Method for \textit{in situ} texture investigation of recrystallization of Cu and Ti by high-energy synchrotron X-ray diffraction

High-energy synchrotron radiation has been used to study \textit{in situ} annealing of cold-rolled Cu and Ti. The measurements were performed using a high-vacuum furnace in transmission geometry and an area detector. The diffraction images were subsequently processed to extract the orientation distribution. The recrystallization process could be followed with a time resolution of the order of 10 s, and good pole figures could be obtained from the very limited amount of data in single diffraction images. The pole figures compare favorably with pole figures of the same material measured \textit{ex situ} with a conventional pole figure goniometer. For Cu, a rapid and complete change from a typical rolling texture to a cube texture was observed after annealing for 20 min at 650 °C. For Ti, changes were more subtle with a tendency for \textit{c}-axes to diminish near the normal direction, as well as for \textit{a}-axes to become aligned with the rolling direction. The method makes it feasible to study the kinetics of recrystallization with quantitative texture analysis.

Keywords: High-energy synchrotron XRD; Recrystallization; \textit{In situ} texture analysis; Cu; Ti

1. Introduction

With the current interest in the dynamics of recrystallization, and the mechanisms that control it [1], \textit{in situ} investigations have become increasingly important. Beside the analysis of the individual grains (orientation and growth) during the recrystallization, also the precise knowledge of the evolution of texture and microstructure that develops during recrystallization can provide insight into mechanical properties of the material under investigation. Many physical and mechanical properties of crystals are anisotropic and, consequently, textured polycrystals will also show directionality and anisotropy.

With high-intensity synchrotron radiation, combined with area detectors, it has become feasible to investigate recrystallization processes of deformed metals \textit{in situ}. If high energies are used, one can perform the X-ray diffraction studies in transmission geometry and, thus, follow these processes throughout the bulk of the material [2]. One of the most prominent features of the recrystallization process is the change in texture. Since an area detector is used, the Debye rings of the lowest-order reflections are recorded simultaneously in a single image. The intensity variations in these rings, and their evolution with time and temperature, can be used to determine the time evolution of texture and infer from it kinetic information about static recrystallization. In addition, particle sizes, nucleation and coarsening can be assessed, based on the shape and size of diffraction spots or the width of the diffraction lines. Because of the lower energies, conventional X-ray sources emphasize mainly surface effects that may not be representative of the bulk material. Many metals oxidize easily at higher temperature and experiments need to be done in vacuum, which is difficult to achieve with a conventional pole figure goniometer. Furthermore, the X-ray flux is generally not high enough to follow the often very rapid recrystallization process and record texture changes \textit{in situ}. Textural changes may occur during the recording of a single pole figure. Neutron diffraction suffers from the same flux limitation.

In this paper, we describe a method and approach for quantitative \textit{in situ} texture studies of recrystallization, which can be extended to phase transformations. We show its application to Cu and Ti.

2. Experimental set-up

All measurements were performed at a side station, ID15C, of the High Energy Beamline, of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The beamline is situated at a multi-pole wiggler insertion device, providing high-energy X-rays up to 250 keV. The beam is monochromatized by a single bounce Si crystal in Laue geometry, and a number of fixed energies are available at the side station, positioned at 6° off the main axis. The experiments reported here were performed at 72 keV (wavelength...
$\lambda = 0.172 \text{ Å}$. A schematic layout of the experimental set-up is given in Fig. 1.

The beam is collimated by two pairs of slits. The first pair defines a beam of $1 \text{ mm} \times 1 \text{ mm}$, and the second pair is set to $1.2 \text{ mm} \times 1.2 \text{ mm}$ and serves to block the scattering from the edges of the first pair. A photodiode is used to monitor the incoming beam intensity. A fast millisecond-shutter determines accurately the exposure time. The samples were mounted inside a custom-made furnace described below. The X-ray diffraction images were recorded with a $1152 \times 1242$ pixel charge-coupled device (CCD) detector coupled to an X-ray image intensifier. Fig. 2 shows some typical images from these experiments. In some of the experiments, the furnace and sample were oscillated over a few degrees about the vertical axis during exposure in order to get sufficient grain statistics in the powder pattern. The sample to detector distance was 326 mm, and was a compromise between angular resolution in the recorded image and available diffraction angle range $2\theta$, and thus the number of diffraction peaks recorded in a single image. An additional advantage of high-energy X-rays, besides penetration depth, is the fact that the corresponding $2\theta$ angles are small, and thus a limited angular range contains a relatively large number of diffraction peaks.

The samples were heated in a locally built furnace (Fig. 3). The furnace covers the temperature range from room temperature to $900 \text{ °C}$ and works under vacuum to prevent oxidation ($10^{-5} – 10^{-6} \text{ bar}$). It fits on an off-center 4-circle HUBER diffractometer and has been designed to perform diffraction experiments in transmission geometry. Samples were placed on a steel holder $100 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ between two water-cooled Cu connectors. A $4 \text{ mm} \times 6 \text{ mm}$ window was placed in the middle of the steel holder to avoid scattering in the transmission geometry. The samples were mounted with Pt wires. Heating was achieved by passing a current through the steel holder and sample, using an Elind Power supply model 30KL38/80. A 0.5 mm thick Pt/Pt-Rh10 % thermocouple is spot-welded onto the steel sample to detector distance was 326 mm, and was a compromise between angular resolution in the recorded image and available diffraction angle range $2\theta$, and thus the number of diffraction peaks recorded in a single image. An additional advantage of high-energy X-rays, besides penetration depth, is the fact that the corresponding $2\theta$ angles are small, and thus a limited angular range contains a relatively large number of diffraction peaks.

The samples were heated in a locally built furnace (Fig. 3). The furnace covers the temperature range from room temperature to $900 \text{ °C}$ and works under vacuum to prevent oxidation ($10^{-5} – 10^{-6} \text{ bar}$). It fits on an off-center 4-circle HUBER diffractometer and has been designed to perform diffraction experiments in transmission geometry. Samples were placed on a steel holder $100 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ between two water-cooled Cu connectors. A $4 \text{ mm} \times 6 \text{ mm}$ window was placed in the middle of the steel holder to avoid scattering in the transmission geometry. The samples were mounted with Pt wires. Heating was achieved by passing a current through the steel holder and sample, using an Elind Power supply model 30KL38/80. A 0.5 mm thick Pt/Pt-Rh10 % thermocouple is spot-welded onto the steel sample holder. The temperature was controlled by a Eurotherm 2408. The samples were kept under light tension during heating by a spring-loaded mechanism to prevent buckling.

The reproducibility of the oven, including the welding of the thermocouple, was tested by observing the recrystallization of steel samples. Two points can be determined very accurately from inspection of the diffraction images. The first point is the start of recrystallization, around $550 \text{ °C}$, which manifests itself with the appearance of a spotty pattern in the image, corresponding to the onset of grain growth. The second point is the appearance of new powder rings around $700 \text{ °C}$, due to the austenite phase. The calibration experiments established that the recrystallization temperature was reproducible within $10 \text{ °C}$, whereas the phase transition temperature was reproducible within $20 \text{ °C}$.

The furnace is covered by an Al chamber with two facing Kapton windows for entrance and exit of the X-rays. The size of the windows was such that the sample could be rotated over $10 \text{ °C}$ around the vertical axis for better grain statistics and pole figure coverage.

The Cu samples were 99.9 % pure Cu, $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$, and cold-rolled to a reduction of 99.3 %. The samples were heated from $50 \text{ °C}$ to $650 \text{ °C}$ over 18 min and kept at $650 \text{ °C}$ for 4 h. Diffraction images were collected every 50 °C while heating up and, once at $650 \text{ °C}$, every 10 min. Exposure times used were 10 s before the start of the recrystallization, and 5 s after recrystallization began. The sample was oscillated over 4 ° during exposure.

The Ti samples were 80 % cold-rolled pure Ti, $10 \text{ mm} \times 10 \text{ mm} \times 0.175 \text{ mm}$ and mounted in a similar way as the Cu samples. In a first experiment, a 4° oscillation was applied. The sample was heated first by ramping the temperature from 75 to $525 \text{ °C}$ over 13.5 min and then annealed at $525 \text{ °C}$ for 1 h. Diffraction data were recorded every 5 min. After 1 h, the temperature was raised over another 2 hours to $650 \text{ °C}$. A second experiment was done without oscillation, to observe better the nucleation event. In that experiment, the temperature was raised from 25 to $550 \text{ °C}$ in 13.5 min, followed by annealing at $550 \text{ °C}$ for 2 h with exposures every 3 min.

3. Data reduction and analysis

The recorded images were corrected for dark current and spatial distortion using the program FIT2D [3, 4], and subsequently scaled with the incoming beam intensity as re-
corded with the photodiode, in order to correct for the beam decay of the synchrotron source. These corrected two-dimensional images were further reduced to a set of one-dimensional intensity versus ring angle plots, by radial integration in steps of 5°. The 72 intensity values for several diffractions \((hkl)\) were subsequently used to determine the orientation distribution (OD).

A few comments about synchrotron texture analysis are in order [5–8]. Fig. 4 shows the geometry of a transmission diffraction experiment with incoming X-rays, sample and Debye cone with an opening angle \(4\theta\), on which diffracted X-rays lie. If the sample is stationary, only lattice planes \(hkl\) that are inclined by an angle \((90° – \theta)\) to the sample surface diffract. In terms of pole figures, the Debye ring corresponds to a small circle at \((90° – \theta)\) from the sample normal \((Z)\). Intensity variations on the Debye ring (as function of angle \(\delta\)) are proportional to pole density variations in the pole figure.

As is evident, coverage of the pole figure from a single image is minimal. The coverage could be improved by tilting the sample around an axis perpendicular to the incident X-ray and recording several images. Each image contains information about pole densities on a rotated small circle on the pole sphere. Unfortunately, in the case of in situ recrystallization, each image records a different state of the sample, and combining images is questionable.

Information about the orientation distribution is not only obtained from pole density variations within a pole figure (i.e., intensity variations on a single Debye ring), but also from intensity correlations between different diffraction rings \((hkl)\). In the case of face-centered cubic (fcc) Cu, there are 5 rings on the image (Figs. 2a, b), and for hexagonal close-packed (hcp) Ti, there are 15 rings on the image (Figs. 2c, d).

We are going to show the general procedure that was followed with the example of cold-rolled Cu. Combining the intensity information from five \((hkl)\)'s (111), (200), (220), (211) and (311), an attempt was made to calculate the orientation distribution with standard methods of quantitative texture analysis [9]. Information for (111), (220) and (200) is shown in Fig. 5a (note that the (111) small circle is broader than (220), because information from (111) and (222) has been combined). Because of the minimal coverage and lack of normalization, the discrete method from Williams–Imhof–Matthies–Vinel (WIMV) was more appropriate than the harmonic method; but even here, diffraction data were not sufficient to obtain a solution for the OD with a \(5° \times 5° \times 5°\) grid of Euler angles. It was then assumed, in a first iteration, that adjacent small circles on the pole figure had identical intensity variations, and with this assumption an OD could be calculated (using the BEARTTEX software [10]), and recalculated pole figures are shown in Fig. 5b. On those, typical features of a Cu rolling texture are visible.

In a second iteration, the directly observed normalized intensity variations on the small circles were used, and for the adjacent small circles, intensity variations from the recalculated pole figures. This is a better estimate than simply assuming that they are the same. With these data, a new OD and corresponding pole figures were calculated and finally the OD was smoothed with a 7.5° Gauss filter (Fig. 5c).

Clearly, this is not the optimal way to obtain quantitative texture information from a sample, and a broader pole figure coverage would be desirable [8]. However, this has not been possible in this experiment because of furnace and sample geometry and because of the dynamic nature of the recrystallization process. In the next section, we will compare the in situ texture analyses with conventional pole figure measurements on the same samples. We were surprised with the excellent agreement between conventional pole figures measured over many sample orientations within hours, and the synchrotron pole figures obtained with minimal diffraction information within seconds. The same method, illustrated here in detail, was applied to all samples studied in this paper.
4. Results

4.1. Recrystallization of copper

In the case of Cu, the first 5 rings, corresponding to (111), (200), (220), (311) and (222) were recorded in the diffraction images (Figs. 2a, b). Cu showed a drastic change in texture over a brief time interval of a few minutes, as the sample was heated at 650 °C. This is illustrated by the patterns on the CCD images as well as corresponding intensity profiles for (200) and (220) (Fig. 6). Annealing not only changed the intensity distribution, but also the grain structure due to grain growth. The smooth variations along Debye rings in the rolling case (Fig. 2a) are replaced by discrete spots, representing individual crystals (Fig. 2b). The (100) pole figures obtained from the diffraction images illustrate a change from a typical rolling texture (Fig. 7a) to a strong cube texture with a single component (Fig. 7c). The cube component is extremely sharp, as we can estimate from the profiles in Fig. 6b, but we should be aware that the peaks on the profiles are on a small circle that is displaced from the periphery and, thus, do not go through the center of the cube components (c.f. Fig. 3) and overall intensities are, therefore, underestimated in the intensities of the Debye ring.

For comparison, pole figures on corresponding samples were also measured ex situ with a conventional pole figure goniometer, using Cu Kα radiation and 5×5 pole figure coverage. From measurements of 2 incomplete pole figures, the OD was calculated with the WIMV method [10], and re-calculated (100) pole figures are shown in Figs. 7b, d. For the rolling texture the agreement between in situ synchrotron pole figures and pole figure goniometer measurements is excellent with similar pole density distributions, as well as peak maxima (2.96 Vs 2.46 m. r. d., respectively). For the recrystallized texture, the synchrotron pole figure displays basically a single cube orientation with {100} poles...
parallel to rolling and normal directions (Fig. 7c). This is also by far the most important component in the \textit{ex situ} pole figure (Fig. 7d). However, in that case, there is a secondary component, about one tenth in peak pole density, that can be attributed to [111] twinning. It is not clear whether this component was overlooked in the synchrotron data, because the small circle does not cover this particular orientation, or if the comparable \textit{ex situ} sample provided was simply different and subject to a different annealing history.

To highlight the dynamic texture changes, intensities perpendicular and parallel to the rolling direction, and integrated over 5° angular intervals are shown in Fig. 8 as function of the annealing time for (220) and (200). It is obvious that orientation changes occurred very quickly, after only a few minutes of annealing, with few changes occurring after the first hour. Clearly, it would have been more effective to sample the first interval at smaller increments or study the process at lower temperature. Unfortunately, there was no opportunity to repeat this experiment.

The documented dynamic changes illustrate the transformation from a rolling to a cube texture. This transformation is well known, particularly for high stacking fault energy fcc metals, such as Cu and Al [11]. In this paper, which emphasizes methodology, we are not going to add any new information about this transformation. We refer readers to the extensive literature [12], documenting that the development of new grain orientations is aided by the movement of high-angle boundaries [13] and microstructural features. Regions of high curvature due to deformation have been called transition bands [14] and are likely regions for recrystallization, which has recently been modeled with finite element simulations [15].

4.2. Recrystallization of titanium

In order to investigate the applicability of the procedure to lower-symmetry materials, we analysed the recrystallization of hcp Ti. Contrary to cubic crystals, in hexagonal crystals there are fewer symmetric equivalent lattice planes. How-

![Fig. 9. Details of the microstructure visible in the (100) (a) and (002) (b) Debye rings of Ti. Originally, the ring is smooth, but with increasing recrystallization and growth, individual grains are visible.](image)

![Fig. 10. \textit{In situ} texture measurements of titanium. OD was constructed from synchrotron diffraction images of 11 Debye rings, using the WIMV method, and pole figures were recalculated from the OD. (a) Starting material, (b) recrystallized material, (c) difference pole figures (starting–recrystallized). (001), (100) and (110) pole figures are represented in equal area projection. Intensity scale is logarithmic for pole figures and linear for difference pole figures.](image)

![Fig. 11. \textit{Ex situ} texture measurements of similar titanium samples. OD was constructed from incomplete pole figures measured with a conventional pole figure goniometer in reflection geometry, using the harmonic method and imposing orthorhombic sample symmetry [18]. (a) Starting material, (b) recrystallized material, (c) difference pole figures (starting–recrystallized). (001), (100) and (110) pole figures are represented in equal area projection. Intensity scale is logarithmic for pole figures and linear for difference pole figures.](image)
ever, there are more diffraction peaks in the $d$-range of interest. In the experiment, we could rely on 11 reflections, though some of them were overlapping.

No drastic changes in texture were observed in the images (Figs. 2c, d), but a detailed look at diffraction lines reveals that nucleation and growth of recrystallized domains are displayed by a spotty pattern (Fig. 9). Intensity variations along 11 diffraction rings were used to calculate an OD, and from the OD, (001), (100) and (110) pole figures were recalculated, both for the initial material and the recrystallized sample (Fig. 10). Comparing the pole figures, we see no drastic texture changes as in the case of Cu. Both display a texture with c-axes in a distribution inclined from the normal direction towards the transverse, and (100) poles concentrated in the rolling direction (Figs. 10a, b). Difference pole figures (coldworked-recrystallized) reveal some subtle changes (Fig. 10c). The c-axes close to the normal direction disappear during recrystallization, and the (100) maximum parallel to the rolling direction weakens. Is this a real difference or merely an experimental artifact? One way to ascertain this is to look at the raw data: The width of the (100) texture peak (full width at half maximum (FWHM)) on the Debye ring near the rolling direction becomes broader with increasing recrystallization, indicating wider dispersion (Fig. 12).

Also here we have compared the synchrotron pole figures with ex situ pole figures measured with a conventional pole figure goniometer [16, 17], (Fig. 11). Note that also in these measurement the patterns and peak intensities are very similar and identical trends are displayed in difference pole figures. The reason for the smoother and more symmetrical appearance in Fig. 11, as compared to Fig. 10, is that the harmonic method was used in those pole figures and orthorhombic sample symmetry was imposed. The synchrotron pole figures that are based on a single small circles of 11 diffraction peaks appear more realistic.

There is no definite answer yet for the cause of textural changes in hexagonal metals during recrystallization [17]. We have done some texture simulations using the viscoplas-
tic self-consistent theory [18] and assuming soft prismatic and harder basal and pyramidal slip, as well as compressional and tensile twinning, and noted that maxima in the difference pole figures, i.e., grains that disappeared during recrystallization, correspond to relatively undeformed (hard) orientations that did not twin during deformation, particularly those grains with c-axes close to the normal direction and (100) poles preferentially aligned in the rolling direction (Fig. 13a). Minima in the difference pole figures, i.e., orientations that increased, correspond to the most highly twinned orientations (Fig. 13b). This would suggest that highly twinned regions with heterogeneous local deformation and large misorientations of domains act as nucleation sites that grow during recrystallization by a mechanism in which nucleation dominates over boundary migration, as was documented for other hexagonal metals [19].

5. Summary and conclusions

The purpose of this note has not been to investigate recrystallization kinetics of metals. Rather, we wanted to introduce a feasible method that now can be used to investigate recrystallization processes and associated textural changes in detail. It has been shown that by applying the high X-ray flux and the high energies available at synchrotron sources, in combination with CCD-based area detectors, it is possible to study the recrystallization behavior of metals in situ on time scales of seconds. With high energies and transmission geometry, textures of bulk samples can be characterized quantitatively, contrary to conventional laboratory X-ray measurements, which analyse thin surface layers. By analysing the time evolution of the texture peak shapes, it has been possible to follow microstructural and textural changes, like grain nucleation and grain growth. The method opens the possibility to study, on a micrometer scale, the recrystallization kinetics of cold-worked metals, which is of major importance for understanding the macroscopic properties of these materials. The spatial resolution will be important in determining the regions where the cube orientation initiates and the relationship to heterogeneous shear bands.

It has also been shown that using very limited data in a single image, it is possible to reconstruct very reasonable orientation distributions and pole figures. We can, therefore, follow the texture evolution on very short time scales with data increments of a few seconds and without a need to rotate the sample. It would be even possible to reach the sub-second timescale by using an optimized beam line with a fast CCD detector.

High-energy synchrotron X-rays have previously been used for the study of texture evolution during deformation at high pressure in diamond anvil cells [20, 21]. Also, a different approach has focused on using synchrotron X-rays for orientation measurements of individual crystals, either with polychromatic radiation [22, 23] or monochromatic radiation with ray tracing [24]. The bulk mechanical properties of polycrystalline materials, however, are more efficiently determined with methods that average grain orientations. Synchrotron diffraction promises to become a powerful tool for in situ characterization of material changes during deformation, recrystallization and phase transformations.

H.-R. Wenk acknowledges the hospitality at ESRF during a sabbatical leave in spring 2001 and for support from the Humboldt Foundation. We are appreciative to N. Bozzolo (Metz) for providing samples of cold-worked Ti, to M. Darcil Rossel (Barcelona) for assistance with experiments and to F. Sandiumenge (Barcelona) for providing the Cu samples.

References


Correspondence address

ESRF
Dr. F. Berberich
BP 220, F-38043 Grenoble Cedex, France
Tel.: +33 4 7688 2813
Fax: +33 4 7688 2907
E-mail: berberich@esrf.fr