Softening of Metals

With new techniques, four distinct processes in the thermal softening of metal systems may be studied.

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During an annealing or thermal softening process a deformed metal may undergo many changes before it is reduced to the completely softened state. These changes are normally described by the terms recovery, polygonization, primary recrystallization, and secondary recrystallization. Recovery is usually looked upon as the loss of physical and mechanical properties of the material without normally visible microstructural changes. Polygonization is generally considered to be that state of softening where subblocks or subgrains are formed within the existing grains. Primary recrystallization is said to have occurred when the deformed structure has disappeared and new grains have been produced, while secondary recrystallization is the movement of the existing grain boundaries. These four processes are usually viewed as not mutually exclusive but as occurring simultaneously within a bulk metal. Thus, in a crude test (and most tests of mechanical properties which measure the bulk characteristics of the material are in this category), only the weighted average effect of these processes is reported. With techniques such as electron diffraction and electron microscopy, the individual processes occurring in selected areas of the material may be studied in greater detail.

Recovery and Polygonization

The change in mechanical and physical properties that occurs in recovery as the material approaches the completely softened state is an indefinite measure of the microstructural processes that occur in this stage of softening. Some properties change almost completely before the onset of recrystallization (this is a visible metallographic change), whereas other properties change only partially or perhaps not at all. It is generally believed that point defects and line imperfections are annihilated during the recovery stage; however, precise mechanisms for specific metal systems are not completely understood.

The change in some physical or mechanical property with time as recovery is occurring takes the form of the curve of Fig. 1. The loss in the property is most rapid in the initial interval and gradually slackens as the recovery period increases. The rate relations implied in Fig. 1 are not compatible with the classical nucleation and growth concept for the structural changes occurring during this stage of the softening process. They are compatible with the concept of the annihilation of dislocations, since according to this view the density of dislocations, and thus the rate of annihilation, is greatest in the initial interval. This rate decreases as the density of dislocations decreases. The amount of recovery occurring prior to recrystallization, however, does affect the kinetics of the subsequent recrystallization processes in certain metal systems. It has been shown by Thornton and Cahn (1) that in aluminum an enhancement of the recovery process considerably reduces and even totally inhibits subsequent recrystallization processes. Hu (2) (working with silicon iron crystals) likewise found that the tendency of the deformed crystal to recrystallize is greatly weakened by prior polygonization of the matrix.

Bollmann (3) has suggested that in the softening of a heavily worked metal the following initial condition exists and the following sequence of events takes place. (i) There are present, initially, cloudy distributions of dislocations which are not homogeneous but which contain small areas that are relatively free of dislocations. (ii) During recovery and polygonization the dislocation clouds contract through the annihilation of dislocations, and this contraction subsequently allows the dislocation-free areas to grow. (iii) The dislocationfree areas or subgrains constitute the "nuclei" of the recrystallized grains, and recrystallization continues the softening process of the worked metal.

The existence of subgrains or dislocation-free areas in worked aluminum has also been indicated by Beck (4), from results with electron transmission microscopy. His results on aluminum of 99.999-percent purity corroborate Bollmann's findings that the dislocationfree areas initially present in the worked material grow in size with the application of an isothermal annealing treatment and increase their degree of perfection as annealing continues.

There is some question concerning the onset of polygonization-whether it occurs during the "cold" working operation or immediately afterwards as a stage in the softening process. Research work in which use is made of the thin film technique of electron microscopy has allowed research workers to observe the distribution of the dislocations at various stages of the working operation. A random distribution of dislocations at low strains changes to a "block" structure with dislocations at the boundaries as the degree of deformation increases. These observations lead to the question of whether or not polygonization as a softening process occurs during deformation itself when the material being deformed is very pure (99.999 percent or better). Or one might ask whether, for materials of an extreme purity of 99.999 percent or better, softening of deformed materials may be normally expected for conditions in which the deformation temperature is at room temperature or below. It is generally recognized that impurity atoms control to a great extent the rate at which a degree of order in the metal is attained. Thus, the kinetics, not the thermodynamics, of the material primarily decides when the onset of softening will occur. Softening, therefore, may well occur as an accompanying process during deformation if the material is sufficiently pure and if it is deformed at such a temperature that

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the softening rates are appreciable. Softening of aluminum 99.999-percent pure occurs readily at room temperature if the degree of deformation is of the order of 80 percent.

Thus, there is evidence that when a worked material containing small areas that are free of dislocations is annealed, movement of edge dislocations out of their slip planes occurs and more dislocation-free areas, of a size to be appropriately termed subgrains, are formed. Furthermore, these new areas, as well as the initial dislocation-free areas, grow in size as annealing continues, and eventually an orderly structure of "polygonized subgrains" is produced throughout a great volume of the sample. It is these subgrains, Bollmann proposes, that are the nuclei of the recrystallized grains.

As annealing is continued the subgrains grow, and the grains that are formed through primary recrystallization originate from those subgrains that are able to withstand the competitive growth processes. Factors affecting this competitive growth appear to be, (i) the initial orientation of the subgrains; (ii) the extent, distribution, and type of the impurity atoms of the materials; and (iii) the physical dimensions and surface conditions of the material that is undergoing softening.

Primary Recrystallization

These factors control the structure and texture of the material formed through primary recrystallization, and to the degree to which they are operating, separately and collectively, govern the production of materials of various textures.

The process of primary recrystallization is described classically as the nucleation and growth of new grains which replace the strained grains of the old matrix. I have defined this process as a gradual and continuous change from the worked state, in which there are regions where the density of dislocations is low, to a state in which the grains are relatively equiaxed and visible by means of light microscopy. The change in the mechanical properties is an indication that recrystallization in the classical sense is occurring as the material is heated to successively higher temperatures. Thus, a loss in the tensile yield strength of a material, such as is shown by the curve in Fig. 2, is usually evidence that recrystallization has oc-

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Fig. 1. Typical recovery curve for some mechanical or physical property of a metal.

curred. The definition of the recrystallization temperature as the temperature at which changes in the microstructure and in the mechanical properties occur is purely arbitrary. Sometimes the recrystallization temperature is defined as the temperature at which the drop in tensile yield strength is 50 percent of the maximum possible drop. In Fig. 2 the recrystallization temperature is indicated by T_{R1} . Alternatively, recrystallization temperature is defined by extrapolation from the straight-line portions of the curve shown in Fig. 2, the intersection T_{R_2} being the recrystallization temperature. The recrystallization temperature for a material is, however, a function of the degree of prior cold work, the impurity content, and the specific microstructural state of the specimen immediately prior to annealing; it has no fundamental significance in itself.

The kinetics of recrystallization have been represented analytically by a number of expressions, the most widely used being that of Avrami (5):

$$X = 1 - e^{-Bt}$$

Here X is the fraction recrystallized, t is the time, and B is a constant dependent on the nucleation rate N and the growth rate G, respectively. Avrami states that for three-dimensional recrystallization the constant k takes on a value between 3 and 4, for two-dimensional or disklike growth k lies between 2 and 3, and for one-dimen-



Softening temperature

Fig. 2. Static recrystallization curve for a typical metal with a constant prior degree of deformation.



Fig. 3. Secondary-recrystallization grain structure of high-purity aluminum (purity, 99.999 percent) revealed by etch (HNO₃, 47 percent; HCl, 50 percent; HF, 3 percent). Etch-pit facets indicate that (100) planes are parallel to the surface of the sheet in all grains, with the cube directions of the grains all parallel to the rolling direction.

sional or needle-like growth k lies between 1 and 2. A derivation of similar rate relations by Mishima (6) leads to an expression of the form

$$\ln \frac{X}{1-X} = Bt^k$$

which is identical to the Avrami relation. The Mishima derivation assumes a power function of the growth rate with time,

$$G = G_o t^m$$

When m = 0 and the growth rate is constant (a frequent experimental observation), the Mishima relation predicts a value of k=3, which according to Avrami lies on the borderline between three-dimensional and two-dimensional recrystallization.

Gordon (7), working with zone-refined aluminum, found that G was not a function of time and that k was equal to 2. He concluded that the reaction was edge-nucleated—that is, that the nuclei formed only on the edges of the matrix grains and that the nucleation sites at the edges were all occupied so early in the reaction that no appreciable error was introduced in assuming that the nuclei were present at zero time. This latter deduction is consistent with observations of Bollmann and of Beck which indicate that the potential nuclei are present initially in the cold-worked material as dislocation-free regions.

Cook and Richards (8) have proposed a rate relationship for recrystallization which can be reduced to the Avrami form:

$X = 1 - e^{-Bt^2}$

with k = 2. They suggest a distinct twostage mechanism for grain formation in deriving their relationship, but the mathematics could apply to a conventional nucleation and growth concept, with the growth rate varying as

$G = G_o/t^{\frac{1}{3}}$

This functional relationship would not be found in materials recrystallizing in a three-dimensional manner but would be found in materials transforming in a two-dimensional way. Gordon found the latter to be the applicable process for recrystallization in zonerefined aluminum.

In alloys of aluminum in which second-phase particles are present, the recrystallized grains first observed frequently form adjacent to the secondphase particles in the early stages of primary recrystallization and then develop outward from these centers. This may be due to differences in the worked state of the material adjacent to the particles, since it has been observed that slip lines sometimes are terminated by the second-phase particles. In some cases it may be due to the existence of a zone denuded of alloying and impurity elements, such as is frequently observed around the second-phase particles. Owing to the heterogeneity of the deformation processes and of the distribution of second-phase particles in alloys, an analysis of rate relations that are developed from data obtained by light or electron metallography is likely to yield only a weighted average result for the heterogeneous processes occurring in recrystallization. Thus, there may be little absolute information that can be derived from rate relations with k = 2, k = 3, and so on, and therefore only relative conclusions are possible. With high-purity material certain absolute statements can be made with less likelihood of error. However, even in this case (with materials of 99.999to 99.9999-percent purity), the past structural history may affect the rate relations and lead to erroneous conclusions concerning the mechanisms of the softening process.

As I have stated, in primary recrystallization the effect of impurity atoms on the kinetics and textures of metals can be appreciable. Beck (9) indicated the correlative effect of the quantity of a dispersed phase (MnAl₈) on the graingrowth characteristics of an aluminummanganese alloy. In general his work indicated that the presence of a finely dispersed phase slowed and even totally inhibited grain growth of the aluminummanganese matrix. Later work by Beck (10) on the same alloy system showed that the volume fraction of the cube texture (11) increased with normal grain growth and that inhibition of the normal grain growth by the dispersed second phase, MnAl₆, limited the volume fraction of the cube-texture component on annealing.

Green, Liebmann, and Yoshida (12) indicate that the degree of preferred orientation of a recrystallized aluminum 99.8-percent pure depends on the amount of iron in solid solution. If the iron is in the form of a precipitate that is, removed from solid solution the effect of a preferred orientation is diminished. These workers indicate that the effect is related to an interaction force between the moving grain boundaries and the foreign-atom iron in solid solution, and that the speed of the moving boundary is determined by the iron atoms diffusing behind it. Thus, the relative orientation of the grains would not be the only factor determining the speed at which boundaries move and hence would not be the only factor determining which grains survive the competitive growth processes and contribute to the gross texture of the material in a primary recrystallized state.

Secondary Recrystallization

Subsequent to primary recrystallization the growth of the primary grains may be selective and the generation of material of a texture different from that which previously predominated may occur. A fine second phase may inhibit the growth of the primary grains and produce a discontinuous type of grain growth in the temperature region in which the second phase goes into solid solution. The end state is large grains that are relatively perfect in terms of the presence of subgrain structures. In the case of aluminum of high purity (99.999 percent), the grains appear to have a cube plane (13) in the surface of the sheet and cube directions (13) that are all parallel to the rolling direction (14) (Fig. 3).

The latter observation raises a question concerning the nucleus of a grain formed through secondary recrystallization. The results suggest that grains of the primary-recrystallization structure which happen to have a "cube texture" are nuclei and have sufficiently rapid growth rates to survive the competitive growth processes to the exclusion, in the limiting case, of grains with other orientations. Factors which clearly influence the competitive growth processes are those mentioned in the section on primary recrystallization-(i) impurity content, type and distribution of the impurity; (ii) thickness of the sample and surface conditions; and (iii) orientation of the grains.

It is likely that the orientation of the grain is the most important of these factors for successful growth; however, it is unlikely that all favorably oriented grains survive the competitive growth processes because of excessive concentrations of impurities at some of their boundaries. Thus, although "cube-oriented" grains may act as nuclei for grains formed through secondary recrystallization (and thus must be considered nuclei in some

systems), cube orientation alone is not sufficient to predetermine which primary grains will survive the competitive growth processes during secondary recrystallization. The restraining force of critical amounts of impurities at some cube boundaries appears never to allow certain grains to become active nuclei in secondary recrystallization.

Aust and Rutter (15) found that in zone-refined lead the presence of an impurity in the solid solution was essential to preferred orientation in the structure of growing grains after primary recrystallization. The impurity must be of a specific type and must lie within a certain concentration range. The observed effect was related to impurity-grain boundary interaction in which the impurities segregated at certain grain boundaries and inhibited their migration. Thus, a preferred orientation was generated by inhibition of the normal rates of migration of certain boundaries.

As I have stated, surface conditions may contribute to the final texture attained after secondary recrystallization. Walter and Dunn (16), working with silicon iron of high purity, found that the type of texture generated in secondary recrystallization depended on the type of atmosphere in which the material was annealed. A strong (110) [001] texture was obtained when the material had a low initial oxygen concentration and was annealed in a vacuum; (100)-oriented grains were grown when a slightly oxidizing atmosphere was used. These workers suggest that the texture generated depends on the surface energy of the material, which is the driving force for the generation of large grains of a certain orientation in secondary recrystallization. Thus, it appears in this case that for secondary recrystallization the prior orientation of the grain is only a partial factor in determining whether the grain survives the competitive growth processes.

Walter and Dunn (17) have also indicated that in a 3-percent silicon iron of high purity, grains having (100) planes at the surface have lower surface energies than grains with (110), (111), and (123) surface planes. These results apply to the initial stages of secondary recrystallization when the material is annealed in a vacuum or in argon. They suggest that the lower surface energy of the grains with (100) planes is responsible for their pref-

erential growth. Grains with (100) planes parallel to the surface would have the lowest energies; their energies would increase as the (100) planes were tilted from the surface plane. Thus, the surface energy of the growing grain plays an important part in determining the final structure in secondary recrystallization. Any factor which alters this surface energy, such as environment or orientation of the grain, will determine, in part, the final texture of the material.

Summary

It should be apparent that while there are many complicating factors in softening processes which tend to render some results inconsistent with others, progress in understanding these processes is being made, and certain unifying concepts have evolved. Realization of the differences in the reaction of metal systems to softening is now well established. Arbitrary division of the softening process into distinct stages has perhaps caused some confusion in the past, but with the use of new techniques, mechanistic details of the entire softening process are now being unfolded.

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