disorder phase transition and stress-induced diffusion in Au-Cu, *Phys. Rev. B* 79, 144-116 (2009).

- [2] Y. Feutelais, B. Legendre, M. Guymont, New enthalpies determination and in situ X-ray diffraction observations of order disorder transitions in Au<sub>0.5</sub>Cu<sub>0.5</sub>, *Acta Mater.* 47, 2539-2551 (1999).
- [3] M. Hirabayashi, S. Weissmann, Study of CuAu I by transmission electron microscopy, *Acta Metallurgica* 10, 25-36 (1962).
- [4] J. Bonneaux, M. Guymont, Study of the order-disorder transition series in AuCu by in-situ temperature electron microscopy, *Intermetallics* 7, 797-805 (1999).
- [5] A.K. Maier, I. Tkalcec, D. Mari, R. Schaller, Grain boundary formation stages in a deformed yellow gold single crystal studied by mechanical spectroscopy, *Mater. Sci. Eng. A - Struct. Mater. Prop. Microstruct. Process* 560, 466-472 (2013).
- [6] M.E. deMorton, G.M. Leak, Zener relaxation in the Copper-Gold system, *Metal Science Journal* 1, 182-186 (1967).

*Received: 10 April 2015.*