ISOCHRONAL COOLING AND ORDER-DISORDER TRANSITION IN STOICHIOMETRIC CuAu ALLOY

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Microhardness of stoichiometric CuAu single-crystal was measured for two different types of isochronal cooling from the disordered state above $T_{O/D} = 410\,°C$. It is shown that there is a difference between the microhardness of the ordered sample measured in the regime of conventional isochronal cooling and the microhardness obtained after an isochronal annealing/quench step, following immediately after a standard disorder annealing of the sample. This difference shows that the state of the sample is influenced by the heating process from room temperature to the annealing temperature in the conventional isochronal regime and explains the absence of thermal hysteresis effects near order-disorder temperature in earlier isochronal resistometric and microhardness experiments on CuAu.

K e y w o r d s: microhardness, copper-gold intermetallic compound, long-range order, isochronal cooling, order-disorder transformation

PŘECHOD POŘÁDEK-NEPOŘÁDEK PŘI IZOCHRONÁLNÍM CHLAZENÍ STECHIOMETRICKÉ SLITINY CuAu

Na monokrystalickém vzorku stechiometrické slitiny CuAu byla měřena mikrotvrdost ve dvou různých režimech izochronálního chlazení z neuspořádaného stavu nad $T_{O/D} = 410\,°C$.

Byl prokázán rozdíl mezi mikrotvrdostí uspořádaného vzorku, měřeného v běžném režimu izochronálního chlazení, a mikrotvrdostí, naměřenou po kombinaci „izochronální žíhání + kalení“, vždy bezprostředně následující po standardním „rozuspořádavacím“ žíhání vzorku.

Pozorovaný rozdíl hodnot mikrotvrdosti svědčí o tom, že při konvenčním izochronálním režimu je stav vzorku ovlivňován průběhem jeho ohřevu z pokojové teploty na žíhací teplotu. To vysvětluje, proč nebyly projevy tepelné hysteréze pozorovány v předchozích izochronálních měřeních mikrotvrdosti a elektrické rezistivity slitiny CuAu.

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1. Introduction

The order/disorder phenomena in stoichiometric CuAu show several interesting features. Below about 410 ℃ the originally disordered face-centered cubic alloy exhibits long-range order (LRO) in two variants: In a shallow region below this temperature (about 385–410 ℃) the orthorhombic long-period antiphase structure CuAuII is found in equilibrium, whereas the tetragonal $L1_0$ CuAuI-phase is stable at lower temperatures [1].

New results of differential scanning calorimetry (DSC) and dynamic resistometric measurements, showing the so-called *retro-effect* [2, 3], are reasons of extensive studies of ordering processes in the CuAu alloy in recent years. For certain thermal pre-treatment of the sample the order-disorder transformation temperature during heating slightly *decreases* upon *increasing* the heating rate, which contradicts to the expected effect of overheating [4]. This fact was interpreted as a result of a 'stabilisation' of the CuAuI phase against complete transition into CuAuII [5, 6]. In order to study a correlation between structural changes in CuAu and the evolution of LRO, microhardness (MH) measurements have been performed recently [7]. The results demonstrate clearly an influence of the LRO on MH, but unlike *in-situ* experiments, where thermal hysteresis of about 60 K was observed [2, 3, 6, 8], within the isochronal temperature intervals of 10 K no hysteresis between heating and cooling experiments could be detected. The same findings were reported in [9] where the author performed a detailed investigation using electrical resistivity measurements with even lower isochronal temperature intervals of 5 and 2 K.

The aim of the present paper is to report the results of a comparative study of MH during two different isochronal cooling procedures, which should elucidate the possible role of the actual heating process from room temperature to the annealing temperature during conventional isochronal procedure.

2. Experimental

The investigation was performed on a single-crystalline CuAu sample with approx. dimensions of $3 \times 3 \times 2.5$ mm. The single crystal was prepared by the Bridgman method, subsequently annealed at 750 ℃ for 22 hours and finally quenched into water. In fact the sample is an actual single crystal in the disordered cubic state only, because in the ordered state a domain structure consisting of different ordered variants and antiphase-boundaries is formed. The composition of the sample was checked by the energy-dispersion analysis in an electron microscope JEOL JEM 2000 FX. The composition of the sample was (51.5 ± 0.5) at.% Au and (48.5 ± 0.5) at.% Cu.

Thermal treatments were carried out in a vertical resistance furnace with the well-defined temperature gradient outside of the temperature plateau. A purified

argon atmosphere was used during annealing in order to prevent surface oxidation and to improve the conditions of thermal equilibration.

For MH measurements a LECO M-400-A microhardness tester was used. MH values (in HV) and their standard deviations were obtained from 10 widely spaced indentations made on the polished sample surface for each thermal annealing step (Vickers pyramid with 100 g load, dwell time of 10 s).

All MH-measurements were done at room temperature. However, prior to the measurement the sample was subjected to an appropriate thermal treatment (temperature program) and mechanical polishing. In this comparative study we used two different temperature programs of isochronal cooling.

The first one – a conventional isochronal cooling – is schematically shown in Fig. 1. The temperature program #1 consists of consecutive isochronal annealing steps (10 minutes) started from the temperature of 500 ℃. Between the individual annealing steps the sample was quenched into water (quenching rate: about 1000 K/s), then MH was measured and re-heated to the new annealing temperature by inserting into the furnace.

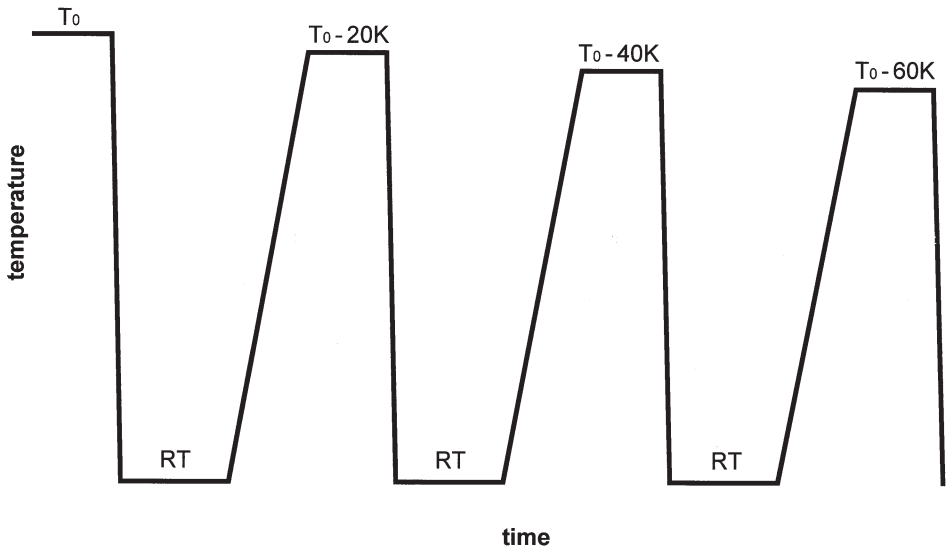

Fig. 1. Schema of a conventional isochronal cooling (temperature program #1) from T_o = = 500 ℃; (ΔT = 20 K, Δt = 10 minutes).

In order to demonstrate the possible influence of ordering processes during the heating periods (from room temperature up to the annealing temperature) on mea-

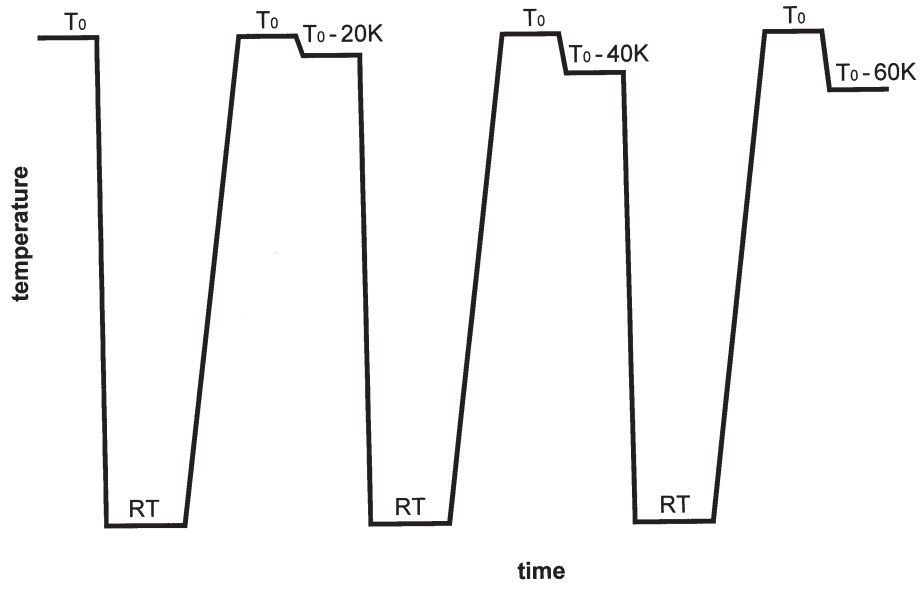

Fig. 2. Schema of the temperature program #2 (T_o = 500 °C, ΔT = 20 K, Δt = 10 minutes).

sured MH-values, we prepared the temperature program #2, which is schematically shown in Fig. 2. The thermal treatment of the sample consists again of consecutive isochronal annealing steps (10 minutes) which were followed by quenching into water for the measurement. Prior to the every isochronal annealing the sample was annealed at 500 °C (10 minutes in temperature plateau of the furnace) and then the sample was transferred fast from plateau temperature into appropriate position in the furnace temperature gradient. This way the sample was cooled from disordered state to the isochronal annealing temperature and its state was not influenced by ordering processes at temperatures lower than the annealing temperature.

The actual temperature of the sample was measured by a thermocouple, the cooling of the sample in furnace did not take more than 20 s.

3. Results

In Fig. 3 the measured MH-values and their standard deviations (SD) are plotted as a function of annealing temperature T_a for both temperature programs of isochronal cooling. It will be shown next to MH-values themselves that also the SD-curves contain a useful information dealing with the ordered state of the

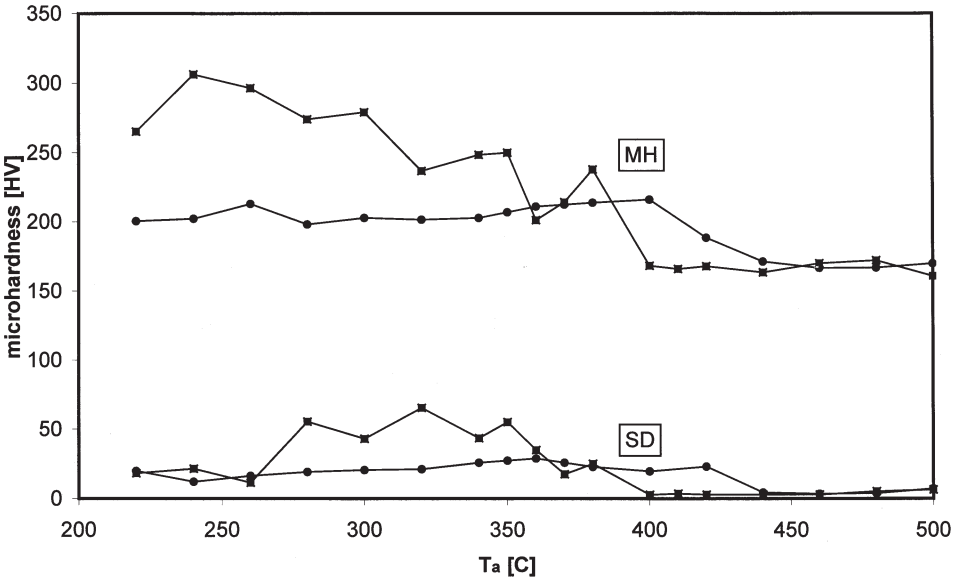

Fig. 3. Temperature dependence of microhardness (MH) and standard deviation (SD) of measured MH-values for a CuAu sample isochronally cooled using temperature program #1 (•) and #2 (■), respectively – see the text. The full lines serve as a guide for the eye.

sample. Up to the temperature of 440 °C the obtained results clearly depend on the temperature program.

In case of conventional isochronal cooling (circles •) we should read the MH vs. T_a dependence from the right to the left (the actual course of experiment). Upon cooling MH shows a steep increase below about 440 °C, a maximum at 400 °C, followed by a plateau in MH down to 220 °C. Note the similar behaviour of the temperature dependence of the standard deviation of the MH-values (circles •). The increase of the SD-values starts also at 440 °C, the "ordering" maximum is reached at 420 °C, below the flat absolute maximum at 360 °C the SD-values decrease monotonically down to about 240 °C.

The curves obtained using temperature program #2 (squares ■) are actually not sensitive to the sequence of the annealing temperatures, because the pre-annealing at 500 °C deletes completely the previous thermal history of the sample. The measured MH-values reflect therefore mainly the state, which was developed during 10 minutes of annealing at the appropriate temperature. The MH remains constant and low in the "disordered" range between 500 and 400 °C. A maximum is achieved at about 380 °C, which exceeds the corresponding value obtained using conventional isochronal cooling. Below 380 °C a local minimum of MH at 360 °C is

detected at the level of the plateau of the curve #1 (circles •). After the next cooling the MH-curve increases continuously (with the absolute maximum at 240 ℃) when considering the scatter and SD of the measured values. The corresponding SD--curve shows a steep increase from low "disordered" values with a broad maximum near 320 ℃, well above the level of the SD-curve #1. Below 260 ℃ the SD-values for both temperature programs are practically the same.

4. Discussion

Both solid-solid transformations in the CuAu are of first order and both are connected with typical thermal hysteresis effects (undercooling, overheating). This can be shown e.g. using data of "half-life" transformation times τ, determined from calorimetry, X-ray and resistivity measurements [10], as discussed in [6]. In the temperature dependence of τ (Fig. 4) two peaks correspond to temperature intervals, where the transformations proceed very slowly – the slowing down is responsible for the thermal hysteresis.

From the MH-curve #1 (circles • in Fig. 3) a typical *order-hardening* [11] can be seen at temperatures below $T_{\mathrm{O/D}} = 410$ ℃, if comparing the microhardness with the plateau level above 440 ℃. Two MH-values, namely for 420 and 400 ℃ are

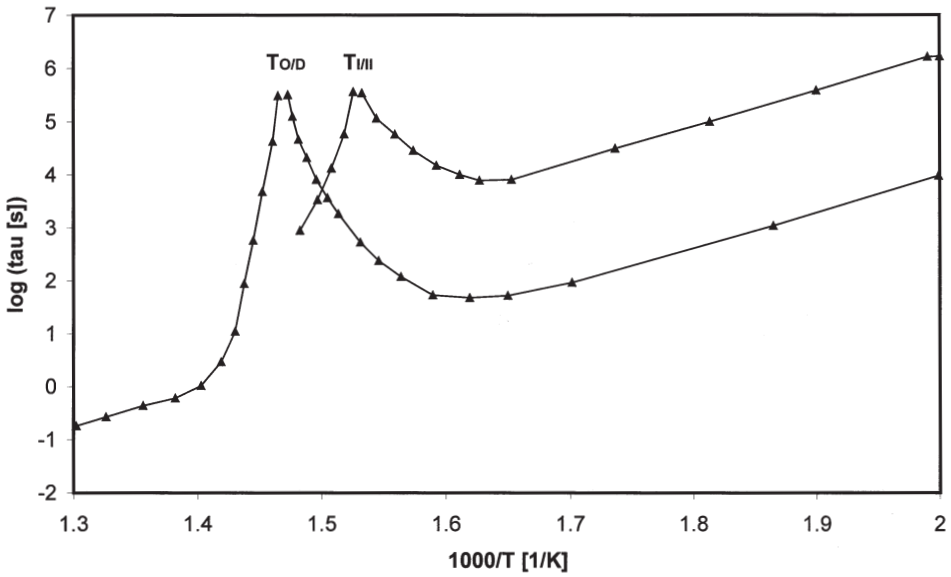

Fig. 4. The logarithm of "half-life" time for transformations in the CuAu against inverse absolute temperature (data from [10]).

worth noting. The former because it was obtained for the annealing temperature above $T_{O/D}$, therefore no LRO should be present in the sample. The latter seems to be in contradiction with the long ordering "half-life" time for 400 ℃ (about 10 hours – see Fig. 4), taking 10 minutes annealing into account. Similar behaviour was found for SD-curve #1 (circles •). On the other hand, the curves measured for the temperature program #2 (squares ■) have not such discrepancies.

The explanation of the difference is simple – the sample, which was after quenching from 440 ℃ inserted into furnace set to the new temperature of 420 ℃ was partly ordered during heating and the ordering was not disordered completely at the annealing temperature, because the disordering "half-life" time is of the order of 10^2 s. The suddenly increased standard deviation of the microhardness at this temperature reflects the fact that the sample is not homogeneous as far as the ordering relates. Different indentations give a scatter of MH-values, because of generally different local arrangement of ordered nuclei or distinct antiphase domains and antiphase boundaries and/or twins generated in the ordered matrix.

The temperature dependence #1 reflects not only an integral influence of all preceding annealings during an isochronal cooling procedure, but all periods of heating from room temperature should be taken into account, as well.

On the other hand, the microhardness-curve #2 reflects mainly results of ordering processes during the individual annealing steps and can be only partially influenced by the cooling resulted from the transfer of the sample from the standard disordered temperature in the furnace.

Low and homogeneous (low SD) microhardness is typical for the disordered cubic state of the CuAu single crystal at temperatures down to 400 ℃ and the *order-hardening* arises at lower temperatures. In spite of the local minimum at 360 ℃ was confirmed by two additional points at 350 and 370 ℃, it is difficult to wonder about its reasons only in terms of phase composition. Moreover, the monotonic increase of MH down to 240 ℃ is a complex problem, because the *order-hardening* is not only process influencing the measured MH-values in this case, but a mobility and/or concentration of mobile dislocations and a development of the internal stress fields must be also considered. On the other hand the starting decrease below 240 ℃ is very probably a result of a slower kinetics of the ordering in this temperature range – compare TTT diagrams in [12, 6] with the annealing time of 10 minutes.

The SD-curve #2 (squares ■) shows also an interesting temperature dependence. As mentioned above low SD-values above 400 ℃ correspond to homogeneous surface of the single-crystalline CuAu sample in the disordered state. The increase and the flat maximum of the SD-values below 400 ℃ reflect a development of LRO and the inhomogeneity of the surface. A lowering of the standard deviations below 280 ℃ is most probably also an effect of the kinetics – an increasing density of ordered nuclei at lower temperatures may be expected. The lower is the temper-

ature, the more of ordered nuclei is hit in the region of an indentation, the more homogeneous is the microhardness.

It is well known that the order-disorder phase transition in CuAu is of the first order and *in-situ* studies are therefore accompanied by a big thermal hysteresis of up to 50–60 K, depending on the rate of temperature change [2, 3, 6, 8]. Isochronal measurements of resistivity change, on the other hand, did not show a hysteresis [13].

Isochronal annealing experiments are of a quasistatic character: The system has enough time during the period of isochronal annealing to relax in the direction of a stable microstructural state corresponding to the actual annealing temperature. Whether or not this 'equilibrium' value is actually reached will be a question of involved relaxation times, annealing temperature and the actual heating process (period) from room temperature to the annealing temperature. On the other hand, during an *in-situ* experiment the microstructural state of the sample is *continuously changed*.

By comparison of curves #1 and #2 in Fig. 3, it follows that the absence of undercooling in case of conventional isochronal cooling experiments is a result of fast ordering processes during heating periods. Paradoxically the isochronal *cooling* curve #1 shows signs of *overheating* (see the MH-value for 420 ℃), because prior to the MH-measurement the sample was quenched from the disordered state at 440 ℃ and subsequently *heated* from room temperature to 420 ℃. The MH-value corresponds to the order-hardening, resulting from the LRO, which persisted after the ten minutes' annealing at 420 ℃ from the fast ordering during the last *heating* period (compare appropriate times in Fig. 4). On the other hand the order-hardening in case of the isochronal MH-curve #2 is shifted to lower temperatures at about 40K (comp. mainly the SD-curves) – it clearly shows the presence of an *undercooling*, i.e. a thermal hysteresis effect, comparable with an *in-situ* experiment.

5. Conclusions

1. Both isochronal cooling MH-curves in Fig. 1 prove the existence of the order-hardening, i.e. a correspondence of the increasing LRO and the hardening in CuAu.

2. The MH vs. T_a dependence is influenced by the temperature program of the isothermal cooling, especially by heating periods from room temperature to annealing temperatures.

3. It was shown that fast ordering processes during heating periods are responsible for the absence of thermal hysteresis by conventional isochronal experiments near order-disorder transition in CuAu.

4. A special temperature program of the isochronal measurement, suppressing the influence of heating periods, leads to similar thermal hysteresis effects, as for *in-situ* experiments.

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