magnitude $Q^{-1} = 10^{-4}$. The overshooting is at least 100 times greater than this in all cases, so it appears that this mechanism alone is not sufficient. Neither does it appear likely that the entire effect could come from arrays of dislocations (e.g., grain boundaries), since specimen grain size has no effect on overshooting.

An experimental study of the effect of dislocations was made as follows: A large-grained specimen was carburized and quenched to room temperature in the usual way. Dislocations were then produced in the specimen by drawing it from 0.030 to 0.026 in. in diam. The specimen was then aged to equilibrium at 300°C. The aging temperature was then increased to 450°C. No overshooting occurred at 450°C; the equilibrium solubility at this temperature was achieved rapidly and directly. This result suggests two things: 1) No carbide was present in the sample; all excess carbon went into dislocations at 300°C, and 2) Overshooting is not caused by the evaporation of carbon atoms from dislocations.

SUMMARY

The results of this work indicate that sudden increases in aging temperatures lead to some form of precipitate dissolution which is unusual in that it results in momentary supersaturation of carbon in the iron matrix. The amount of this supersaturation ("overshooting") is dependent primarily on the amount of carbon which was in solution prior to the low-temperature aging; that is, overshooting is dependent on the size and number of carbide precipitates formed during low-temperature aging. To a somewhat lesser degree, overshooting is dependent on the difference between initial and final aging temperatures. The effect increases slightly with increasing temperature difference. Grain size appears to have no effect on overshooting.

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Grain Boundary Migration in High-Purity Lead and Dilute Lead-Tin Alloys

The motion of individual grain boundaries under a constant driving force was investigated for zone-refined lead, with and without solute tin additions. The rate of boundary migration was found to depend strongly on tin content and on the orientation relationship between the adjacent grains. The results are compared with the theory of impurity-controlled grain boundary migration developed by Lücke and Detert. Evidence was found that grain boundaries separating grains which have the Kromberg-Wilson orientation relationships of 38 and 22 deg about <111> and 28 deg about <100>, correspond to boundaries of high mobility. The results are discussed in relation to the formation of annealing textures in metals and the structure of high-angle boundaries.

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It is generally known that small amounts of impurities in solid solution greatly influence the recrystallization behavior of metals. For example, the addition of 0.005 at. pct. of tellurium to copper,1 or 0.005 at. pct. of silver to lead,2 or 0.01 at. pct. of manganese or nickel to aluminum3 greatly decreases the rate of recrystallization of these metals. However, this effect may be the combined result of a decrease in the rates of both nucleation and growth; recrystallization experiments do not separate these two factors. Bolling and Winegard4 determined the effects of small quantities of tin, silver, and gold on grain growth in polycrystalline zone-refined lead.

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Experimental observations are presented which show the effect of relative crystallographic orientation on the rate of grain boundary migration. The importance of this data is discussed in relation to the formation of annealing textures in metals.

EXPERIMENTAL PROCEDURE

Single crystals of zone-refined lead containing various additions of tin from 0 to 0.10 wt pct, were grown from the melt in a horizontal graphite boat. Master alloys of tin in lead and seed crystals containing known tin concentrations were used in order to obtain specimens of known composition. The dimensions of these single crystals were generally about 6 mm square in cross section by 8 to 10 cm in length. The conditions of freezing were maintained nearly identical for each specimen; the speed of freezing was from 5 to 8 mm per min and the temperature gradient present in the liquid during freezing was approximately 10°C per cm. When the desired length of crystal had been grown, the remaining liquid was decanted by rapidly separating the solid and liquid during freezing in order to obtain a representative solid-liquid interface for microscopic observation. Examination of such interfaces revealed the absence of the hexagonal cell structure and, therefore, of the impurity segregation of which it is a manifestation, in crystals containing less than about 0.01 wt pct Sn.

The melt-grown crystals contained striation boundaries having misorientations of up to several degrees as shown by X-ray observations made by means of the usual back-reflection method as well as by the Berg-Barrett technique. The striation boundaries in crystals containing 0.01 wt pct Sn or less were observed to form an irregular pattern, Fig. 1, as reported by Atwater and Chalmers. The addition of about 0.1 wt pct Sn produced a pattern of uniform, continuous striations of the type studied by Teighsouinan and Chalmers.

Over thirty striated single crystals, having various concentrations of tin, were grown. The orientations of these crystals are shown in Fig. 2. A number of the crystals, in the as-grown condition, were annealed for 1 hr or longer at 305°C in an argon atmosphere. This treatment produced no observable change in the striation structure of the crystals, thereby demonstrating the high stability of this structure. No evidence of the formation of new grains was found on annealing the as-grown crystals. New grains were then introduced into each crystal by a plastic compression of a small, localized region at one end of the sample. X-ray photographs from the deformed area showed the presence of numerous small recrystallized grains which formed at room temperature. On annealing at temperatures from 250°C to 300°C in argon, one or two of these recrystallized grains were observed to grow into the undeformed part of the striated crystal. In this way, it was often possible to obtain a single grain produced by recrystallization growing into a striated, melt-grown crystal, and, therefore, the motion of a single, known grain boundary under a constant driving force could be studied.

Fig. 1—Macrophotograph showing growth of a new striation-free crystal into a striated crystal in zone-refined lead. X2 1/2. Reduced approximately 12 pct for reproduction.

Fig. 2—Stereographic plot of specimen axis or growth direction (0) and normal to top surface of crystal (C), for five starting orientations, A to E.
Fig. 1 shows an example of such growth; it will be seen in the photograph that a new grain has grown into the melt-grown crystal at the expense of the striation structure. In order to measure the rate of grain boundary movement, the grain boundary positions before and after various annealing treatments were revealed by lightly etching the sample in a solution of 5 pct nitric acid in methyl alcohol.

RESULTS AND DISCUSSION

a) Driving Force Considerations—Several observations clearly demonstrated that the striation substructure provides the driving force for grain boundary migration in the present experiments. It was found that migration of a grain boundary into a striated crystal removes the striations in the volume through which the boundary has passed, as illustrated by Fig. 1, suggesting that the energy of the striation structure has provided the driving force for migration of the grain boundary. New grains were introduced, by a second localized deformation and recrystallization, into the striation-free crystal thus formed. No growth of this second set of recrystallized grains could be obtained into the striation-free crystal. This indicates a correspondence between removal of the striations and removal of the driving force for boundary migration. In addition, it was observed that intersection of the striation boundaries by the grain boundary is necessary to obtain grain boundary motion. A grain boundary will not advance into the striated crystal if the striation boundaries are parallel to the grain boundary rather than intersecting it. A number of the melt-grown crystals used in this work contained regions which were free of striations. In such cases, it was found that a new grain would not grow into the striation-free region while another new grain grew continuously into the striated portion of the same crystal. It is evident, therefore, that an interaction must be geometrically possible between the striation boundaries and the grain boundary in order for grain boundary migration to occur and that the energy associated with the striation structure does provide the driving force for grain boundary migration in the present experiments. While variations in the striation pattern were sometimes observed, as discussed above, it was possible to obtain a reasonably uniform and reproducible striation structure by careful control of the conditions of freezing of the samples.

An estimate of 4000 ergs per cm$^3$ for the driving energy provided by the striation structure was obtained from measurements of the average orientation difference (3 deg) and average spacing of the striation boundaries (0.04 cm) combined with previous data on grain boundary energies in lead. The number of dislocations comprising a striation boundary can be calculated on the assumption that the boundary is of the simple tilt type. On this basis, the number of striation boundaries observed in the crystals used in this investigation corresponds to a dislocation density of approximately $7 \times 10^7$ lines per sq cm. Removal of the striations by passage of a grain boundary, therefore, indicates a dislocation density difference of about $7 \times 10^7$ lines per sq cm between the new grain and the striated crystal.

The striation structure is not measurably changed by annealing of the undeformed, striated crystal for long periods at 300°C. Consequently, this substructure provides a stable driving force for grain boundary migration. In addition to the case of lead, the striation structure has also been observed to support grain boundary migration in melt-grown crystals of zone-refined copper, aluminum, and tin. The present technique for studying grain boundary mobility should, therefore, have general applicability.

b) The Influence of Tin on the Rate of Grain Boundary Migration—The rate of grain boundary migration in crystals of zone-refined lead to which no impurity had been added was observed to be as high as 8 mm per min at 300°C. With a driving energy of 4000 ergs per cm$^3$, this rate corresponds to a grain boundary mobility (i.e., rate per unit of driving energy) of $2.5 \times 10^{-5}$ cm$^2$/erg-sec at 300°C. This mobility is at least one hundred times greater than any previous values reported for metals in the literature. The addition of tin as solute to the zone-refined lead was found to have a very large effect on the rate of boundary migration. A single crystal was grown in which the tin concentration was 0.001 wt pct along part of its length and 3.015 wt pct in the remainder. Into the 0.001 wt pct Sn section of this crystal was introduced a new grain which was related to the striated crystal by a rotation of 32 deg about the axis shown in Fig. 3. In the first 2 hr of annealing at 300°C, the grain boundary moved through the striated region containing 0.001 wt pct Sn at a rate of 0.1 mm per min, Fig. 3. When the boundary reached the region containing 0.015 wt pct Sn, very little further movement occurred after an additional annealing time of 88 hr at 300°C. The rate of migration in this region was less than or equal to 0.0001 mm per min. In crystals containing 0.05 and 0.10 wt pct Sn, no observable boundary migration at the expense of the striation structure could be obtained in annealing times of the order of 100 hr.

The rate, $v$, of migration at 300°C of various

![Graph showing grain boundary displacement vs time at 300°C for a "double-concentration" specimen.](image)

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*Fig. 3—Grain boundary displacement vs time at 300°C for a "double-concentration" specimen, i.e., 0.001 and 0.015 wt pct Sn. Orientation relationship for grain boundary is shown in stereographic triangle.*
high-angle grain boundaries separating crystals of random relative orientation, is plotted as a function of tin concentration, C, in Fig. 4. Both the rate and concentration scales are logarithmic in this figure. It will be seen that an increase in tin content from 0.0004 to 0.006 wt. pct decreases the speed of boundary migration by a factor of 1000. This illustrates both the extremely large effect of a small amount of tin on the rate of migration and the remarkably strong dependence of migration rate on solute tin concentration. Also, \( \log v = 10.7 - 2.5 \log C \)

where \( v \) = speed of migration in cm per sec and \( C \) = tin concentration in atom fraction.

Below a concentration of about \( 4 \times 10^{-6} \) wt fraction Sn, the \( \log v \) vs \( \log C \) plot deviates from the linear relation which holds at higher concentrations, the concentration dependence becoming much smaller, as shown in Fig. 4. Nevertheless, in this range, the addition of less than \( 10^{-8} \) wt concentration Sn still produces an easily measurable effect on the rate of boundary migration.

As noted above, the grain boundary-migration rate was observed to change by a factor of about 1000 as the tin concentration was varied from 0.0004 to 0.006 wt. pct. This large change in boundary-migration rate with solute concentration is not due to variation of the striation driving force, since no appreciable variation in the striation structure was observed in this concentration range. In fact, the variation in driving force from specimen to specimen is believed to be less than a factor of two, based on the observed reproducibility of the striation structure and the internal consistency of the results. Consequently, the observed dependence of migration rate on tin concentration is attributed to a corresponding variation in grain boundary mobility. Fullman has also concluded that solute atoms affect primarily grain boundary mobility rather than driving force in grain growth processes.

The experimental results described above may be compared with the quantitative theory of impurity-controlled grain boundary migration proposed by Lücke and Detert. This theory is based upon the concept that interaction forces exist between foreign atoms in solid solution and a grain boundary, so that the concentration of foreign atoms is increased in the boundary. It proposes that at high concentrations or low temperatures, a moving grain boundary is held back by this interaction so that its speed is controlled by the speed at which the foreign atoms can diffuse along with the boundary as it moves; at low concentrations or high temperatures, the interaction is insufficient to hold the boundary, “breakaway” occurs, and the boundary moves much faster. On the basis of these considerations, Lücke and Detert derive the following equation describing impurity-controlled grain boundary migration:

\[
v = \frac{G (2r)^2 \Lambda}{KT} \frac{a^2}{4\sqrt{2}} \frac{D_o}{C} e^{-\left(\frac{Q_D + V}{KT}\right)}
\]

where

- \( v \) = speed of boundary migration
- \( G \) = shear modulus
- \( r \) = atomic radius of base metal
- \( \Lambda \) = dislocation density being removed by the migration process
- \( K \) = Boltzmann’s constant
- \( T \) = temperature in °K
- \( a \) = lattice constant of the material
- \( D_o \) = diffusion constant for bulk diffusion of the solute atoms
- \( C \) = concentration of solute in bulk crystals
- \( Q_D \) = activation energy for bulk diffusion of the solute atoms
- \( V \) = energy gained by putting a foreign atom in the grain boundary

The variation of migration speed with concentration, calculated from this equation using values of the parameters valid for tin in lead under the conditions of experiment used in the present work, is plotted as a dashed line in Fig. 4. Values used in the calculation were: \( G = 0.5 \times 10^{11} \) dynes per sq cm; \( 2r = 3.49 \times 10^{-8} \) cm; \( \Lambda = 7 \times 10^7 \) lines per sq cm; \( K = 1.38 \times 10^{-16} \) ergs per °C; \( T = 573 \) °K; \( a = 4.94 \times 10^{-8} \) cm; \( D_o = 3.96 \) sq cm per sec; \( Q_D = 26,200 \) cal per mol.
The interaction energy, $V$, was calculated by means of Cottrell's formula, as quoted by Lücke and Detert,

$$V = \frac{4}{3} r^3 G \left( \frac{1 + \sigma}{1 - \sigma} \right) n$$  \hspace{1cm} [2]

where $\sigma$ is Poisson's ratio and $n$ is given by:

$$n = \frac{r - r'}{r}$$  \hspace{1cm} [3]

The quantity $r'$ is the radius of the foreign atom in solid solution. Using $\sigma = 0.45$ and $r' = 1.508 \times 10^{-8}$ cm for the case of tin as solute in lead gives a value of $V$ equal to $1.3 \times 10^{-22}$ ergs. An alternative formula given by Lücke and Detert gives the same value for $V$. It should be noted that these calculations of $V$ take into account only an elastic interaction between the impurity atoms and the boundary. It will be seen from Fig. 4 that the theoretical curve describes the experimental data within about an order of magnitude over the composition range studied experimentally. In view of the necessary approximations made in deriving the theoretical curve, this agreement must be considered to be good. In addition, the theory predicts a linear variation of $\log v$ with $\log C$; this was found experimentally over a considerable range of composition. However, the slope of the log $v$ vs log $C$ plot should be unity according to the theory, whereas a value of 2.5 was found by experiment, indicating that $v$ is proportional to $C^{-2/3}$ rather than $v$ is proportional to $1/C$ for the case of tin as solute in lead. To account for this discrepancy by a variation with composition in the driving force for boundary migration would require that the driving force vary by approximately a factor of 30 as the solute concentration decreases from 0.005 to 0.0005 wt pct Sn. Such a variation in driving force is very unlikely, as discussed above. It must be concluded that the dependence of grain boundary mobility on composition is considerably greater for the case of tin in lead than that predicted by the theory.

The theory of Lücke and Detert predicts that, at any given temperature, the grain boundary–impurity interaction will be sufficient to restrict the motion of the boundary only if the impurity concentration is above a certain critical value. This critical concentration is given by:

$$C = \frac{a^2}{4\sqrt{2}} G \frac{(2\gamma)^3}{V} \Lambda e^{-\frac{V}{kT}}$$  \hspace{1cm} [4]

where the symbols are as defined for Eq. [1]. Substituting values of the parameters noted previously gives a critical concentration of $1 \times 10^{-2}$ atom fraction. This may be identified with the break which occurs in the curve of Fig. 4 at about $10^{-6}$ wt fraction. The discrepancy is roughly one order of magnitude. It should be noted, however, that the speed does not rise to "much higher values" below $10^{-6}$ wt fraction, as Lücke and Detert assume will occur when "breakaway" has taken place. On the other hand, the boundary migration would be expected to show very much less dependence on solute concentration when the boundary is "broken away" from an impurity atmosphere than when it is carrying the impurity along with it. It seems reasonable, therefore, to interpret the region of Fig. 4 below about $10^{-6}$ wt fraction of tin as describing the motion of boundaries which are free of an atmosphere of solute atoms.

The speed at which "breakaway" will occur has been given by Lücke and Detert as:

$$v_{\text{max}} = \frac{V D_0}{2\pi kT} e^{-\frac{(q\phi)}{kT}}$$  \hspace{1cm} [5]

Again, the symbols are as defined for Eq. [1]. Substituting appropriate values for the quantities in Eq. [5] gives a value of $v_{\text{max}}$ equal to 11 mm per min. This may be compared to the speed of about 1 mm per min at which the break occurs in the curve of Fig. 4.

It should be noted that a residual impurity content in the zone-refined lead equivalent to $3 \times 10^{-7}$ wt fraction of tin would be sufficient to bring the experimental points below $4 \times 10^{-8}$ wt fraction onto the same straight line as the points above that concentration. While it is believed that the lead used in this investigation had an impurity content considerably less than $10^{-6}$ wt fraction of tin or other equivalent impurities, no direct method of verification of its purity was available with the necessary degree of sensitivity. Consequently, the experimental observations below about $10^{-6}$ wt fraction of tin must be viewed with this reservation. It is hoped that it will be possible in the near future to obtain a better evaluation of solute concentrations below $10^{-6}$ wt fraction.

c) The Effect of Orientation Relationship on the Speed of Boundary Migration—During the determination of the data presented in Fig. 4, grain boundaries were observed from time to time which moved at speeds very much higher than expected. One case
of this phenomenon is illustrated in Fig. 5, which shows distance vs time plots for three grain boundaries. The lower line in Fig. 5 represents the motion of a grain boundary in a sample containing 0.001 wt pct Sn. The speed of this boundary was 0.1 mm per min. The intermediate line shows the motion of another boundary, in a sample containing 0.0005 wt pct Sn. The reduction in tin concentration compared with the first boundary resulted in an increase in migration speed to 0.4 mm per min, as would be expected from Fig. 4. The upper line in Fig. 5 shows the grain boundary motion in a sample containing 0.003 wt pct Sn; this boundary moved at 1 mm per min in spite of the fact that the tin concentration was higher than that in the other two specimens. The latter grain boundary corresponds to an orientation difference of 39 deg about \( <111> \), which is similar to the high-mobility boundaries observed by Liebmann et al. in aluminum.

More detailed investigation showed that these fast-moving boundaries always separate crystals which have relative orientations near one of a few particular relationships. The three relationships giving rise to fast-moving boundaries which have been observed in this study to date are such that the striated crystal and the growing grain are related by a rotation of 36 to 42 deg about a common \( <111> \) direction, by approximately 23 deg about a common \( <111> \) direction, or by approximately 26 to 28 deg about a common \( <100> \) direction. For convenience of terminology, grain boundaries separating crystals, the lattices of which are related as described above, will be referred to as "special" boundaries. This definition, of course, neglects the possible effect of boundary orientation; since the advancing grain boundary was usually curved, as depicted in Fig. 1, the influence of the orientation of the grain boundary itself could not be evaluated in the present study.

Data obtained on the speed of migration at 300°C of these "special" boundaries as a function of composition of the specimen is presented in Fig. 6 along with the data of Fig. 4 for comparison. Note that the speed scale is logarithmic and the composition scale linear in Fig. 6. It will be seen that the difference between the migration rate of a "special" boundary and that of a random, high-angle boundary is a function of the composition of the specimen. Depending on the composition of the sample, the speed of a "special" boundary may be up to approximately one hundred times faster than that of a random boundary under the same conditions. As was pointed out by Lücke and Detert, their theory does not take into account the type of grain boundary being considered. It is evident from Fig. 6 that the boundary-migration rate for the "special" grain boundaries is much less dependent on tin concentration than that for the "random" grain boundaries. If \( \log v \) is plotted vs \( \log C \) for the "special" boundaries, a slope of approximately unity is obtained, although the velocities \( v \) are about a factor of 100 greater than the theoretical values shown in Fig. 4 for the tin concentration range covered.

A large number of recrystallized grains form at room temperature as a result of the localized deformation technique used to introduce new grains into the sample. It is to be expected that, by chance, a few of these recrystallized grains will bear special orientation relationships to the striated crystal. On the basis of the data presented in Fig. 6, the boundaries separating striated and recrystallized grains in special orientation relationship will, in a sample of suitable composition, have a much higher rate of migration than other boundaries. Consequently, it is to be expected that the rapid growth of such a special grain will result in termination of the growth of less favorably oriented grains, so that the successful growing grain produced by this technique will frequently bear a special orientation relationship to the striated crystal if the sample composition is in the proper range.

The orientation relationship between the recrystallized grain which grew most successfully and the striated crystal into which the growth occurred was determined for the specimens used in this investigation. The results for a number of samples of zone-refined lead, with no tin addition and with tin additions less than 0.0001 wt pct, are shown in Fig. 7(a). In this figure are plotted in the standard stereographic triangle, the single axes (open circles) which relate, by the smallest rotation, each successful new grain to the striated crystal into which it grew. The rotations about the axes shown varied from 25 to 60 deg. In some of the
pure lead specimens, it was found that a number of grains grew to a marked extent, with one of them becoming the sole growing grain only after a considerable amount of boundary migration had taken place. In these instances, the orientation of the last grain grown out by the most successful one was also determined; data for these grains are plotted as full circles in Fig. 7(a). On the basis of Fig. 6, it would be predicted that random relative orientations should be found between the successful recrystallized grains and the striated crystals because the difference between the speeds of random and special boundaries becomes very small as zero tin concentration is approached. This expectation is borne out by Fig. 7(a), which shows that the relative orientations are random. In Fig. 7(b) are plotted the axes of minimum rotation, relating each successful new grain to the striated crystal into which it grew, for a number of samples of zone-refined lead to which various amounts of tin, from about 0.0005 to 0.004 wt pct, had been added. It is clear from Fig. 7(b) that there is a very marked preference for the growth of grains having the special orientation relationships noted above, as would be expected from the large difference in migration rate shown in Fig. 6.

A number of attempts were made to obtain fast-moving boundaries in samples containing 0.005 to 0.010 wt pct Sn, by the same technique which was successful for the 0.0005 to 0.004 wt pct Sn range. No fast-moving boundaries were obtained. This observation implies that the migration speeds of special and random boundaries become nearly equal at concentrations above about 0.005 wt pct Sn under the conditions of temperature and driving force used in these experiments; it is not, however, conclusive evidence that the rates do become equal.

The results of Fig. 7(b) are in general agreement with the oriented growth theory of annealing textures, which predicts that successful new grains which grow preferentially into a single crystal will be related to the starting crystal by a \langle 111 \rangle rotation of 30 to 40 deg in the case of face-centered-cubic metals. However, it is evident that only under certain conditions is oriented growth an important or controlling factor since these special orientation relationships were only found in the range of solute concentration from 0.0005 to 0.004 wt pct Sn in zone-refined lead, under the present conditions of driving force and temperature. It is not surprising, therefore, that conflicting results have been obtained in previous studies designed to test this prediction of the oriented growth theory, where the composition, driving force, and temperature have not been maintained identical from one investigation to another.

The special orientation relationships observed during the present work are similar to several of those which Kronberg and Wilson presumed would be favorable for boundary migration. They suggested that, for a series of discrete rotation angles around a common \langle 111 \rangle axis (22 and 38 deg) and around a common \langle 100 \rangle axis (28 deg) in face-centered-cubic structures, the atomic movements necessary for transition between the two misoriented lattices are particularly short and, therefore, easy to accomplish. In fact, 14 pct of the atomic sites in the adjoining lattices would coincide, requiring no movement at all.

One possible interpretation of the data of Fig. 6 is that solute atoms may have less tendency to segregate to “special” boundaries compared to random boundaries at tin concentrations below about 0.004 wt pct. On this basis, the difference in migration rates between the two types of high-angle boundaries could then be explained as due to the special boundaries moving free of impurities while the random boundaries carry an impurity atmosphere with them. This interpretation would be in agreement with the view of Kronberg and Wilson.
that the "special" boundaries are ones across which the lattice matching is unusually good, since the accommodation of impurity atoms would be expected to be less favorable at such interfaces than at random boundaries.

However, it may also be argued that a boundary across which the two crystal lattices fit poorly would better allow the atom movements necessary for boundary migration than one of good fit. On this basis, it might be expected that a special boundary is one of unusually poor fit which may then tolerate a higher concentration of solute before its motion is seriously impaired. While no conclusions can be drawn concerning the detailed nature of different high-angle boundaries, it should be noted that, since certain large-angle boundaries have been shown to have different mobilities under the same conditions, as well as different sensitivities to the presence of solute atoms, their structures must be considerably different.

The orientation relationships observed for the special boundaries are in common with various reported observations of new orientations produced by secondary recrystallization in face-centered-cubic metals, e.g. (18), (19). Consequently, it appears that any theory which attempts to explain these annealing textures must take into account the remarkable growth selectivity demonstrated by the present experiments.

While the phenomenon of grain boundary migration, as described in this paper, offers a technique for producing single crystals which are free of lineage, it also may present a difficulty to be overcome in growing high-purity metal crystals from the melt. When growth of a crystal is initiated from the melt, without the use of a seed crystal, the striation structure does not appear immediately. Appreciable misorientations develop only after a considerable distance, often about 1 cm, has been frozen. Consequently, a stray crystal, introduced during growth of a high-purity single crystal from the melt, can grow to appreciable size without developing striations. This may result in the formation, during freezing, of a grain boundary which separates a striation-free crystal from the striated one which is destined to propagate. The striation-free crystal formed in the way can grow by grain boundary migration at the expense of the striation structure of the desired crystal, thereby terminating its propagation. A number of instances have been observed in which a grain boundary formed by the accidental introduction of a stray crystal migrated several cm during the solidification operation, thereby transforming not only the desired crystal, but also a large part of the seed used to initiate its freezing, to the orientation of the stray. In extreme cases, the seed crystal may be lost as a result of the grain boundary migration.

Experiments are now in progress to determine the temperature dependence of grain boundary migration in zone-refined lead crystals with various tin additions as well as the effect of solute atoms other than tin.

SUMMARY

1) The striation structure of melt-grown single crystals provides a stable driving force for grain boundary migration.

2) The striations are removed by passage of the grain boundary through the striated crystal.

3) The addition of a small amount of impurity to zone-refined lead has a very large effect on grain boundary migration rate under the present experimental conditions.

4) The dependence of migration rate on concentration of tin is very steep: the rate of migration, \( v \), is decreased by a factor of about 1000 as the tin concentration, \( C \), is increased from 0.0004 to 0.006 wt. \( v \) is proportional to \( C^{-6.2} \) in this concentration range.

5) Theoretical values of grain boundary migration rate, calculated on the basis of the theory of Lücke and Detert, agree with the experimental observations within approximately one order of magnitude. However, the dependence of boundary-migration rate on tin concentration, mentioned in 4) above, is considerably greater than that predicted by the theory.

6) Grain boundaries separating crystals which are in special orientation relationship were found to move at speeds up to one hundred times greater than boundaries separating crystals of random orientation difference, under the same conditions. Special relationships observed were those which relate the two crystals by a rotation of 36 to 42 deg about a common \(<111>\) axis, by 23 deg about a common \(<111>\) axis, and by 26 to 28 deg about a common \(<100>\) axis.

7) The difference in migration rate between "special" and "random" boundaries is markedly dependent upon the concentration of impurity present. This difference in speed is small for zone-refined lead and increases to a factor of about one hundred at a tin content of about 0.004 wt. pct under the conditions of the present experiments.

8) Only in the concentration range where the difference in boundary-migration rates is large was it found that the recrystallized grain which grew most successfully into the striated crystal was frequently related to it by one of the special orientation relationships noted in 6) above. This indicates that the growth selectivity represented by the difference in migration rates plays a major role in determining which grains will grow most successfully.

9) The special orientation relationships noted in 6) above are similar to several of the Kronberg-Wilson orientation relationships.

10) The special orientation relationship of 36 to 42 deg about a common \(<111>\) axis is essentially that which is predicted by the oriented growth theory of annealing textures.
The Nickel-Titanium-Carbon System

A tentative 870°C isothermal section, the solidus equilibria, and the solubility of TiC and graphite in the nickel solid solution have been determined with arc-cast specimens. Each of the Ni-Ti intermetallics forms two-phase fields with TiC; only Ti₄Ni has a measurable solubility for carbon. A quasi-binary eutectic exists between TiC and a titanium-rich nickel solid solution; ternary eutectics occur on either side, with TiNi₃ or with graphite. Graphite is in equilibrium with a nickel solid solution containing a ratio of Ti/C which increases below the solidus.

DURING the past decade, titanium-carbide cermets containing nickel or cobalt alloy binders have been widely studied for high-temperature and wear-resistant applications. Recent work has emphasized control of the carbide grain size and distribution and the thermal expansion match between the phases. The present study was initiated to determine the phase compositions during the sintering or infiltration process, and during subsequent heating. Although the effect of additives and impurities in commercial compositions are important, it was necessary to consider first the pure ternary, Ni-Ti-C. Emphasis was placed on the nickel corner, since the nickel solid solution is the continuous phase in compositions having highest strength.

Early metallographic work by Zarubin and Molkov showed that solid solubility at either end of the section Ni-TiC is small. Edwards and Raine reported that nickel dissolves between 3 and 5 wt pct TiC at 1250°C, on the basis of microstructures of annealed, vacuum-melted powder mixtures. Although the solubility of nickel in TiC has not been measured, TiC formed by the menstruum process in liquid-iron solution contains as little as 0.06 wt pct Fe.

BINARY SYSTEMS

The most recent determinations of the three binary systems are summarized in Fig. 1. Titanium carbide (6) is predominant among the binary phases, and it melts above the boiling point of nickel.

The Ni-C binary is based on separate liquid solubility and solid solubility measurements. The eutectic temperature, 1328°C, is taken from the solidus description below. However, thermal analysis data by Morrogh and Williams also show eutectic arrests in this vicinity in the absence of supercooling.

The Ni-Ti binary is taken from the work of Poole.