

Recrystallization of copper under hydrostatic pressure up to 15 kbar

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Hydrostatic pressure (up to 15 kbar) during annealing results in retardation of recrystallization during initial recrystallization of copper; the rate of nucleation and growth of new grains are both retarded. The effect of pressure on the nucleation rate is extremely high and a finer crystalline structure results during annealing under pressure.

The difference in the rate of formation of recrystallization nuclei and their growth under uniform pressure is connected with the considerable role of volume diffusion in nucleation of the recrystallized structure.

1. Introduction

There have been a number of recent experimental studies showing that physical properties of crystalline bodies may exhibit considerable changes under pressure and these changes are frequently irreversible in the sense that the properties of the body are found to have been changed (when compared with the initial state) after the pressure is removed. This is true above all to mechanical properties. Thus, after mechanical working under hydrostatic pressure up to 10 kbar materials which are brittle under standard conditions (for example, chromium [1], marble, sapphire [2], etc) become extremely plastic. Iron samples of high purity at 8 kbar show [3] a considerable decrease in the lower and upper yield limit. Under hydrostatic pressure shearing strength exhibits an abrupt increase [4] and the strength characteristics of polycrystalline materials subjected to pressure increase [5, 6].

The above effects, the list of which could be further extended, are naturally associated with structural changes being developed in crystals under uniform pressure. However, data on the problem discussed are scarce in the literature and are not always unambiguous. Arkharov and Bulychev [7] found that recrystallization of sintered samples of copper is slow in conditions simulating uniform compression. The same conclusion was arrived at by Tanner and Radcliffe [8] who studied recrystallization of cast copper under pressure at similar temperatures (80 to 170°C). On the other hand, at high

temperatures (close to melting) uniform pressure enhances grain growth [9].

This paper presents experimental results on the effect of pressure on recrystallization kinetics of copper plastically pre-deformed (> 90%).

2. Experimental procedure

The material used in this study was copper of commercial purity (with impurity content < 0.02%). The ingot from which the samples were obtained was pre-annealed at 930°C for 8 h, and then rolled 95% at room temperature. After this treatment the ingot showed a well expressed (110) [111] rolling texture. The samples were cylinders 2 mm diameter and 3 mm high.

Recrystallization-annealing was carried out in a high pressure chamber [10] which allows pressures up to 15 kbar. After annealing, the samples were studied by X-ray diffraction and metallographic analysis. The relative volume of the recrystallized material was determined from the data on the intensity of the (200) diffraction line. It has been found [11] that the development of the (100) [100] cubic texture is characteristic of severely deformed copper with (110) [111] deformation texture when it is annealed. The (200) intensity I_t that corresponds to annealing time, t , is determined by the relative volume, X , that has recrystallized by that time:

$$I_t = I_0 + X(I_{\max} - I_0) \quad (1)$$

where I_0 is the initial intensity of reflection, I_{\max} is the reflection intensity of a fully recrystallized sample. The intensity measurements were carried

out using a diffractometer. The error in these measurements was within 3%.

Apart from the metallographic measurements of the total recrystallized volume, the number of growing recrystallized grains was determined by X-ray diffraction. For this purpose X-ray diffraction patterns were taken by both Hirsch and Kellar's technique [12] and by another procedure [13], the latter allowing X-ray patterns of reflection only from regions immediately adjacent to the sample surface to be obtained. A primary X-ray beam falls on the sample at angle ϕ rather than at right angles, the former given by

$$l(1 + \sin \psi / \sin \phi) = 1/\mu \quad (2)$$

where μ is the shear coefficient of the monochromatic X-ray absorption of the sample, l is the thickness of the reflecting layer, and ψ is the angle between the reflected beam and the sample surface. If l is smaller than the average size of a diffracting unit (nucleus), the superposition of reflections from units located at different depths from the sample surface (within the half-value layer) is neglected and the resolution improves, which enables nuclei of $\sim 5 \times 10^{-5}$ cm to be revealed.

3. Experimental results

Experimental data on the total volume recrystallized during isothermal annealing at different temperatures and pressures are given in Fig. 1a and b. With the reference to the double-log co-ordinates (b), one can see that the dependence of X on annealing time is described as

$$X = 1 - \exp \left[- \left(\frac{t}{\tau} \right)^m \right] \quad (3)$$

i.e., it agrees with the representations of the formal theory of recrystallization [14]. The values of the index m for different annealing temperatures and pressures which were found from the straight line slopes of Fig. 1b are listed in Table I.

The data given in Table I show that within the measuring error the index m does not exhibit any regular change in the temperature range 140 to 200°C and in the pressure range 1 bar to 15 kbar and as a first approximation, it may be regarded as a parameter independent of p and T .

In correspondence with the experimental data the factor $1/\tau$ can be expressed as $1/\tau = K_0 \exp(-Q_r/RT)$ and it changes markedly with change of temperature and pressure. Unfortunately it was impossible to arrive at an unam-

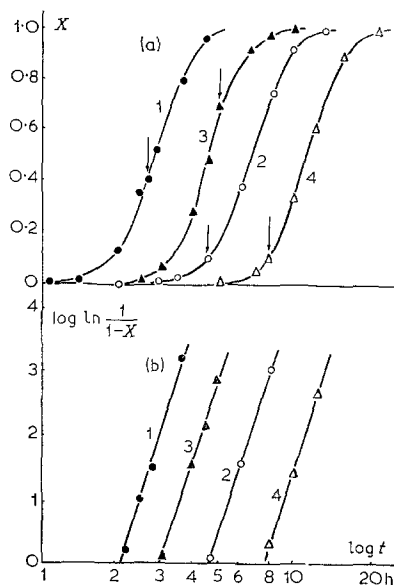


Figure 1 X (volume fraction recrystallized) and $\log 1/(1-x)$ versus $\log t$ (t = isothermal annealing time) for copper samples deformed 95%. 1. $T = 180^\circ\text{C}$, $p = 1$ bar; 2. $T = 180^\circ\text{C}$, $p = 8$ kbar; 3. $T = 140^\circ\text{C}$, $p = 1$ bar; 4. $T = 140^\circ\text{C}$, $p = 8$ kbar. Arrows indicate first appearance of spots on the diffraction rings.

TABLE I

T (°C)	Pressure	$K_0 \times 10^{-7}$ (sec)	m	Q_r , (kcal (g mol) ⁻¹)
120	1 bar	12.5	3.8	28 ± 1
140			3.7	
160			3.8	
180			3.8	
140	8 kbar	9.3	3.7	28 ± 1
160			3.8	
180			3.7	
200			3.6	
140	14 kbar	7.5	3.6	27 ± 1
160			3.7	
180			3.6	
200			3.7	

biguous conclusion as to the degree of changes in Q_r , which can be regarded as the effective activation energy of recrystallization, with pressure. In fact, by using published values of activation energy, which are characteristic of different diffusion processes, it is easy to demonstrate that the changes in Q_r in the pressure range 1 bar to 15 kbar do not exceed 2 kcal g.mol⁻¹, i.e. they are within the error of determination of the quantity. K_0 is practically independent of

temperature in the temperature range studied in this work and decreases as the pressure increases.

The data presented here show that the values of the effective activation energy of recrystallization for severely deformed copper of commercial purity are well below the activation energy of volume diffusion and exceed the activation energy of grain-boundary diffusion. It may be assumed that the process of initial recrystallization is determined through superposition of different atomic mechanisms. Apart from grain-boundary diffusion which in general terms determines the kinetics of the growth of recrystallization nuclei, volume diffusion is also likely to make a certain contribution to the general kinetics of the recrystallization process.

The arrows in Fig. 1a show the annealing times where the initially blurred lines of the X-ray diffraction patterns first reveal spot reflections corresponding to the growing nuclei of the recrystallized phase. With a reasonably high resolving power of the X-ray technique ($\sim 1 \mu\text{m}$) used in our investigations, we succeeded in revealing early stages of nucleus growth. As is shown in the figure, the times required for the nuclei to grow to sizes capable of being revealed by X-ray diffraction, increase as the pressure increases, but the first spots are seen at smaller volume fraction of recrystallization for the samples annealed under pressure (which are also coarser grained)*.

At ambient pressure and a temperature of 180°C , for example, the appearance of spot reflections is observed at the annealing stage where the relative volume X of the recrystallized phase equals $\sim 80\%$. During annealing at 8 kbar, similar changes in the diffraction pattern occur at values of $X \simeq 10\%$, although the annealing time required for nuclei to grow to 1 to $2 \mu\text{m}$ is approximately 1.5 times longer in the latter case.

4. Discussion

The differences observed in the kinetics of the change in the total volume of the recrystallized phase and in the recrystallization nucleus growth is likely to result from different effects of pressure on the kinetics of nucleation and growth processes. However, these two processes are differently retarded by pressure; nucleation is

more sensitive to hydrostatic pressure than the growth process.

Assuming that the recrystallization nuclei, separated from the unrecrystallized matrix by large-angle boundaries, represent domains of ~ 0.1 to $1 \mu\text{m}$ [15], the data on the variations in the number of spots on the X-ray diffraction pattern during annealing can be used as a first approximation to find the characteristics of the nucleation kinetics. Data for different tempera-

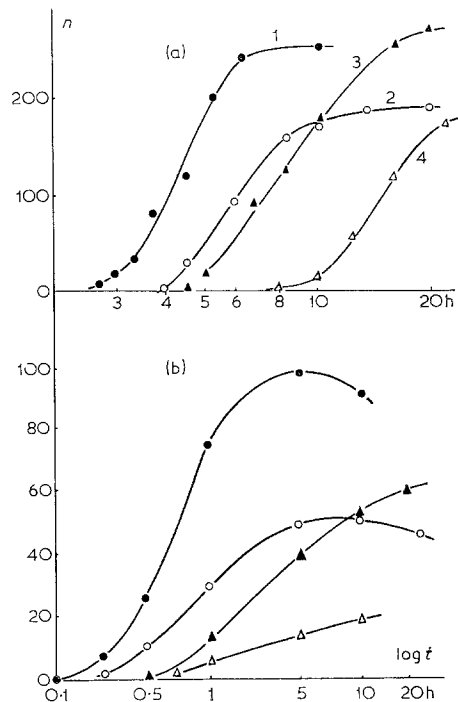


Figure 2 X-ray spot number, n , versus annealing time, t , at different temperatures and pressures. (a) 1. $T = 180^\circ\text{C}$, $p = 1$ bar; 2. $T = 180^\circ\text{C}$, $p = 8$ kbar; 3. $T = 140^\circ\text{C}$, $p = 1$ bar; 4. $T = 140^\circ\text{C}$, $p = 8$ kbar. (b) 1. $T = 450^\circ\text{C}$, $p = 1$ bar; 2. $T = 450^\circ\text{C}$, $p = 8$ kbar; 3. $T = 240^\circ\text{C}$, $p = 1$ bar; 4. $T = 240^\circ\text{C}$, $p = 8$ kbar.

tures and annealing times are shown in Figs. 2 and 3. It is clear that the spot reflection density on the X-ray diffraction patterns obtained from the samples annealed under pressure is always smaller than that from the samples annealed under similar conditions without pressure. This regularity could be confirmed at every stage of

*The fact that the appearance of the first spots is observed at a comparatively late stage of recrystallization, may be corrected with the relatively high impurity content of the copper and the low annealing temperature, which make for the formation of a very fine-grained structure.

initial recrystallization up until its completion. As the density of recrystallization nuclei is reduced during annealing under pressure, the mutually competitive action of the growing nuclei exhibits itself only at some later stages of annealing (see Fig. 2), and a coarser structure results.

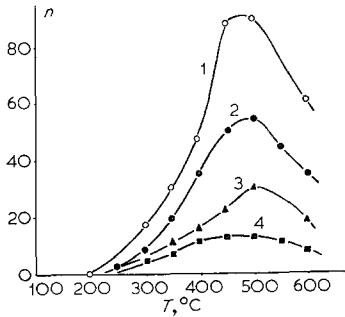


Figure 3 X-ray spot number, n , versus annealing temperature, T . Annealing time = 1 h. 1. $p = 1$ bar; 2. $p = 5$ kbar; 3. $p = 10$ kbar; 4. $p = 14$ kbar.

Different degrees of retardation of nucleation and growth during annealing under pressure can be easily understood if we assume different diffusion mechanisms to be responsible for the recrystallization process. The theoretical model [16] is supported by experimental data [17, 18], according to which coalescence of neighbouring subgrains makes a great contribution to nucleation. According to [16], this process, which leads to the formation of large-angle boundaries, can proceed either through the co-operative climb of dislocations, or co-operative diffusion of vacancies. The mechanism that controls both the rate of coalescence subgrain rotation and the rate of nucleation is, therefore, volume self-diffusion in both cases.

With a vacancy mechanism of diffusion the change of the self-diffusion coefficient D under pressure is given by

$$\frac{\partial \ln(D/a^2\nu)}{\partial p} = - \frac{\Delta V_a}{RT} = - \frac{1}{RT} (\Delta V_f + \Delta V_m) \quad (4)$$

where a is the lattice parameter, ν is the atomic frequency, ΔV_a is the total activation volume, ΔV_f is the partial molar volume of vacancies, ΔV_m is the change of the activation volume corresponding to volume changes in the case of

vacancy migration.

From published estimates [19-21] we find $\Delta V_f \simeq (0.5 + 0.6)V$, $\Delta V_m \simeq 0.15\bar{V}$ (\bar{V} is molar volume) for fcc metals. The increase of activation energy of vacancy formation, therefore, plays a major role in retardation of diffusion under pressure.

The rate of growth of the recrystallization nuclei isolated from the matrix is accomplished through migration of large-angle boundaries and it would be determined by the values of the grain-boundary diffusion coefficients. Both activation energy and activation volume of grain-boundary diffusion are very close to the values of the corresponding characteristics of the vacancy migration process.

Hence, the effect of uniform pressure on grain-boundary diffusion should be weaker than on

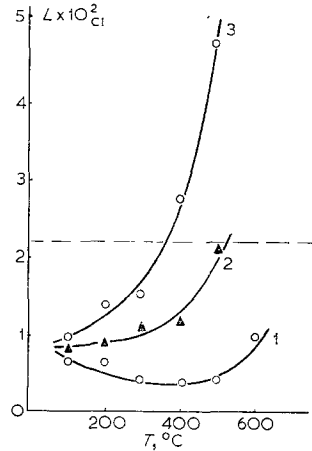


Figure 4 Mean linear grain size, L , versus annealing temperature, T , under different pressures. Annealing time = 1 h. 1. $p = 1$ bar; 2. $p = 5$ kbar; 3. $p = 14$ kbar. Dashed line is for the initial (undeformed) grain size.

volume diffusion and, therefore, the rate of migration of the growing recrystallization nuclei boundaries limited by grain-boundary diffusion must be less sensitive to pressures than the rate of nucleation.

The above considerations are also evidenced by the data characterizing the variations in the average grain size at the annealing stages under pressure which correspond to the beginning of grain growth (Figs. 4 and 5). If the number of growing recrystallized grains is small, then by the time of complete disappearance of the deformed matrix, the grains would become

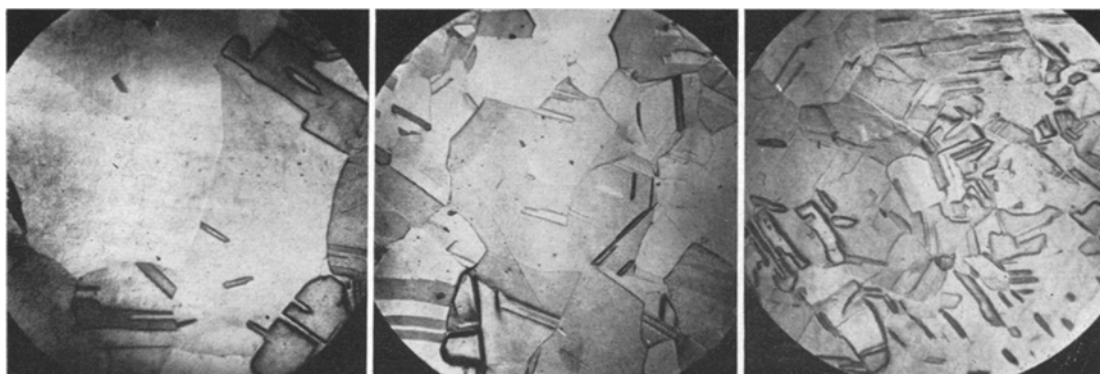


Figure 5 Photomicrographs of copper samples after annealing under pressure, (a) 1.1 bar; (b) 8 kbar; (c) 14 kbar. Annealing temperature = 600°C, annealing time = 1 h ($\times 64$).

larger than for similar annealing conditions without pressure. By retarding the recrystallization kinetics in general, pressure contributes to the formation of a more coarse-grained structure. This effect is most clearly seen at fairly high annealing temperatures (Fig. 5) when nucleation is fast.

5. Conclusions

1. The initiation of recrystallization of cold-rolled commercial copper cold-worked is retarded when the metal is annealed under hydrostatic pressure.
2. According to X-ray diffraction data, the process of nucleation is more sensitive to pressure than the rate of nucleus growth.
3. The difference in retardation of the two processes under pressure is one of the factors responsible for the formation of a coarser structure when annealing under pressure.

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