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# Mechanism of Diffusion Induced Recrystallization in Single Crystals of Copper

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**Abstract.**

The microstructure evolution during diffusion induced recrystallization (**DIR**) on the surface {011} of Cu single crystals has been experimentally studied in detail by using a scanning electron microscope. The selected area channelling pattern technique was used for measuring the orientation of the grains in the polycrystalline layer formed by Zn diffusion from the vapour phase. The misorientations of adjacent grains were then determined in terms of rotation angle and axis. The relation between twinning and low-angle grain boundaries depends on the Zn concentration, heat treatment temperature and time.

## Introduction.

In a layer where bulk diffusion occurs, elastic stresses can arise due to the dependence of the lattice parameter on the concentration of the diffusing element. The relaxation mode of these stresses depends on several factors, such as the extent of crystal lattice distortion or annealing temperature. One of the most interesting relaxation processes is the diffusion induced recrystallization (**DIR**). **DIR** at the surface of Cu polycrystals during annealing in a Zn atmosphere was first reported by Chongmo and Hillert [1] in their study of diffusion induced grain boundary migration (**DIGM**) in the Cu–Zn system. Since this initial study several studies [2–7] have been performed to clarify the **DIR** behaviour. Unfortunately, many important features of this fascinating process have not yet been investigated. Of particular interest are the influence of the temperature, annealing time and surface Zn concentration (being the driving force of **DIR**) on the evolution of microtexture. The mechanism of **DIR** has not yet been thoroughly tested experimentally. Most of the investigations of **DIR** [4-6] have been rather limited to characterisations of the macroscopic phenomena and detailed nucleation but growth processes have not been reported. The aim of the present paper is to investigate the mechanisms of **DIR** on a fcc metal. Recent developments in the methods for local crystallographic measurements permit one to characterise the recrystallization not only in terms of grain size and average texture. These methods, particularly the selected area channelling pattern technique (**SAC**), allow the determination of the orientation of individual grains. Based on these data, the misorientation parameters of individual grains can be calculated and the appearance of the grain boundaries (**GBs**) of different types can be analysed [8–10].

## Experimental

The **DIR** studies were carried out on the {011} surface of Cu single crystals. These crystals were grown from high purity Cu (5N8) by the Bridgman technique and sectioned perpendicular to the [011] tilt axis by spark erosion. Four different Cu–Zn alloys with Zn contents of 22.5, 25, 27.5 or 30 wt.% were used as diffusion sources. The ampoules with samples were annealed at 693 K for 500 or 700 h. The samples for the **SAC** method were carefully polished to produce better surface contrast in the scanning electron microscopy (**SEM**) [13]. The **SAC** method of SEM allows the microstructure to be observed and the orientation of individual grains in the **DIR** layer to be determined. The physical background and experimental aspects of channelling phenomena are presented in detail in some reviews [11,12]. For every sample the orientations of 200 to 500 grains and the mutual misorientations of neighbouring grains were determined.

## Results

We investigated the microstructure evolution of the {110} surface of monocrystal Cu as a function of the heat treatment time and Zn concentration $c_{Zn}$ in the diffusion source. After diffusion anneals new small grains can be seen on the surface sample, including twins and the regions of the original {110} surface of monocrystal Cu. **DIR** grains were formed in the layer of bulk diffusion of Zn and were uniform in size. The grain boundaries between the Cu matrix and newly formed grains are highangle .Inside newly formed grains are twins of order 1,2 and 3. As a rule, the surface of newly formed grains was nearly {110} , and the surfaces of twins were {114}, {100}, {013}, {112}. Fig. 1 displays the mean grain size $d$ in the **DIR** layer for two annealing times $t$ and four values of Zn concentration $c_{Zn}$ in the diffusion source. The grain size increases with increasing $t$ and $c_{Zn}$.

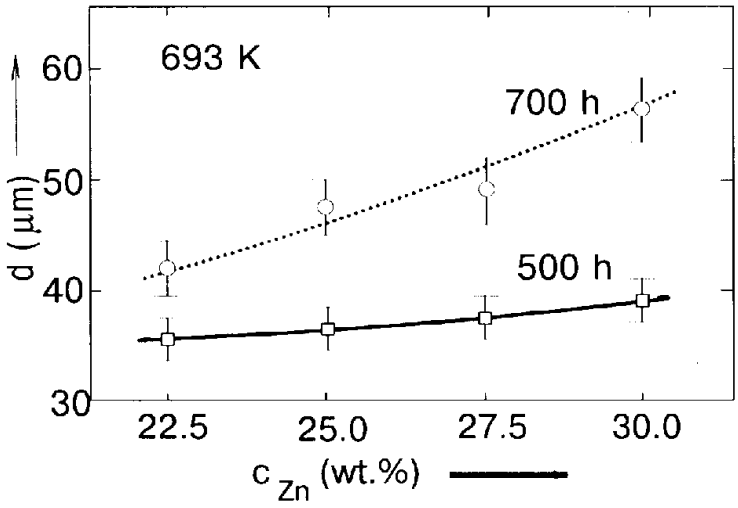


Figure 1. The dependence of the mean grain size $d$ on the Zn concentration in the diffusion source $c_{Zn}$ after annealing at 693 K for 500 and 700 h, respectively.

The grains in the **DIR** layer can be primarily characterised by their orientation, e.g. by the cristallographic direction of the grain which is parallel to the normal direction (**ND**) of the sample surface. The surface of the sample is in all cases a {011} plane.

The microstructure of the polycrystalline **DIR** layer consists of three kinds of grain regions:

- The ND of the investigated grains differs slightly from [011], the orientation of the single crystal. Such regions occupy 40% of the structure for an annealing time of 500 h and 50% for an annealing time of 700 h.

- Populations of grains (clusters) where the ND deviates very little from [114], [001], [112] or [012] lead to the majority of GBs with low-angles. Such regions occupy 20–30% of the structure. Table 1.
- Randomly oriented grains. The majority of GBs are high-angle GBs. Such regions occupy 20% of the structure.

Table 1 . The clusters of grains in **DIR** layer .

| | | ND to the surface of grain | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | [114] | | [112] | | [012] | | [100] | |
| % Zn | Heat treatment time, hours | The number of clusters | The number of grains in clusters | The number of clusters | The number of grains in clusters | The number of clusters | The number of grains in clusters | The number of clusters | The number of grains in clusters |
| 22.5 | 500 | 5 | 10 | 3 | 20 | 6 | 20-30 | | |
| 25 | 500 | 5 | 30-40 | | | 3 | 20-30 | | |
| 27.5 | 500 | | | | | 2 | 20 | 4 | 25 |
| 30 | 500 | | | | | | | | |
| 22.5 | 700 | 5 | 20 | | | | | | |
| 25 | 700 | 20 | 20-30 | | | 13 | 30 | | |
| 27.5 | 700 | 4 | 10-16 | | | | | 2 | 10 |
| 30 | 700 | 3 | 10 | | | 2 | 10 | | |

The analysis of the microstructure demonstrates that the grains of the preferred orientations [114], [112], [012] and [001] are not distributed absolutely randomly over the specimen surface. They form clusters containing at least several tens of grains. These grains are separated from one another by a low-angle GB, which is consequently a low-mobile GB. As a rule, a cluster is surrounded by a high-angle GB.

In **DIR** layer there are many low angle GBs. Practically, all high-angle GBs are twins $\Sigma = 3^n$ ($n$ = 1, 2 or 3, $\Sigma$ is the reciprocal density of coincidence sites). Fig. 2 shows the fraction, $f_{la}$ of low-angle GBs among all GBs in the **DIR** layer for different $c_{Zn}$ . $f_{la}$ increases with annealing time. After an anneal for 500 h $f_{la}$ decreases with increasing $c_{Zn}$. After an anneal of 700 h the maximum value of $f_{la}$ appears at the concentration of 25 wt.% Zn.

Fig.3 shows the grain size distribution for $c_{Zn}$ after an anneal of 700 h. For the grain with ND to the grain surface near [110] the size distribution is wider, than for grains with ND to the grain surface [114]. Grain size distribution for grain with ND to the grain surface [110] changes significantly with increasing $c_{Zn}$ .It means that there is the growth of grains with ND [110] mainly .

For most crystalline solid solutions the lattice parameters vary with composition. If the lattices to remain coherent in the presence of a composition variation, work has to be performed in straining the lattice. Stresses are concentrated in the very thin coherent layer. During the heat treatment under the stress the process of polygonization starts. As a result there are low angle grain boundaries.- dislocations walls. During anneals under stress dislocations walls can move and combine. It is process of creating high angle grain boundaries - newly formed grains with different

orientations. For materials with a low stacking fault energy, stress relaxation can occur also by twinning - creating new grains with low mobility grain boundaries .

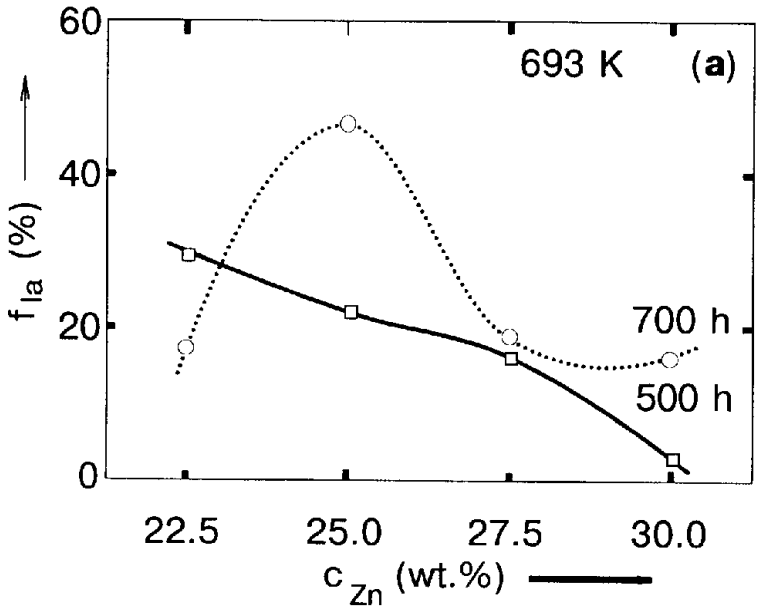


Figure 2. The dependencies of the fraction of low-angle GBs in the **DIR** layer $f_{la}$.

**Discussion.**

The results of this work display some important features of the **DIR** process. Some facts can be easily understood due to the similarity with the usual processes of recrystallization and grain growth. Other peculiarities are specific to **DIR**.

The increase of the mean grain size $d$ with increasing annealing time is one of the common features of **DIR** and usual recrystallization. The increase of $d$ with increasing $c_{Zn}$ can be also explained if we take into account that $d$ was measured in the upper layer of the sample which is enriched by Zn. The addition of 20 wt.% Zn to Cu lowers the melting temperature $T_m$ of a Cu–Zn alloy by about 100 K [14]. Therefore, the recrystallization in a Cu–Zn solid solution proceeds at a higher homological temperature $T/T_m$ than in pure Cu, and the recrystallization rate increase with increasing $c_{Zn}$ as well as with increasing $T$.

The number of different grain orientations present in the **DIR** layer decreases with increasing annealing time. This fact can be understood if we suppose that the grains with the most energetically favourable orientations consume the grains having the orientations which are energetically less favourable. The analogue of this process is the secondary grain growth in the recrystalized sheets driving by the difference in the surface energy of the grains with different orientations. Therefore, the observed process is a kind of a diffusion - induced secondary recrystallization.

Small angle GBs possess a lower energy than high-angle GBs. Only the CSL GBs can have an energy comparable with the energy of low-angle GBs. In the case studied practically all of CSL GBs in the polycrystalline layer **DIR** were twins of different order having low energy. There is a tendency to increase the small-angle GB fraction in the **DIR** layer with increasing time $t$. Therefore, basing on the data of orientation measurements for individual grains we can suppose that the decrease of Gibbs energy of the system during **DIR** is connected not only with the increase of $d$, but also with the time displacement of the GB energy distribution towards the GBs with low energy.

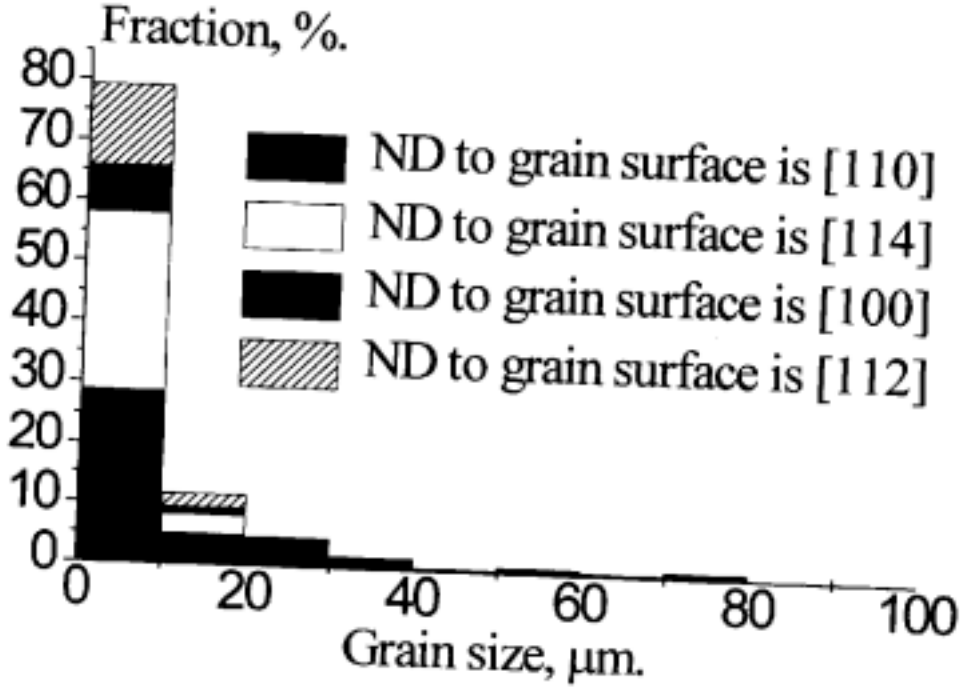


Fig.3 a.The grain size distribution for different grain orientations in **DIR** layer on surface of monocrystall Cu at 22.5%Zn .

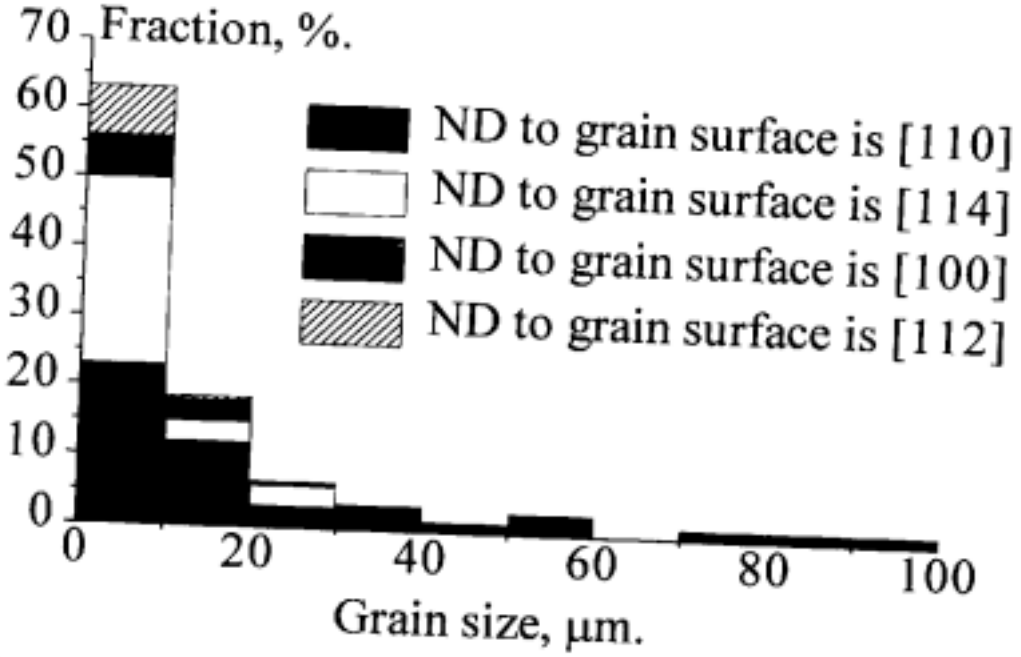


Fig.3 b.The grain size distribution for different grain orientations in **DIR** layer on surface of monocrystal Cu at 30% Zn.

**Conclusion.**

We can suppose that the internal stresses formed in the layer of bulk diffusion relax during **DIR** in two ways:

- By *high temperature poligonization.* In this case the grains are formed with the orientation which differs only slightly from the original [011] orientation of Cu single crystal.
- By *twinning.* In this case grains with an orientation different from the original [011] orientation of a single crystal are present in the **DIR** layer . Clusters with [114], [112], [012], and [001] orientations were found. The grain boundaries between [011] and cluster orientations are twinning grain boundaries, special ones with misorientation angles close to the coincidence misorientations $\Sigma = 3^n$ .The relation between different twinning grain boundaries depends on the Zn concentration in the vapour phase, heat treatment temperature and heat treatment time.

We suppose that the properties of such materials having a grain structure which is strongly determined by the special $\Sigma = 3^n$ grain boundaries would be significantly different from the properties of polycrystals containing random grain boundaries .

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