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Diffusion Induced Recrystallization in Single Crystals of Copper[3]

By

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The microstructure evolution during diffusion induced recrystallization (DIR) on the {011} surface of Cu single crystals is experimentally studied. The selected area channelling technique is used for measuring the orientation of the grains in the polycrystalline layer formed by Zn diffusion from the vapour phase. The misorientation of adjacent grains is determined in terms of rotation angle and axis using a direct matrix method. The fraction of low-angle boundaries increases with annealing time during DIR. The number of the low-angle boundaries correlates with the fraction of grains possessing a (114) texture. The fraction of the grain boundaries with coincidence misorientations remains roughly the same during DIR.

Экспериментально изучена эволюция микроструктуры в процессе диффузионно-индуцированной рекристаллизации (DIR) на поверхности {011} монокристаллов меди. Ориентация зерен в поликристаллическом слое, образующемся на поверхности монокристалла меди в результате объемной диффузии цинка, определялась с помощью каналирования электронов по методу избранной площади. Затем рассчитывались параметры взаимной разориентации соседних зерен (ось и угол разворота) с помощью прямого матричного метода. Доля малоугловых границ зерен в слое DIR возрастает со временем. Количество малоугловых границ коррелирует с долей зерен, имеющих текстуру (114). Доля границ зерен, имеющих разориентации совпадения, остается в течение DIR приблизительно постоянной.

1. Introduction

In the layer of bulk diffusion elastic tensions can arise due to the dependence of the lattice parameter on the concentration of the diffusing element. The relaxation mode of these tensions depends on several factors, like 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 Hillert and Chongmo [1] in their study of diffusion induced grain boundary migration (DIGM) in the Cu–Zn system. Since this initial study several studies [2 to 7] have been performed to clarify the DIR behaviour. Unfortunately, many important features of this fascinating process are still not investigated. Of particular

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interest are the influence of the temperature, annealing time, and surface Zn concentration (being the driving force of DIR) on the evolution of microtexture. Recent developments in the methods for local crystallographic measurements permit one to characterize the recrystallization not only in terms of grain size and average texture. These methods, particularly the selected area channelling technique (SAC), permit to determine the orientation of individual grains. Basing 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 to 10].

2. Experimental

The DIR studies were carried out on the {011} surface of Cu single crystals. The single crystals were grown from high purity Cu (5N8) by the Bridgman technique and sectioned perpendicular to the ⟨011⟩ tilt axis (parallel to {011} planes) by spark erosion. These surfaces were then chemically cleaned with a 50% HNO_3 aqueous solution and ground with 4000 SiC paper. To eliminate any residual stresses or plastic deformation the samples were then annealed for 15 h at 1123 K. No recrystallization was observed on the {011} surface. For DIR annealing, the samples described above were encapsulated in a single chamber silica ampoule under an Ar–20% H_2 mixture at 2×10^4 Pa along with chips of a Cu–Zn alloy, which served as a Zn source, a Ta foil, and a piece of high purity graphite, which served as an O_2 getter. Four different Cu–Zn alloys with a Zn content of 22.5, 25, 27.5, and 30 wt% were used as diffusion sources. The ampoules with samples were then annealed at 693 K for 500 and 700 h in a tube furnace controlled to ± 1 K. In all cases care was taken that the surface to be studied was maintained in a horizontal position facing upward to guarantee even deposition of Zn. After removing the specimens from the ampoule some samples were mounted in lucite for metallographic observations of the layers parallel and perpendicular to the Zn-rich surface after grinding with a 4000 SiC paper and polishing with 3 and 1 μm diamond paste. The samples were etched by swabbing with a solution containing 3.5 ml H_2O, 1.5 ml NH_4OH, and 0.3 ml 3% aqueous H_2O_2 for 10 to 30 s. Here the etchant had to be freshly prepared. The samples for the SAC method were not mounted. Instead of this they were carefully polished by hand with 3 and 1 μm diamond paste and chemically polished with a solution of nitric acid, phosphoric acid, and acetic acid in same parts for a short time (10 to 15 s). This procedure was chosen to remove the deformation layer caused by polishing and to get a better surface contrast in the scanning electron microscopy (SEM).

The SAC method of SEM permits to see the microstructure of the sample and to determine the orientation of the individual grains in the same experiment. Therefore, many grains can be analysed and an overall picture of the misorientation distribution can be obtained. The SEM-SAC method has been used by us in order to determine the orientation of individual grains in the DIR layer. The physical background and experimental aspects of channelling phenomena are presented in detail in some reviews [11, 12]. We have measured the orientation by hand from an electron channelling pattern. A grain orientation can be obtained from a screen using only a ruler and a standard map. This method was adopted as a computer program for routine orientation measurements, and requires the operator to identify poles in the channelling pattern. The orientation of a grain with respect to the specimen frame may be equally described both by rotation angles and rotation axis or by proper orthogonal matrices. It is well known [13, 14] that there are 24 geometrically different, crystallographically

equivalent rotations for cubic systems, each of which describes completely the orientation of a grain with respect to the specimen frame.

After the determination of the orientation of individual grains, the misorientation parameters, namely the axis and misorientation angle, for the GBs between the neighbouring grains can be determined using a special computer program [15]. After that the GBs can be classified as follows:

— low-angle GBs with a misorientation angle less than $15°$;

— high-angle GBs with a misorientation angle more than $15°$;

— GBs of coincidence type [or coincidence site lattice (CSL) GBs].

Under CSL GBs we understand the GBs with misorientation parameters lying near the coincidence misorientations with a low value of the reciprocal density of the coincidence sites Σ. Geometrically, the CSL exists for any value of Σ and only for the misorientation angles of the exact coincidence. Experimentally, GBs possess a special structure and special properties a) only for Σ values which are small enough and b) in some angular interval $\Delta\theta$ near the coincidence misorientation θ_Σ [16]. The cut-off value of Σ at which the CSL ceases to have any physical significance depends on the temperature; $\Delta\theta(\Sigma)$ depends on Σ and decreases with increasing Σ [16]. Different investigators set the upper limit for Σ usually between $\Sigma = 25$ and 49. In this work we have chosen the cut-off value $\Sigma = 27$ [17, 18]. A GB was classified by us as CSL GB if its misorientation angle θ differs from the corresponding θ_Σ no more than $\Delta\theta(\Sigma)$. For every sample the orientations for 200 to 500 grains and the mutual misorientations for neighbouring grains were determined. During these measurements the region of interest has been located in the image. After that the orientation data can be collected without further reference to the image. The operator moves the sample in a linear traverse and measures the orientation every time the channelling pattern changes. This method of data collection permits one to estimate the grain size together with the orientation measurements. After the whole width of the sample has been traversed, the process can be repeated along a different trajectory. The distance between the trajectories is equal to the mean grain size in the section to be investigated.

3. Results

After diffusion anneals new small grains can be seen on the surface of Cu single crystals. These DIR grains were formed in the layer of bulk diffusion of Zn. 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}.

The grains in the DIR layer can be primarily characterized by their orientation, e.g. by the crystallographical 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 coincides with $\langle 011 \rangle$, being the orientation of the investigated 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.

— The ND deviates very little from $\langle 114 \rangle$, $\langle 001 \rangle$, or $\langle 012 \rangle$. The majority of GBs in these regions are low-angle GBs. Such regions occupy 20 to 30% of the structure.

— Randomly oriented grains. The majority of GBs are high-angle GBs. Such regions occupy 20 to 40% of the structure.
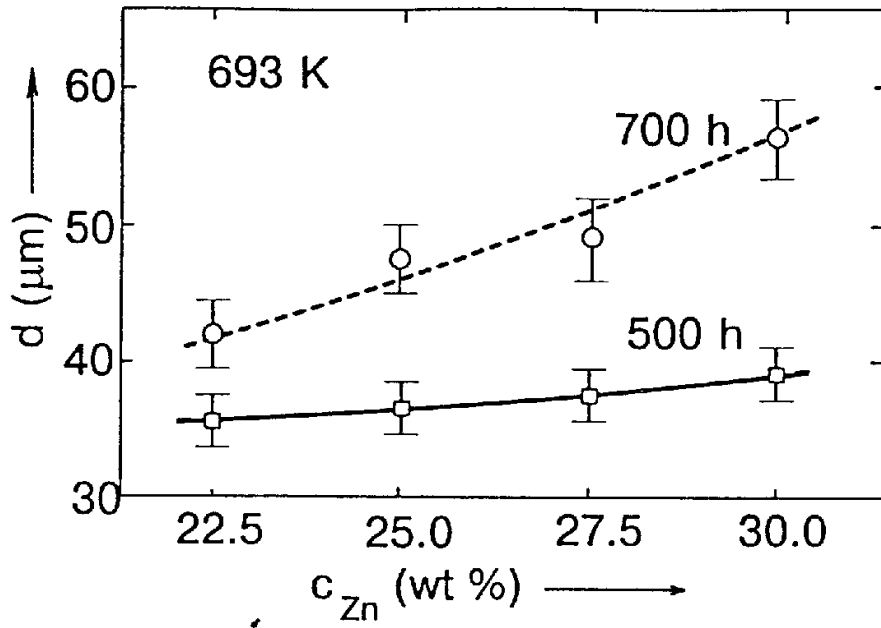
Fig. 1. The dependence of the mean grain size d on the Zn concentration in the diffusion source c_{Zn} after annealing at 693 K for 500 and 700 h, respectively

The most frequent orientations of DIR grains were $\langle 011 \rangle$, $\langle 114 \rangle$, $\langle 112 \rangle$, $\langle 001 \rangle$, and $\langle 012 \rangle$. Other orientations, like $\langle 013 \rangle$, $\langle 015 \rangle$, $\langle 116 \rangle$, $\langle 122 \rangle$, $\langle 123 \rangle$, $\langle 125 \rangle$, $\langle 127 \rangle$, and $\langle 223 \rangle$, were very seldom (about 5% of all DIR grains). The number of different orientations decreases with increasing annealing time. The analysis of the microstructure demonstrates that the grains of the preferred orientations $\langle 114 \rangle$, $\langle 112 \rangle$, $\langle 012 \rangle$, and $\langle 001 \rangle$ are not distributed absolutely randomly over the specimen volume. They form clusters containing at least several tens of grains. These grains are separated one from another by a low-angle GB, which is consequently a low-mobility GB. As a rule, a cluster is surrounded by a high-angle GB. The increase of the volume fraction of grains having orientations $\langle 114 \rangle$, $\langle 112 \rangle$, $\langle 012 \rangle$, or $\langle 100 \rangle$ proceeds by an expansion of these clusters.

Fig. 2 displays the relative number of grains having the most frequent orientations $\langle 011 \rangle$, $\langle 001 \rangle$, $\langle 114 \rangle$, and $\langle 112 \rangle$ after anneals for 500 and 700 h for different c_{Zn}. Most frequently (27 to 43%) appear the $\langle 011 \rangle$ grains having an orientation coinciding with the orientation of the single crystalline substrate. Their number increases with increasing t and c_{Zn}.

Fig. 3 shows the fraction, S_{or}, of the surface area for the grains with the orientations $\langle 011 \rangle$, $\langle 001 \rangle$, $\langle 114 \rangle$, $\langle 012 \rangle$, and $\langle 112 \rangle$ after anneals for 500 and 700 h for different c_{Zn}. Some features not displayed in Fig. 3 can be clearly seen. The area fractions of $\langle 011 \rangle$ and $\langle 114 \rangle$ grains definitely increase after longer annealing time on the cost of the other components. For example, the component $\langle 012 \rangle$ completely disappears after 700 h.

In the DIR layer there are many low-angle and high-angle GBs, but only a few CSL GBs (about 5 to 10%). Practically, all these GBs were twins of different order: $\Sigma = 3^n$ (where $n = 1, 2,$ or 3). In the grain clusters $\langle 114 \rangle$, $\langle 110 \rangle$, and $\langle 012 \rangle$ the orientation of the individual grains has a very low deviation from the corresponding cluster orientation. Therefore, there are many low-angle GBs in the DIR polycrystalline layer. Fig. 4a 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 anneal for 500 h f_{la} decreases with increasing c_{Zn}. After an anneal of 700 h the high maximum of f_{la} appears at the concentration of 25 wt% Zn. For comparison, Fig. 4b shows the evolution of S_{or} for grains with a $\langle 114 \rangle$ orientation for different c_{Zn}. Interesting is the comparable behaviour of f_{la} and S_{or}.
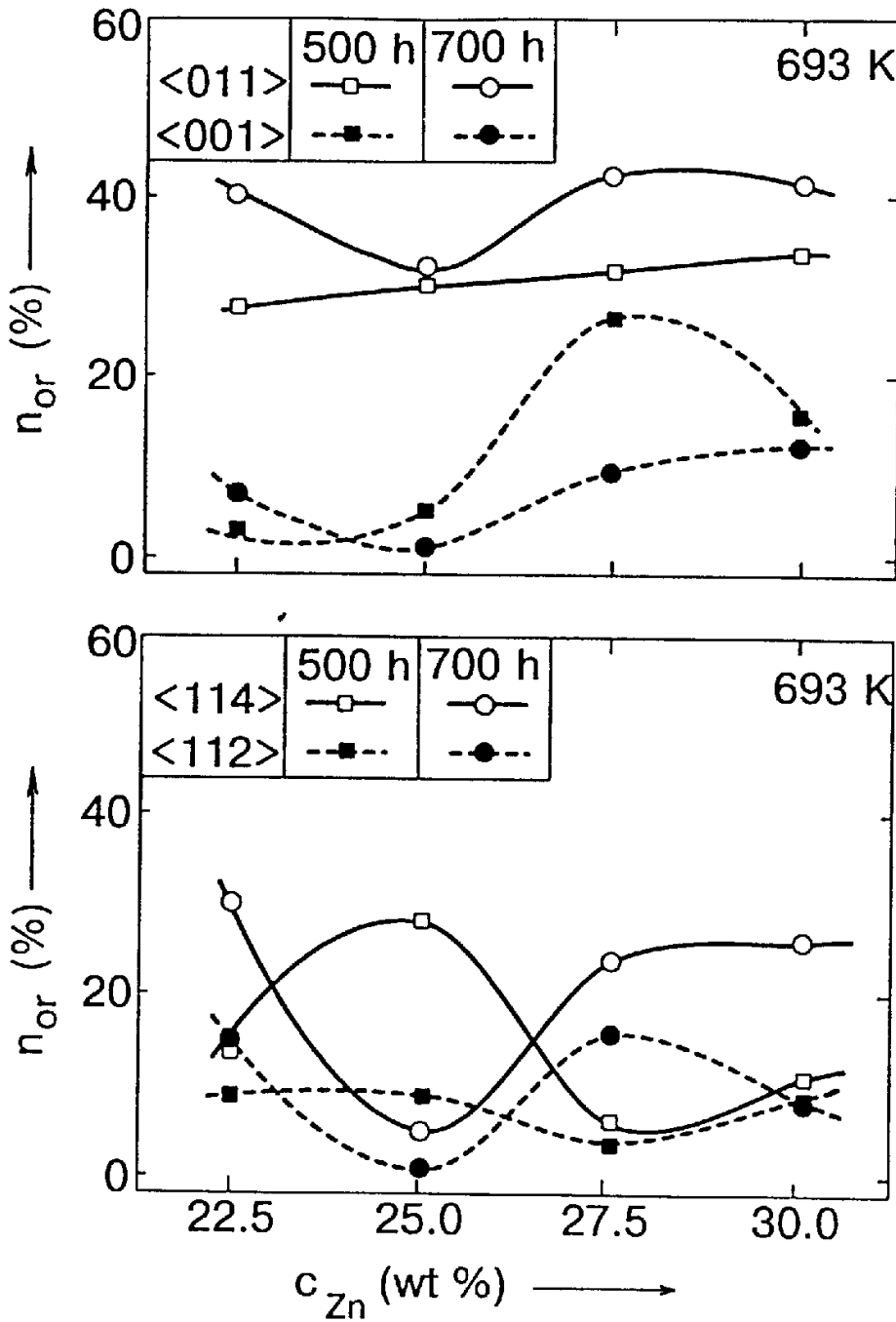
Fig. 2. The dependencies of the relative number, n_{or}, of grains having the most frequent orientations $\langle011\rangle$, $\langle001\rangle$, $\langle114\rangle$, and $\langle112\rangle$ on the Zn concentration in the diffusion source c_{Zn}

4. Discussion

DIR is one of the important processes which may accompany the interdiffusion process at low temperatures. During DIR new (small) alloyed grains form in the diffusion zone. The new grains initiate at the original GBs and progressively, by an avalanche type of process, repeated nucleation of new grains occurs on the surface of the previously formed new grains until eventually the interface is completely composed of a fine-crystalline alloy layer [4]. New grains grow by diffusion induced grain boundary migration (DIGM). The DIR process has been found to be the dominant mass transfer mechanism in regions of high
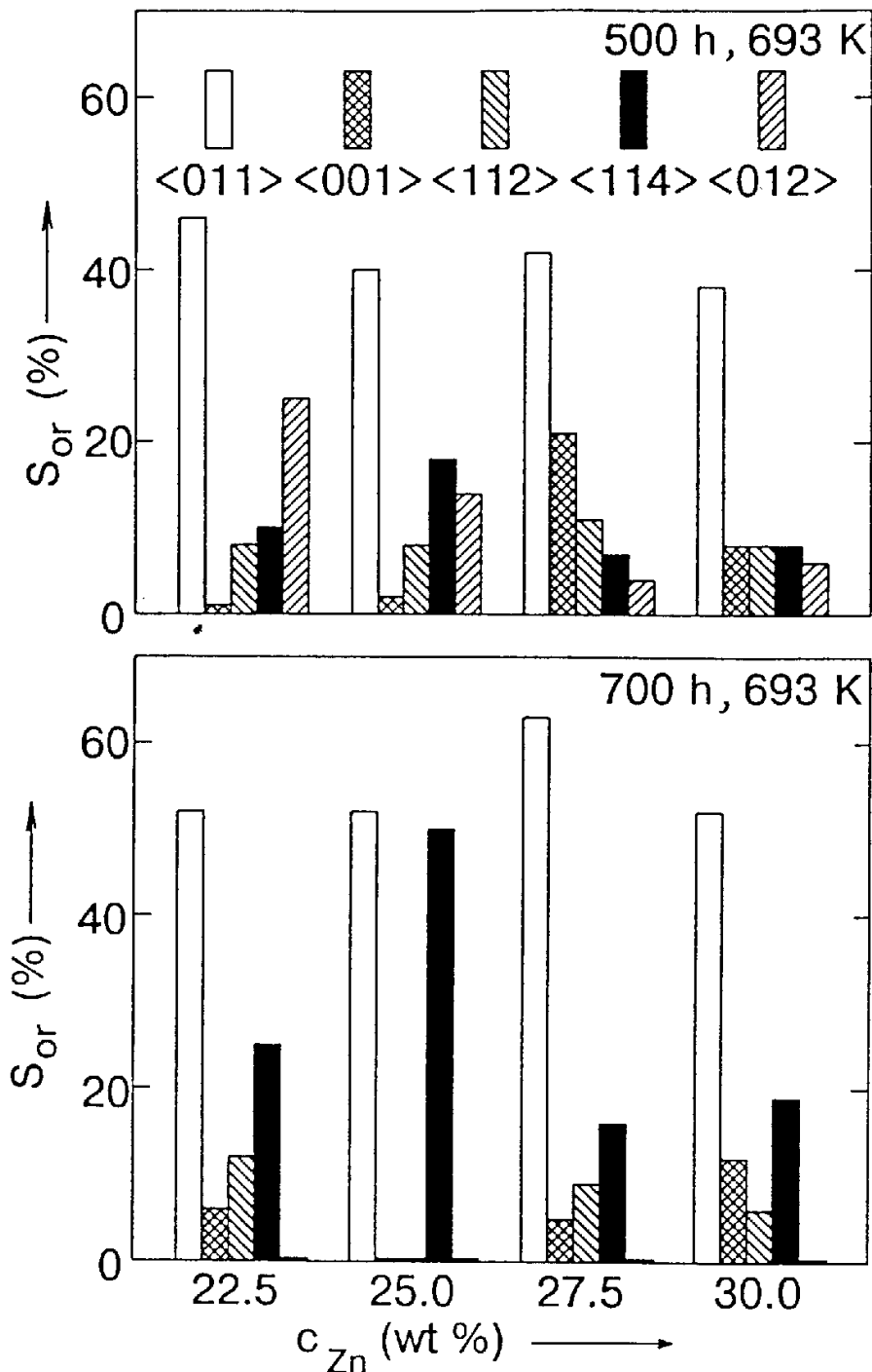
Fig. 3. Fraction of the surface area, S_{or}, of the grains with the orientations ⟨011⟩, ⟨001⟩, ⟨114⟩, ⟨012⟩, and ⟨112⟩ for different Zn concentrations in the diffusion source c_{Zn}

concentration gradients, and to be even more important there than DIGM. The mechanism of the nucleation of new grains by DIR still remains an object of discussion.

Parathasarathy and Shewmon [6] in their study of the diffusion of iron from the vapour phase into nickel explained the formation of Fe Ni alloy DIR grains at or close to migrating GBs as due to the tensile stresses which develop in regions near the boundaries because of the faster GB out-diffusion of nickel compared with the GB in-diffusion of iron. These tensile stresses then would be relieved by the volume expansion which occurs on alloying nickel with iron. This explanation is contradicted by the observation of DIR along copper
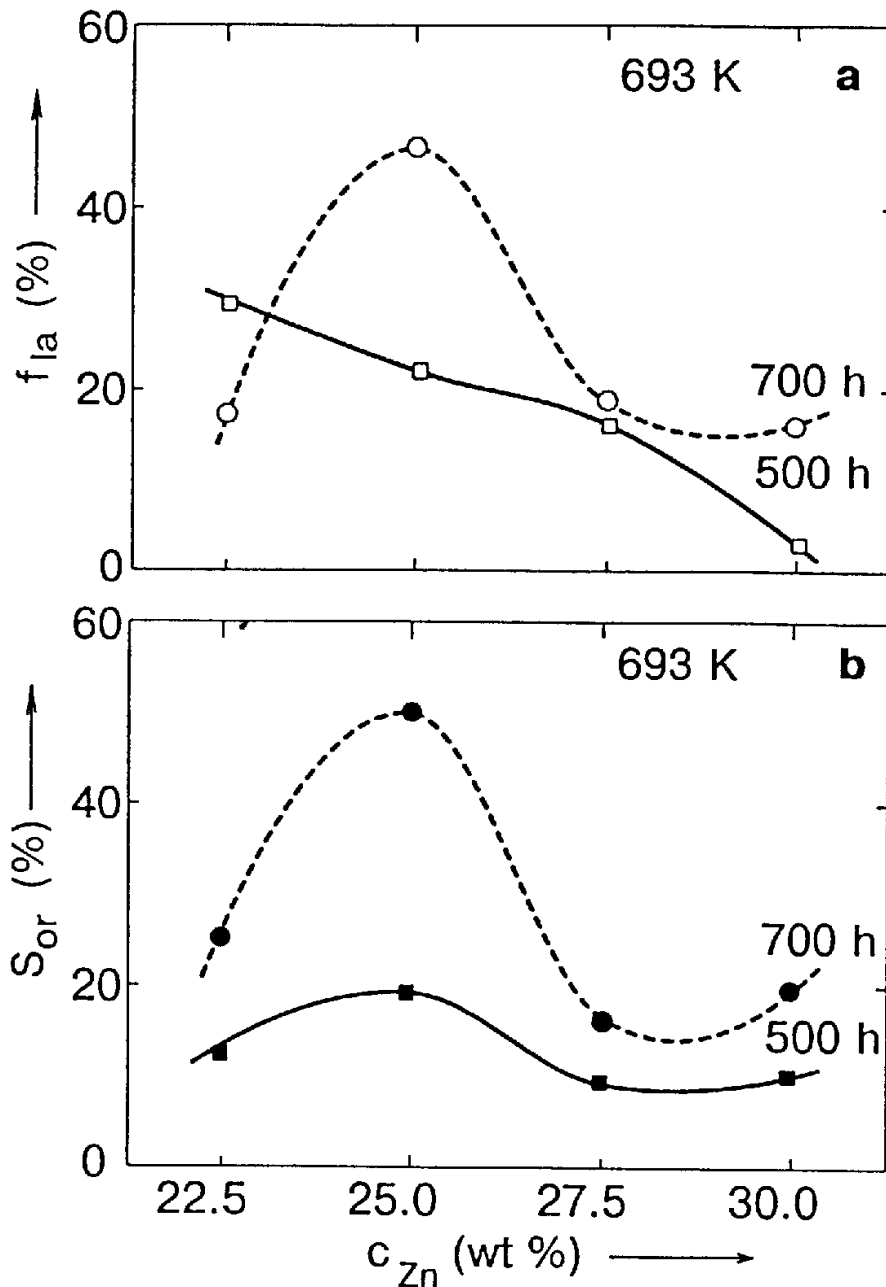
Fig. 4. The dependencies of the fraction of a) low-angle GBs in the DIR layer f_{la} and b) of the surface area for the grains with the orientation $\langle 114 \rangle$ S_{or} on the Zn concentration in the diffusion source c_{Zn}

GBs in Cu Ni diffusion couples [19]. Here, tensile stresses are also expected to develop owing to the faster GB diffusion of copper than that of nickel, but alloying copper with nickel brings about a *decrease* in the molar volume. It is therefore unlikely that the occurrence of DIR is to be associated with a particular stress situation to be relieved by the lattice parameter change on alloying. Instead, in [4] was suggested that, when the net mass or vacancy flow along the GBs is very violent, drastic structural rearrangements in these GBs occur, leading to the emission of dislocations by glide into the grain interiors. Here these dislocations may coalesce by climbing into dislocation walls which eventually form new GBs.

Indeed, below the temperatures of DIR the nickel grain interiors were shown by transmission electron microscopy to have a very high dislocation density [19]. The temperature at which DIR started to be observed was about the same as that needed to

induce normal primary recrystallization of parts of the sample which were cold worked by cutting and scratching. This observation indicates that the microscopic processes which are activated to initiate DIR are the same as those that bring about normal recrystallization, i.e. dislocation wall formation by lattice dislocation climb; after dislocation emission from the original GBs. Therefore, the studies of the orientation distribution of new grains formed by DIR and its evolution are important for decovering the DIR mechanism. 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 [20]. 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 increases with increasing c_{Zn} as with increasing T.

The number of different grain orientations present in the DIR layer decreases with increasing annealing time. For example, it can be seen (Fig. 3) that the orientation ⟨012⟩ exists in the sample after an anneal of 500 h, but disappears after 700 h. 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 recrystallized 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.

Remarkable is the similarity in behaviour of the fraction, f_{la}, of small-angle GBs in the DIR layer and area fraction, S_{or}, of grains with ⟨114⟩ orientation (compare Fig. 4a and b). Both curves have a maximum at 25 wt% Zn for $t = 700$ h. This behaviour shows that the quick growth of the grain clusters with the ⟨114⟩ orientation proceeds due to the nucleation of new slightly misoriented ⟨114⟩ grains.

It is interesting to compare the $f_{la}(c_{Zn})$ dependence (Fig. 4a, $t = 700$ h) with the behaviour of the recrystallization in Al foils [15]. The maximum of the low-angle GB fraction f_{la} was there revealed on the dependence of f_{la} on the annealing time. The disappearance of the low-angle GBs in Al with increasing t was driven by the beginning of the secondary recrystallization. The increasing temperature shortens t for the transition to the secondary recrystallization [21, 22]. In our case, the increase of c_{Zn} acts like an increase of temperature. Therefore, we can suppose that the gradual disappearance of the small-angle GBs in Cu has something in common with the process studied in Al [15] though Cu and Al have very different stacking-fault energies and different recrystallization behaviour.

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 studied case the fraction of CSL GBs in the polycrystalline layer DIR was about 5 to 10%, but practically all of them 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. Kinetically, the formation of the low-angle GBs is also favourable as a simplest way for dislocations formed in the distorted bulk diffusion layer to relax into the low energy configurations like walls or networks.

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