A study of order-disorder transformation in CuAu alloy under an external load

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Abstract

In-situ microscopic video cinematography of the sample in a compression test machine and *post-mortem* 3-D atomic force microscopy (AFM) were used for the surface study of the order-disorder transformation on CuAu single- and polycrystalline samples. A special control of the compression force allowed to determine the thermal expansion of the sample in the compression axis.

The change of symmetry from the disordered fcc structure to the tetragonal CuAuI-phase or the orthorhombic long-period structure CuAuII is accompanied by the anisotropy of lattice parameters and also by local generation of c-variants of structural domains. Macroscopic results of these processes can be observed as a dynamic change of the surface morphology and external dimensions of the sample. These effects are connected with orientation of c-variants with respect to the surface of the sample (so called *surface effect*) and with respect to the compression axis (so called *stress ordering effect*).

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

1. Introduction

The phenomena connected with the structural order/disorder transition in stoichiometric CuAu can be observed *in situ* on the surface of the sample. Below approximately 683 K the originally disordered face--centered cubic alloy exhibits Long-Range Order (LRO) in two variants: In a shallow region below this temperature (about 658–683 K) the orthorhombic long-period antiphase structure CuAuII is found in equilibrium, whereas the tetragonal $L1_0$ CuAuI-phase is stable at lower temperatures [1].

A simultaneous application of modern *in situ* experimental methods provides new results and is therefore one of reasons of extensive studies of ordering processes in the CuAu alloy in recent years [2–10].

In order to study a correlation between structural order changes in CuAu and thermal history and external load (compression stress), a combination of *in--situ* microscopic video cinematography of the sample in a compression test machine and *post-mortem* 3-D Atomic Force Microscopy (AFM) has been used for the surface study of the order-disorder transformation on CuAu single- and polycrystalline samples. The aim of the present paper is to report and summarize the main results of performed measurements and observations.

2. Experimental

The investigation was performed on a single--crystalline CuAu sample in a cylindrical form with the diameter of 3.90 mm and the height of 3.66 mm. The crystal was prepared by the Bridgman method, subsequently annealed at 1023 K for 22 hours and finally quenched into water. The orientation of the disordered single crystal was determined by Laue method, Miller indices of the basal plane of the cylinder were (7 3 22). The sample is in fact a 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.

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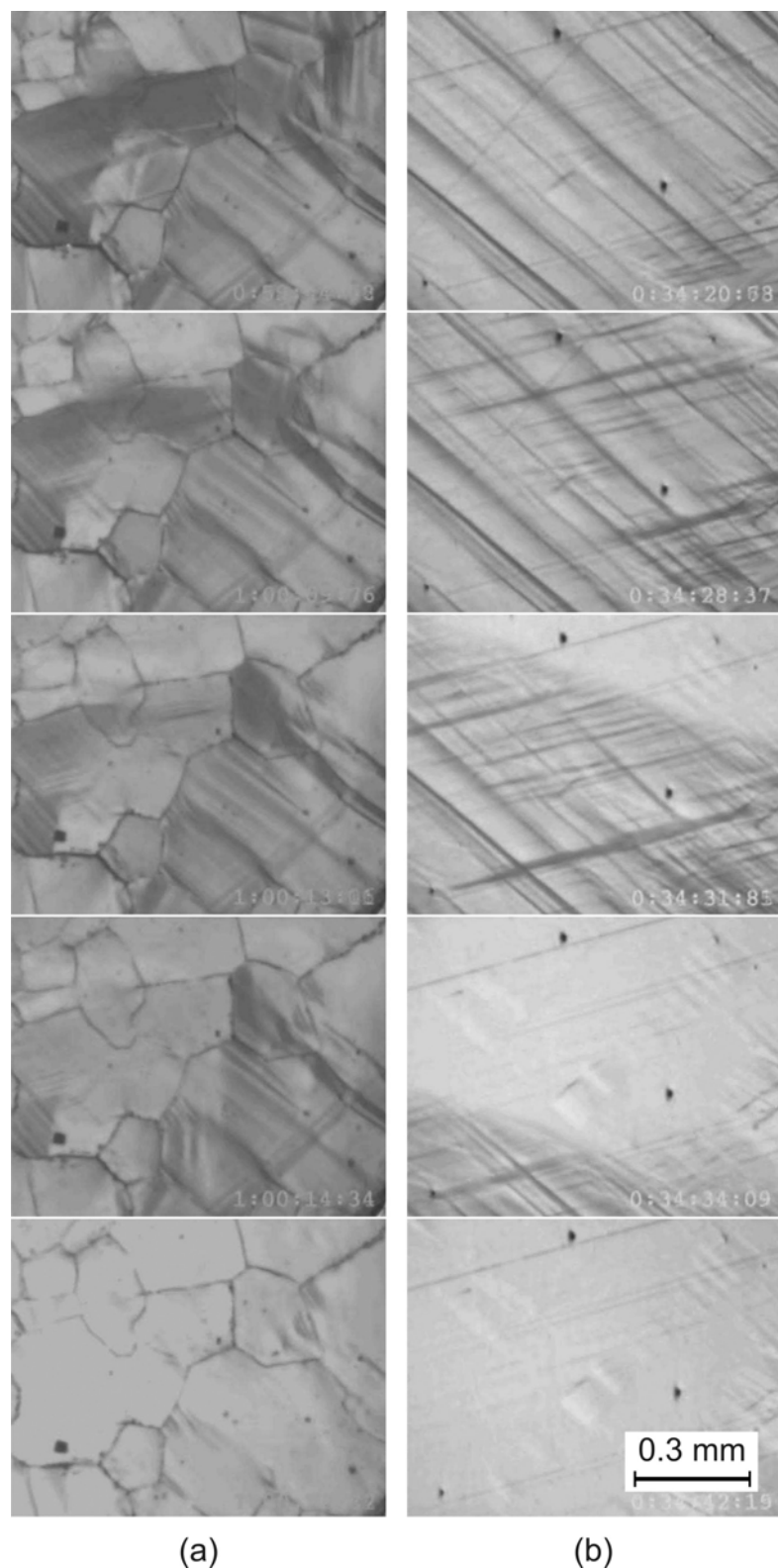
Fig. 1. Cinematography of the order-disorder transformation in CuAu (heating rate $= 10$ K min^{-1}, transformation time approximately 6 s at about 793 K): a – polycrystalline sample under compressive stress about 1 MPa, b – single crystal, stress-free conditions.

The cylindrical polycrystalline sample (diameter of 4.92 mm, height of 4.64 mm) was prepared by arc

melting of pure metals in argon atmosphere, the subsequent treatment was the same as for the single crys-

tal. The composition of both samples was checked by the energy-dispersion analysis in an electron microscope JEOL JEM 2000 FX. The composition of the samples was identical: (51.5 ± 0.5) at.% Au and (48.5 ± 0.5) at.% Cu.

The arrangement for the *in-situ* microscopic video cinematography was the following: the sample was fixed by ceramic plates between deformation machine heads in a vacuum chamber and heated by eight focused infrared lamps – the rates of linear heating were in the range of $3–20 \, \text{K} \, \text{min}^{-1}$. A flat area of the sample surface was prepared by fine polishing. Observations on this area were made by a microscope QUESTAR QM-100, enabling the observation of the sample from a distance of about 150 mm with the lateral resolution of $1–2 \, \mu\text{m}$. The magnification was set up so as the TV screen, displaying the image made by a CCD-camera, represented the area of $1 \, \text{mm}^2$ of the sample surface. The external compressive stress (about $3–5 \, \text{MPa}$) was applied in a computer controlled creep regime and the appropriate deformation (dimension changes) of the sample was recorded as a function of time and temperature.

Atomic Force Microscopy (AFM) observations were performed at room temperature using Rasterscope 4000.

3. Results and discussion

All performed experiments reflect clearly only effects related to the order-disorder transition. The order-order transition between tetragonal CuAuI and orthorhombic CuAuII cannot be practically observed due to structural similarity of both structures and relatively long transformation time of this transition [9] when compared with characteristic times of used *in-situ* methods.

The study of the order-disorder transformation using Microscopic Video Cinematography (MVC) simultaneously with applied compressive stress in creep regime was focused on observed surface phenomena and their sensitivity to external parameters of the experiment, i.e. external stress, heating rate and initial state of the sample.

3.1. Polycrystalline sample

The evolution of the morphology of the polycrystalline sample during disordering process is shown in Fig. 1a. The sample was quenched from the disordering temperature 773 K, polished and heated at $10 \, \text{K} \, \text{min}^{-1}$ at a compress stress of 0.4 MPa. During the heating from room temperature at first the ordering proceeds and slightly above $T_{\text{O/D}} = 683 \, \text{K}$ the disordered state is restored. This process takes about six seconds and is manifested by gradual disappearing of

systems of dark stria in individual grains. Transformation fronts start to move either from grain boundaries or from a boundary between two stria. In the latter case a pair of fronts is generated whose mutual distance increases. The motion of a front terminates either at a grain boundary or annihilates with another front. The motion of fronts in individual grains is not mutually correlated. Individual grains do not transform all at once. Even a type of reversible grain boundary sliding may be observed. In spite the sliding process being in general an irreversible process of plastic deformation, the observed reversibility is caused by the restoration of the original form of grains during the transformation into disordered cubic state. Apart from some grain boundaries, above 703 K the surface relief returns to the state prior to heating.

This shape-restoration seems to be connected with reversible strain effects of twinning; i.e. the ordering of the quenched sample produces predominantly a system of twins, which disappear in the disordered state. This behaviour can be expected for {101} twins, as {101} are mirror planes in the disordered state [11].

On subsequent cooling of the sample from 773 K no changes of the surface relief down to about 643 K were observed. Around this temperature, systems of dark stria gradually (without a visible front) appeared in each grain as a result of ordering in the sample. This new surface relief is not as sharp as the relief arising during heating of quenched disordered state.

In order to test the reversibility of ordering process in polycrystalline sample we polished now the sample in ordered state and checked, whether or not the flat surface is restored after subsequent disordering (heating) and ordering (cooling). As expected, the surface relief at temperature of 703 K became corrugated, representing a negative or inverted picture of domains in ordered state. At subsequent cooling we obtained only a partially smoothed surface of ordered sample. During the transition into disordered state individual grains therefore restored their original form independently of external load. On the other hand, in ordered state the distribution of domains is partly influenced by external load.

The noticeable thermal hysteresis of the order--disorder transformation, which can be seen in principle at all thermal *in-situ* experiments, is seen in the record of dimension changes of the polycrystalline sample during the measuring cycle (see curves 3 and 5 in Fig. 2). The change of the linear dimension of the polycrystalline sample is caused by the difference in molar volume of the disordered and ordered phase ($V_{\text{ord}} < V_{\text{disord}}$).

In general, the influence of external compressive stress on the observed effects in polycrystalline CuAu was negligible. This fact can also be clearly seen by comparison curves 3 and 5 in Fig. 2 – the results of dilatometry (in stress-free conditions) [12] are qualit-
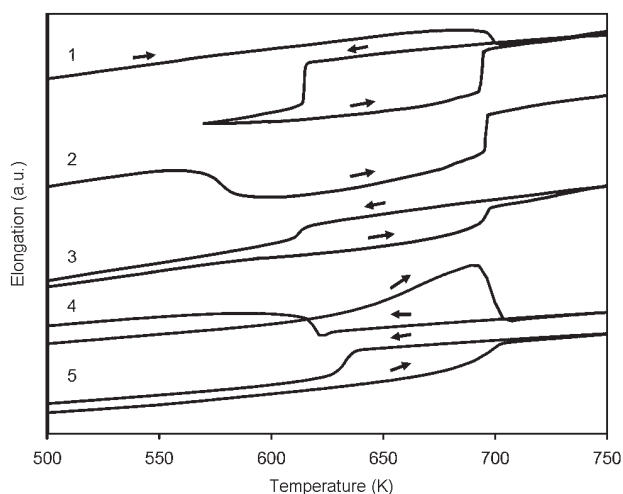
Fig. 2. Elongation of CuAu samples measured as a function of temperature during a thermal cycle: curve 1 – single crystal, deformation machine (see the text); curve 2 – single crystal, deformation machine, heating from quenched disordered state; curve 3 – polycrystalline sample, deformation machine; curve 4 – single crystal, dilatometer [12]; curve 5 – polycrystalline sample, dilatometer [12].
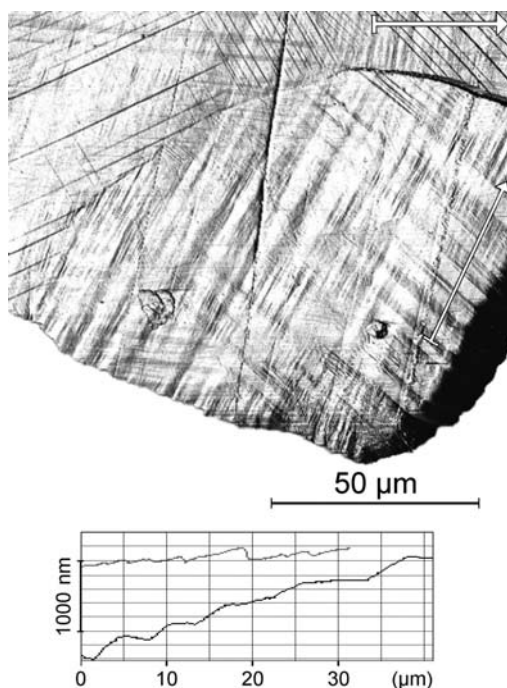

Fig. 3. Two-dimensional AFM-picture of ordered CuAu polycrystalline sample, the height profiles correspond to the white arrows in the picture [10].

atively the same as the measured dimension changes under external stress. The applied stress does not influence significantly the ordering process in the polycrystalline sample. The stress is probably significantly lower than the local internal stresses in the material.

In Fig. 3 the surface topology of the ordered polycrystalline sample observed by AFM is shown. Aside of a grain boundary relatively broad parallel bands and sharp lines are observed on the surface. The height profiles, corresponding to two arrows across appropriate parts of the surface, clearly document that the lines have a character of sharp steps. The profile of bands has an arch or triangle form. The lines belong to irreversible changes of the surface morphology and are the deformation traces (slip lines or {111} deformation twins [13]). The bands consisting of fine stria disappear in the disordered state – they seem to be connected with {110} twins.

3.2. Single crystal

Figure 1b shows an example of surface morphology effects connected with disordering transformation in the CuAu *single crystal* in the absence of external load. The sample was quenched from 773 K, polished and subsequently heated (10 K min^{-1}). The situation slightly above $T_{O/D}$ is displayed on the picture showing the newly ordered state transforming into the disordered cubic phase. Similarly as in the polycrystalline sample the transformation takes about six seconds. The cinematography analysis revealed only a single transformation front travelling across the surface with a velocity of about 150 μm s^{-1}. Note the new twins created and travelling on the ordered side of the transformation front. Above 703 K the surface relief returns to the state prior to heating.

On subsequent cooling dark stria gradually (without a visible front) appeared. Repeated heating and cooling confirmed the reversibility of observed effects.

The known crystallographic orientation of the surface in disordered cubic state enabled to determine the indices of observed traces and quantitatively evaluate the AFM observations (e.g. heights and widths of observed surface steps and their slopes). The main results can be summarised as follows (details are in [14]):

– In all used thermal treatments of the material the order-disorder in CuAu is accompanied by deformation in both {111} and {101} planes. It was confirmed that the deformation in {101} planes vanishes in disordered state, whereas the deformation in {111} planes persists. The deformation in {111} planes is not present exceptionally only in the absence of external load.

– The height of individual steps in {111} planes is (77 ± 25) nm, independently on external load. The height of steps in {101} planes is between 200 and 450 nm in an absence of external load, for experiments under load it was (49 ± 15) nm only. The height of steps does not depend on used heating or cooling rate.

– From the ratio between the height and the width of deformation steps the slope angle can be estimated. For $\{101\}$ and $\{111\}$ planes the slope was $1.8° \pm 1.1°$ and $5.6° \pm 2.3°$, respectively.

In contrast to the polycrystalline sample the influence of external compressive stress on the observed effects in the single crystal was substantial. The surface morphology of the state ordered under stress differs surprisingly little from the disordered state, only a few irreversible deformation traces on the surface were formed and no dark and bright bands were formed. The surface of the ordered state is almost flat similarly as in the disordered state. During the heating the disordering is accompanied by a single passage of the transformation front, "changing" the flat surface into flat surface again. In the vicinity of the front often signs of plastic deformation (slip lines or twins of the type $\{111\}$) can be observed. The influence of external stress on the ordering in an originally disordered cubic single crystal has surprisingly large macroscopic effect. Note that our experimental configuration is unusual – we observe the basal plane of cylindrical single crystal, while the vertical applied stress is perpendicular to the horizontal cylinder-bore axis. If the cross section of cylindrical single crystal was circular in disordered state then after ordering under external load the cross section got an elliptical form with ellipticity up to 0.9. After subsequent disordering and quenching, or disordering and ordering in stress-free conditions, the sample got its original circular cross section. The explanation of this behaviour is very simple. It is based on the influence of compressive stress on generation of c-variants of ordered domains, so called *stress ordering effect* [15] – see below.

The influence of the external stress can be also seen from a comparison of thermal elongation measured by a dilatometer (in stress-free conditions) and dimension changes measured under external load in deformation machine (see curves 4 and 1 in Fig. 2). The curve 1 consists of three parts – heating, cooling and repeated heating of the single crystal. Before the beginning of this measurement the sample was ordered under external load and then the crystal was turned about the horizontal cylinder-bore axis by $90°$ in grips of the deformation machine. The lattice parameter c of the ordered structure is lower than the cubic lattice parameter, the ordered regions therefore are compressed along the c-axis and expanded across the c-axis in comparison to the dimensions in disordered state. These simple facts may explain the effects in dilatometry of a long cylindrical CuAu single crystal (curve 4), assuming the so-called *surface effect*. The c-axes tend to arrange themselves normal to a free surface, in particular in the stress-free conditions of ordering [16]. This arrangement of ordered domains in the sample is responsible for the elongation of the cylindrical sample in the ordered state. The
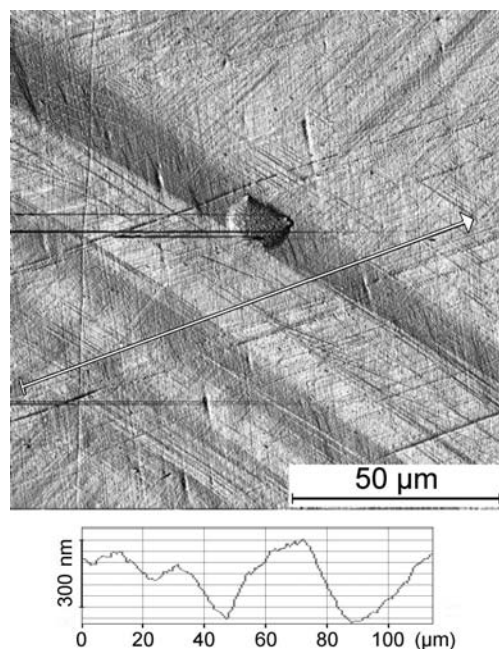

Fig. 4. Two-dimensional AFM-picture of ordered CuAu single crystal, the height profile corresponds to the white arrow in the picture [10].
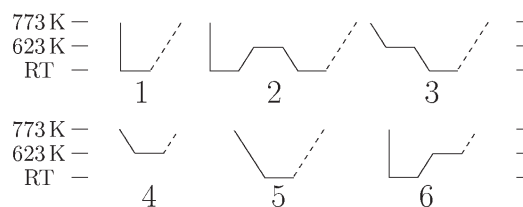

Fig. 5. Schema of various thermal regimes for thermal treatment of CuAu samples prior their heating.

record of measured dimension changes under external stress (curve 1) differs substantially from the results of dilatometry – the "hysteresis curve" corresponds qualitatively to the *stress ordering effect*, because the compression axis favours the nearest possible c-axes of ordered domains and the number of c-variants is reduced in the single-crystalline matrix. The resulting domain structure is then responsible for the contraction of the ordered sample along the compression axis. The first heating part of the curve 1, started as described above, is in fact very similar to the results of the dilatometry measurements, reflecting the influence of the *surface effect*. In this case naturally the observed contraction above $T_{O/D}$ is caused by a combined effect of previous *stress ordering* and rotation of the crystal before the heating. The curve 2 was measured by heating of quenched disordered single crystal, the curve clearly shows a contraction, coming from the ordering process influenced by the *stress ordering effect*. Above $T_{O/D}$ the disordering is accompanied by

sample elongation (compare with the first and third part of the curve 1). The *stress ordering* is in a close relation to the shape restoration effect as observed in CuAu e.g. in [17]. We did not recognise any qualitative difference in *stress ordering* for applied stress in the range of 1–5 MPa.

In Fig. 4 the surface topology of the ordered CuAu single crystal, as observed by AFM, is shown. Ordering is again connected with the presence of broad parallel bands on the surface. Their height profile is qualitatively the same as in case of the polycrystalline sample.
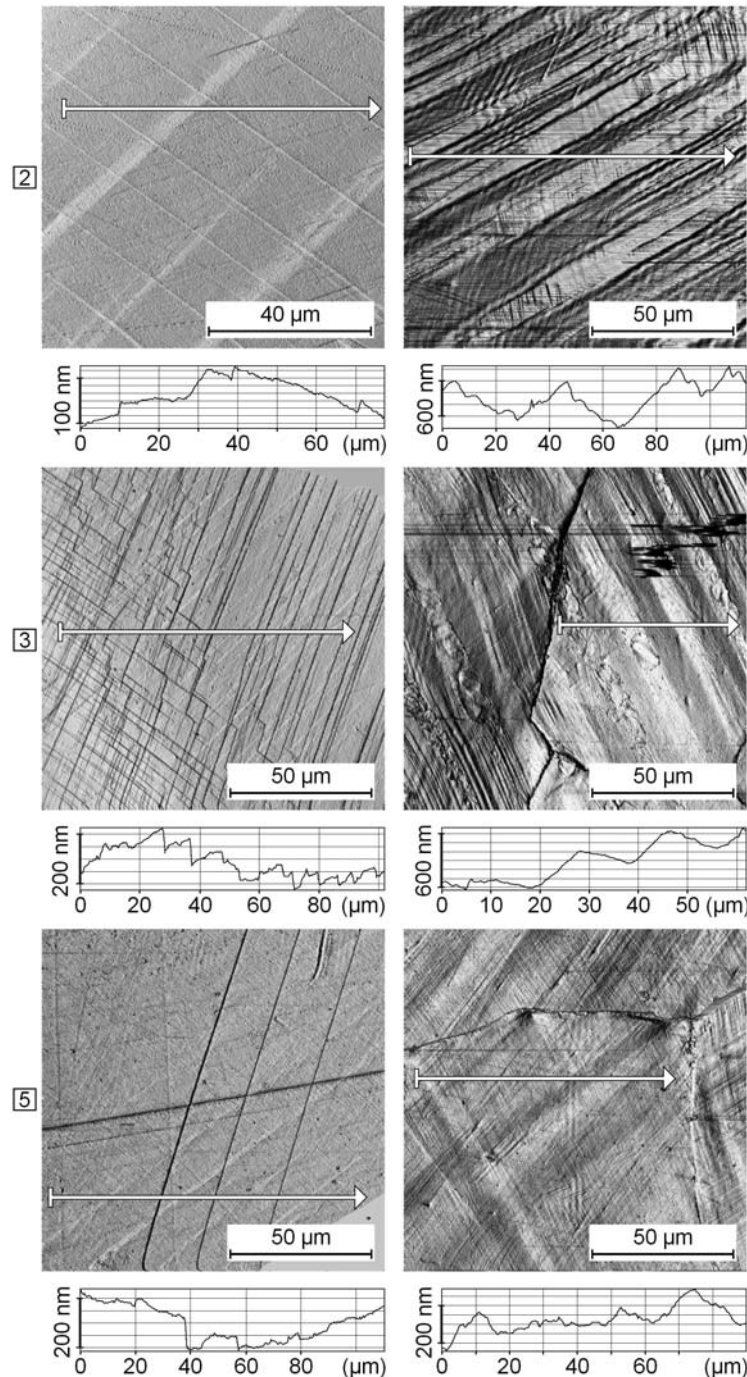

Fig. 6. Two-dimensional AFM-pictures of ordered CuAu single crystal (left) and polycrystalline sample (right), the height profiles correspond to the horizontal arrows in the picture. The numbers in squares correspond to thermal treatment regimes shown in Fig. 5.

3.3. Thermal history effects

Properties of CuAu alloy in disordered state are independent of thermal history of the sample. On the other hand, the morphology of ordered domains and related properties depends on ordering conditions (thermal history, external load). We examined polycrystalline samples and the single crystal in six different thermal regimes, as schematically shown in Fig. 5. The detail description of differences observed by MVC can be found in [14]. Using AFM only final ordered states morphology arising from regimes 2, 3 and 5 at room temperature could be observed.

The comparison of corresponding AFM pictures is summarised in Fig. 6. The relief arising from ordering of quenched disordered state (regime 2) is the most pronounced, the height of individual bands is up to 1 μm. On the other hand, the height of bands observed in regime 3 is about 0.5 μm for the polycrystalline sample, the single crystal shows only permanent deformation traces in {111} planes. The relief of regime 5 shows the lowest contrast. The height of bands is only about 0.1 μm for the polycrystalline sample, while the surface of the single crystal is almost smooth showing only exceptionally permanent deformation traces in {111} planes.

4. Conclusions

1. The order-disorder transition in CuAu can be observed by *in-situ* MVC both on polycrystalline and single crystal samples. The transformation is accompanied by deformation in both {111} and {101} planes. It was confirmed that the deformation in {101} planes vanishes in the disordered state, whereas the deformation in {111} planes persists. The shape--restoration in disordered state seems to be connected with reversible strain effects of twinning; i.e. the ordering of the quenched sample produces predominantly a system of {101} twins, which disappear in the disordered state.

2. The influence of external compressive stress on the observed effects in polycrystalline CuAu is negligible. The applied stress does not seem to be able to influence significantly the ordering process in the polycrystalline sample. It is probably low compared with the local internal stresses in the material.

3. The influence of external compressive stress on the ordering in an originally disordered cubic single crystal has surprisingly large macroscopic effect coming from the ordering process influenced by the *stress ordering effect*. On the other hand, in stress-free conditions of ordering a long cylindrical CuAu single crystal shows the so-called *surface effect* when *c*-axes of ordered domains tend to arrange themselves normal to a free surface of the crystal.

4. The properties of CuAu alloy in disordered state are independent of thermal history of the sample. On the other hand, the morphology of ordered domains and related properties depends on ordering conditions (thermal history, external load). The surface relief arising from ordering of quenched disordered state is the most pronounced, the height of individual bands is up to ten times higher than that of bands arising from ordering of slowly cooled sample.

Acknowledgements

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