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Rapid growth of single crystals in the solid state utilizing a massive transformation

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A method is described for rapidly growing single crystals in the solid state, utilizing the massive transformation. The technique involves moving a necked specimen through a thermal gradient and it has been shown to be successful in alloys of the Ag-Al system near 24.5 at.% Al. Single crystals of the hcp ζ phase have been grown from the bcc β phase at rates between 0.01 and 1.2 cm sec^{-1}. X-ray observations indicate the development of misorientations and a substructure with increasing crystal growth velocity. Metallographic observations on numerous crystals demonstrate that the occurrence of single crystal growth is closely related to the relationship between the undercooling at the transformation interface and the interface velocity. Favourable conditions require that the velocity of the transformation interface be near the maximum value possible under the imposed thermal conditions. Success in growing a single crystal decreases with increasing undercooling and no crystals could be grown when the undercooling exceeded about 20°C. Solid state crystal growth utilizing the massive transformation has many features in common with crystal growth resulting from undercooled liquids.

1. Introduction

It is now well established that many metals and alloys can undergo a crystal structure change in the solid state by the process of a massive transformation [1]. In the process the parent crystal structure changes into a new structure, during cooling or heating, and the growth of the new incoherent grains is accomplished through a rapid, non-co-operative, transfer of atoms across relatively high-energy interfaces. There is no change of the overall composition and, since only a few jumps may be sufficient to transfer each atom from one structure to another, most of the atomic mobility is limited to the interphase region. Furthermore, massive transformations exhibit nucleation and growth characteristics which are thermally activated.

Experiments [2] have shown that most massive phases are difficult to nucleate but, once nucleated, the new grains are incoherent with respect to the parent matrix and can grow at speeds exceeding 1 to 2 cm sec^{-1}. This situation allows several parent grains to be absorbed by one growing massive grain and, hence, provided the flow of heat is controlled directionally and only one nucleus is encouraged to grow, a single crystal can result. This possibility has been demonstrated in the Cu-Ga system during the bcc → hcp ($\beta \rightarrow \zeta_m$) massive transformation [1, 3].*

In order to produce a massive transformation it is necessary to ensure that other possible competing reactions do not occur. In cases where a two-phase field is crossed prior to a massive transformation, the heating or cooling rates must be sufficiently rapid to suppress processes involving volume diffusion, such as the equilibrium phase separation. However, such rates may not be the most advantageous for the growth of a single crystal. Hence, in order to study this particular feature, a good alloy system is one in which a two-phase field need not be crossed prior to a massive transformation. This situation occurs between the β and ζ phases in the Ag-rich portion of the Ag-Al system at 24.5 at.% Al, as shown in Fig. 1, where the two-phase fields touch one another at a congruent point.

In the present paper we report on the growth of single crystals of the hcp ζ phase in the Ag-Al system, utilizing the massive transformation

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*The subscript m is commonly used to indicate that the product phase ζ_m is the result of a massive transformation.

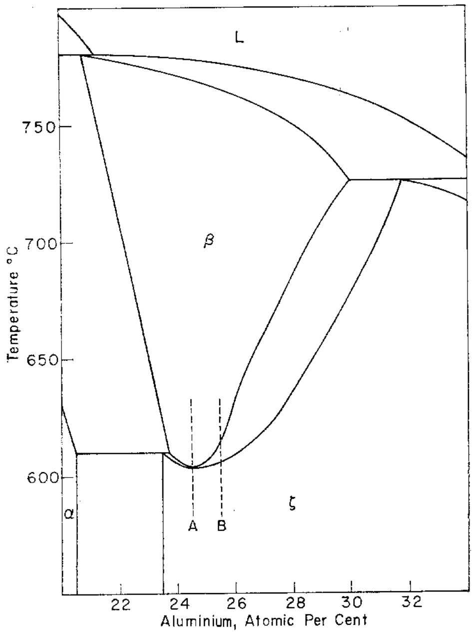

Figure 1 Portion of the Ag-rich side of the Ag-Al phase diagram.

($\beta \rightarrow \zeta_m$) in alloys near the congruent composition.

2. Experimental procedures

2.1. Specimen preparation

All of the experimental work was conducted on alloys with compositions of Ag-24.5 at. % Al and Ag-25.5 at. % Al, referred to as A and B subsequently. As indicated in Fig. 1, the A alloy corresponds to the composition of the congruent point relationship between the β and ζ phases at 603°C. The B alloy is slightly off the congruent composition and the β and ζ phases are separated by a narrow (β + ζ) two-phase field.

Both the Ag and Al used to prepare the alloys were obtained from the United Mineral and Chemical Corporation with a stated purity of 99.999%. After weighing, the constituent elements were compacted together in a hydrostatic press into pellet-shaped slugs of 25 g. The pellets were levitation-melted in an induction furnace which had been evacuated and backfilled with half an atmosphere of argon. The vigorous mixing induced by the levitation coil produced a homogenous liquid on melting. To minimize segregation during casting, each molten alloy was chill cast into a rectangular copper mould coated with graphite. The alloys were homogenized in the β phase at 700°C for 2 days, in fused silica capsules which had been evacuated, heated to bake out any adsorbed water, and backfilled with half an atmosphere of helium. Homogenization was terminated by quenching in an iced 10% NaOH solution (−5°C). The ingots were carefully weighed after casting, and again after homogenization, and in all cases no weight losses, were detected greater than 0.025% of the initial weight or 0.07 at. %, if all the loss is attributed to Al. Confirmation of the intended composition was obtained also from X-ray lattice parameter and electron beam microprobe measurements. The details were the same as in an earlier study with these alloys [4].

The alloys used for the single crystal experiments were reduced to the desired thickness by rolling, with intermediate anneals in the ζ phase. In order to avoid the formation of the extremely brittle μ phase in this composition range* during cold rolling, the ingots were annealed for about 2 min in the ζ phase before each reduction of 10%. The ingots were quickly transferred to the rolls after each anneal. This procedure proved to be satisfactory in fabricating ingots into sheets 0.25 mm thick, and subsequently into strips 3 mm wide and 7 cm long. Specimens for the single crystal experiments were manually filed to produce a tapered neck geometry with a neck angle of about 10 to 15°. The specimens were mounted on brass plates with double-sided adhesive tape and given a final polishing treatment with 0.3 μm alumina powder.

2.2. Massive transformation in a thermal gradient

Single crystals were produced by utilizing one of the distinguishing features of a massive transformation; namely, that once nucleated, massive phase grains exhibit rapid and incoherent growth. The key to the production of single crystals was the directional control of the growth of a single grain. Three important aspects of the experiments were devised with this in mind: the apparatus involving a temperature gradient, the specimen geometry and preparation procedure, and the heat-treatment schedule.

The basic requirement of the apparatus design was that the resultant heat flow in the specimen be unidirectional. The design is relatively simple and consists of a quartz tube surrounded by a furnace. Flowing helium fills the tube which

*For the composition range between the A and B alloys, the μ phase is stable below about 450°C.

contains the specimen. One end of the specimen is maintained at a high temperature (i.e. in the β phase) by the furnace while the other end is spot-welded to a heat-sink which rests in a reservoir of flowing water maintained at room temperature. The heat-sink, which can be any material with good thermal conductivity (a piece of Ag-Al alloy was used in the present case), enhances heat transfer to the water and maximizes the fraction of the specimen that is converted into a single crystal. With this heating arrangement, the temperature gradient that is established along the length of the specimen is then moved at various speeds by the use of synchronous motors that either raise the furnace or lower the specimen at a controlled rate. The specimen holder consists of a clamping device that holds the specimen in a fixed position, or allows it to descend at a controlled rate during cooling.

A narrowed necked region is the most important feature of the specimen design. Utilization of a necked geometry encouraged the migration of only a single β/ζ_m interface by providing a constraint which made it very difficult for more than one interface to pass through the neck. An alternative specimen shape was also tried in which the specimen was tapered to a point at an angle of about 10 to 15°. However, the taper geometry was not as successful in producing single crystal growth as the neck geometry.

Arrangement of the temperature distribution in the specimen was planned to ensure that the critical regions along its length were initially in the appropriate phase fields; and to provide a rapid enough cooling rate to initiate the massive transformation. To accomplish this, a temperature gradient of about 150°C cm^{-1} was needed between the bottom of the furnace and the reservoir of water. Inside the furnace this gradient levelled off, but the temperature was still high enough to maintain the entire region, from just below the neck upwards, in the β phase. Initially each specimen consisted of a recrystallized ζ structure, and a standard anneal of 5 min in the temperature gradient was employed prior to cooling to establish the presence of the β and ζ phases in the required regions along the length. A plot of a typical temperature profile along the specimen chamber during an experiment is shown in Fig. 2.

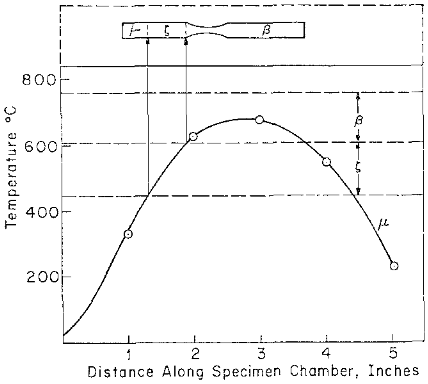

Figure 2 Temperature profile along specimen chamber prior to single crystal growth.

2.3. Optical and X-ray studies

After each experiment, the specimen was polished and examined metallographically with polarized light. Since the massive ζ_m phase is optically anisotropic, the use of polarized light produced contrast between ζ_m grains. This contrast was enhanced by applying a light etch (alcoholic $FeCl_3$) to the surface. If a single crystal was produced, the region that had the β phase structure at high temperature consisted of a single ζ_m grain after transformation. Confirmation of this observation was obtained using Laue back-reflection X-ray photographs. From a series of X-ray photographs taken along the length of the specimen, it was possible to verify that the specimen was a single crystal, and also to establish the orientation of the basal plane of the ζ_m phase with respect to the specimen surface containing the cooling direction.

3. Results and discussion

3.1. Growth of single crystals

By controlling the growth of the massive ζ_m phase during the $\beta \rightarrow \zeta_m$ massive transformation, it has been possible to propagate a single β/ζ_m interface through many specimens and convert them into single crystals of the ζ_m phase. Two examples of successful runs are given in Figs. 3 and 4 for an A specimen grown at a rate of 0.29 mm sec^{-1}, and a B specimen grown at a rate of 0.28 mm sec^{-1}.* In both cases, heat was extracted from the region labelled I.

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*The crystal growth velocity was determined by measuring the transit time for the β-ζ_m interface to travel a fixed distance. Such measured growth velocities showed a complex dependence upon the amount of undercooling and are reported elsewhere [5]. As a result of numerous runs single crystals were grown at velocities ranging between 0.01 and 1.2 cm sec^{-1}, with undercooling not exceeding about 20°C.

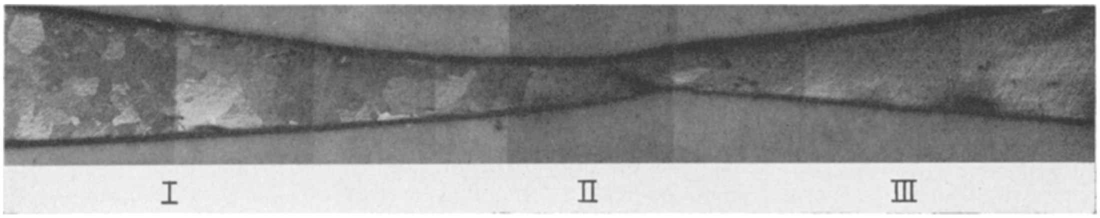

Figure 3 Single crystal of the ζ_m phase (area III) in an A alloy produced during the $\beta \rightarrow \zeta_m$ massive transformation (×7).

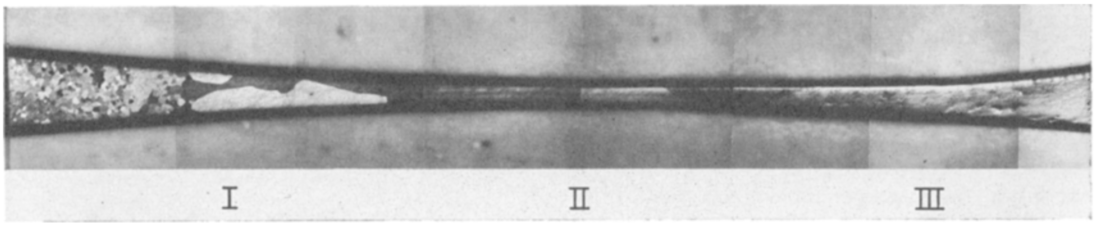

Figure 4 Single crystal of the ζ_m phase (area III) in a B alloy produced during the $\beta \rightarrow \zeta_m$ massive transformation (×7).

In addition to indicating that a single β/ζ_m interface has converted region III in Figs. 3 and 4 into a single ζ_m grain, these photomicrographs contain other microstructural features that are of interest. Initially, in region I, the grains in the ζ phase are relatively small and have shapes indicative of an equilibrated single phase structure. As the neck region, II, is approached, new grains have formed which are larger than in region I and possess the highly irregular shape representative of the massive ζ_m phase. Clearly, in this region the formation of the ζ_m phase involved the nucleation of new grains from the β phase. In the neck region, the ζ_m grain size is comparable to the width of the neck so that only one or two grains fill the specimen. The trend of increasing grain size as the neck region is approached suggests that growth of existing ζ_m grains was favoured over nucleation of new ζ_m grains. The increase in grain size most likely resulted from the operation of a competitive growth process whereby only those grains that were growing at near maximum velocity were able to survive. As the result, on the region III side of the neck, the last β/ζ_m interface to arrive at the neck has emerged as the sole transformation front able to convert the remainder of the specimen into a single crystal.

While a single interface passed through each specimen that was converted into a single crystal, occasionally there was evidence of some additional nucleation. For example, in Fig. 3 a stray grain formed in region III, but its growth velocity must have been slower than that of the main transformation front because it is seen to have been completely engulfed by this front, so that it appears as an island. There is evidence, also, that a small grain formed at the upper edge of the specimen, in region III and was by-passed by the main transformation front before it experienced much growth.

The $\beta \rightarrow \zeta$ transformation in Ag-Al alloys, at about the composition Ag-24.5 at.% Al, has been established by Hawbolt and Massalski [6] to be massive at cooling rates exceeding 10^3 °C sec^{-1}. In the present case the cooling rates employed were about 100 times slower, but the reaction mechanism during single crystal growth is also massive. This is evidenced by several of the features contained in Figs. 3 and 4. Firstly, the characteristic irregular boundaries present in region I in both figures as the neck area is approached are representative of a microstructure resulting from a massive transformation. Secondly, the existence of a single grain in region III can only mean that a single transformation interface has passed through this area. Since region III had a polycrystalline β phase structure before transformation, numerous instances of parent-phase grain-boundary crossing must have occurred. This suggests that no orientation relationship existed between the parent and product phases during the growth as in typical massive transformations. Lastly, in the B crystal, the growth of the ζ_m phase occurred without any solute partitioning despite crossing of the narrow two-phase field. Had partitioning occurred, the two-phase ($\beta + \zeta$) region present before cooling in region I of Fig. 4 would have persisted in regions II and III. This would have resulted in a composition difference across the β/ζ interfaces such that upon further cooling into the single phase ζ range, only the remaining β phase would transform to ζ. However, the latter ζ phase would then have a different composition from the ζ phase that formed initially. In order for a single crystal of the ζ phase to result from this initial condition by competitive grain growth, the composition difference between ζ grains would have to be eliminated. A volume diffusion process would thus be required to accomplish the levelling of the composition difference, but in the limited time available, even at the slowest cooling rate, this would not have been possible. Therefore, the passage of a single β/ζ interface through the specimen implies that solute partitioning, as might be expected to occur from an equilibrium reaction during the crossing of the equilibrium two-phase region during cooling, did not occur, but instead the β phase was converted into ζ_m by a composition-invariant massive reaction. The condition of composition invariance is also satisfied for the growth of an A crystal, but in this case it is not as significant because the presence of a congruent point between β and ζ at this composition precludes solute partitioning.

Not all of the attempts at single crystal growth were successful. Sometimes, especially at the high growth rates and high cooling rates, the formation of new ζ_m grains ahead of the advancing transformation interface would, either partially or completely, block its further motion. With partial blocking, if the main transformation front was moving rapidly enough, the newly formed grains would be by-passed and contained at their point of origin; otherwise, they would compete with the main transformation front. An example of a case in which newly formed grains were contained by the main transformation front is given in Fig. 5. The new grains are lighter in colour and appear elongated in the growth direction, which was from left to right.

In Fig. 6 the main transformation interface was not able to by-pass the newly formed grains and single crystal growth gave way to growth of several grains. A notable feature in Fig. 6 is that while most of the interfaces between ζ_m grains are curved and irregular, some examples of straight boundaries are also present. The straight boundaries are most likely traces of

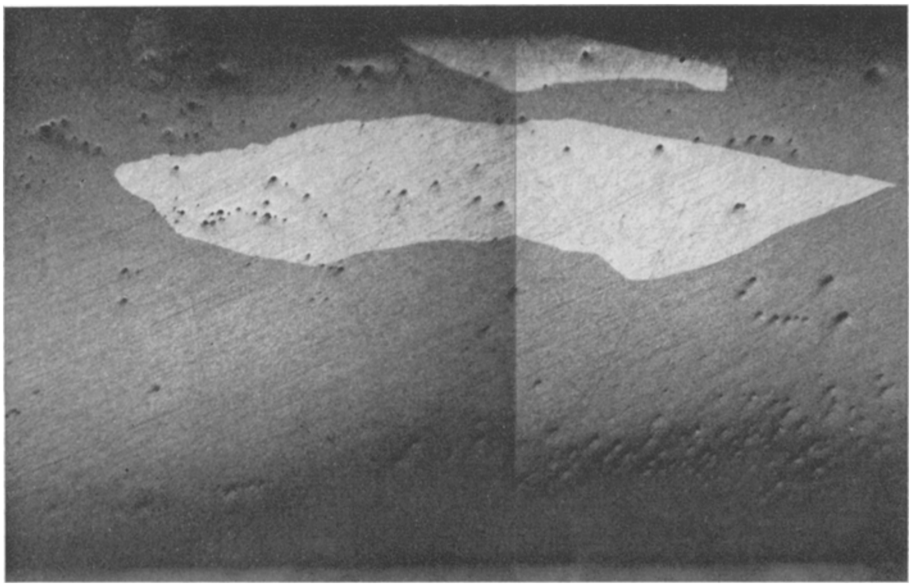

Figure 5 Example of stray ζ_m grains in an A alloy that occasionally formed during single crystal growth (× 34).

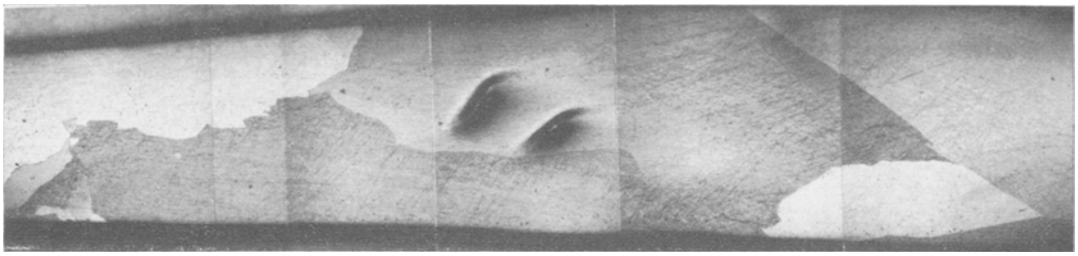

Figure 6 Illustration of breakdown of single crystal growth in a B alloy. The two dark areas in the centre of the specimen are indentations caused by spot-welding a thermocouple (× 15).

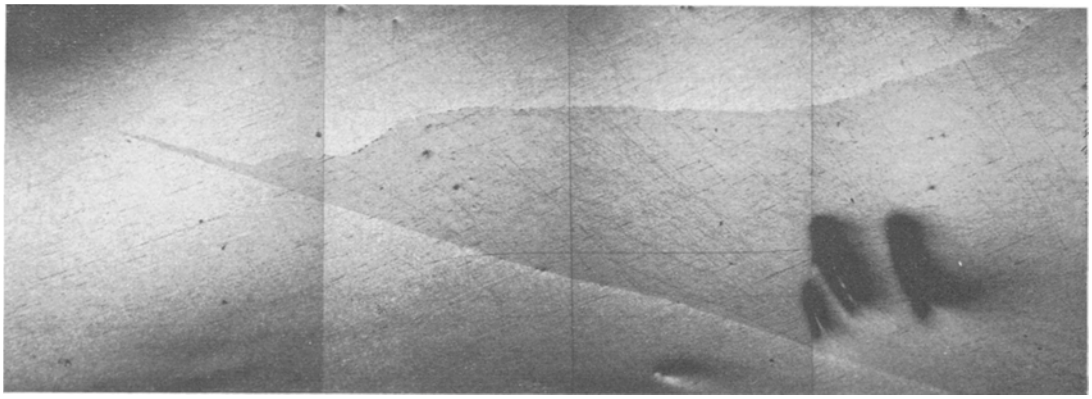

Figure 7 Different types of interfaces observed between ζ_m grains after the $\beta \rightarrow \zeta_m$ reaction in an A alloy (× 43).

planes with a twin orientation, which is the $(10\bar{1}1)$ twin plane for the ζ_m phase.* This suggests that transformation twinning, of the kind observed during the $\beta \rightarrow \zeta_m$ transformation in Cu-Ga alloys [7] and interpreted by Gleiter and Massalski [9], has taken place.

Another example of the occurrence of both highly curved and straight interfaces is illustrated in Fig. 7. In this case, the lower boundary is remarkably straight over its entire length, while the upper boundary is generally curved, especially near the tip of the dark-coloured grain. The small dark areas outlining the upper boundary are precipitates of the μ phase which were formed by annealing this specimen at 200° C for 1 min. The large number of precipitate particles on the upper boundary, particularly in areas of high curvature, suggests that the curved interfaces have a higher energy compared to the straight portions.

Unless the main transformation interface is moving at the maximum velocity for the cooling conditions in effect, its progress may be obstructed by the formation of additional grains. This condition is illustrated by the sequence of transformation events recorded in Fig. 8. As the main transformation front (grain a), was progressing to the right, it encountered a new grain (b). However, before grain (b) had a chance to advance much further its path was blocked by the formation of two other new grains (c and d). During the competitive growth of the main reaction front, (a) and grain (d) both encountered a fault in the specimen (vertical black rectangular area). Since (a) was able to sweep around this obstacle before (d), it must have had a higher velocity. Further evidence for this point is provided by the increase in size of grain (a) at the expense of grain (d) in the area to the right of the fault. Competition during growth also occurred between grain (c) and the main grain (a). In this case (c) appears to have had a higher velocity because it was able to block off com-

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*These straight boundaries were not analysed to determine if they corresponded to the $(10\bar{1}1)$ twin plane. However, in the cases in which straight boundaries between ζ_m grains have been analysed [7, 8] they have always been found to be the $(10\bar{1}1)$ planes.

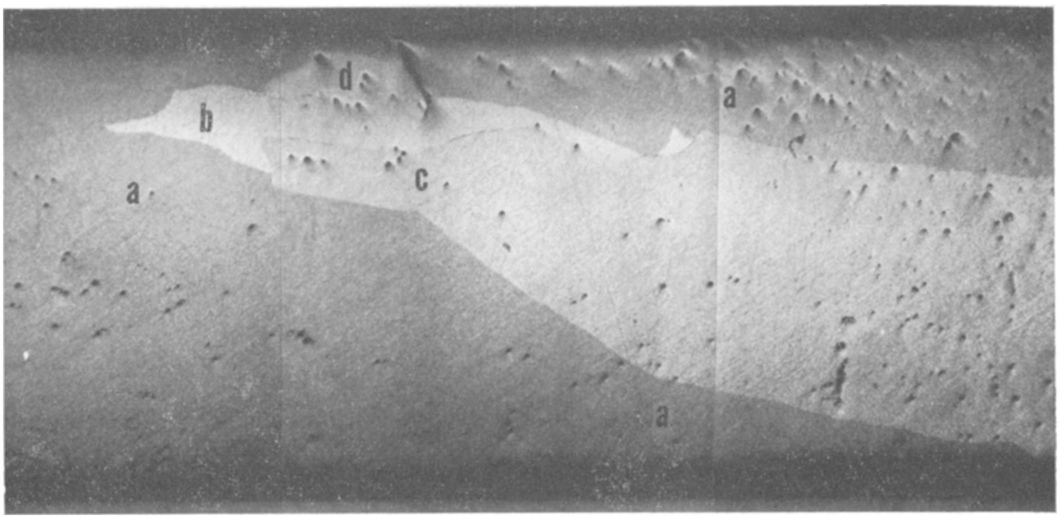

Figure 8 Competition between the main grain (a) and additional ζ_m grains (b, c and d) during massive growth in an A alloy (× 32).

pletely the lower segment of (a) and prevent the upper segment of (a) from increasing in size.

3.2. Details of crystal structure

In addition to providing confirmatory evidence that single crystals were obtained, the results of the X-ray observations also indicate the relationship between growth velocity and crystal perfection. This is illustrated in Fig. 9 for the A alloy. For crystals grown at low velocities of 1.1 mm sec^{-1}. sharp, well-defined, diffraction patterns (Fig. 9a) were obtained. This type of pattern is typical of a fairly perfect crystal, with little substructure. As the growth velocity was increased, there was a noticeable difference in the appearance of the diffraction spots. For crystals grown at 5.4 and 8.5 mm sec^{-1}, the diffraction spots tend to be elongated and split (Figs. 9b and c), indicating the development of a strained mosaic substructure. A much more pronounced distortion produced by a crystal grown at 12.0 mm sec^{-1} is evident in Fig. 9d. It is clear that several slightly misoriented strained subgrains are present. The diffraction patterns obtained from crystals of the B alloy grown at progressively higher velocities indicated a similar trend.

Each of the diffraction patterns presented in Fig. 9 was taken from a crystal oriented with the (0001) plane of the ζ_m phase normal to the incident beam. Initially, the crystals were oriented so that the surface of the specimen containing the cooling direction (i.e. the length axis of the specimen) was normal to the incident beam. After analysing the diffraction patterns, the amount of angular adjustment necessary to bring the (0001) plane normal to the incident X-ray beam was determined. Some representative results are plotted on the stereographic projection in Fig. 10, for crystals of the A alloy. The points plotted in this figure represent the orientation of the single crystals with respect to the standard (0001) plane. They show that in each case the (0001) plane of the ζ_m phase was within less than 20° of the cooling direction. Furthermore, there was no systematic trend observed with changing velocity. Again, similar results were obtained for single crystals of the B alloy.

3.3. Relationship between undercooling and interface velocity

It is customary to denote T_0 as the temperature at which the free energies of the two structures involved in the transformation are equal. For the A alloy, T_0 corresponds to the congruent point temperature in the phase diagram. The driving free energy for the transformation is derived from a certain degree of undercooling, ΔT, below T_0 and, hence, the temperature at the transformation interface, T_i, may be expressed by

$$T_i = T_0 - \Delta T. \qquad (1)$$

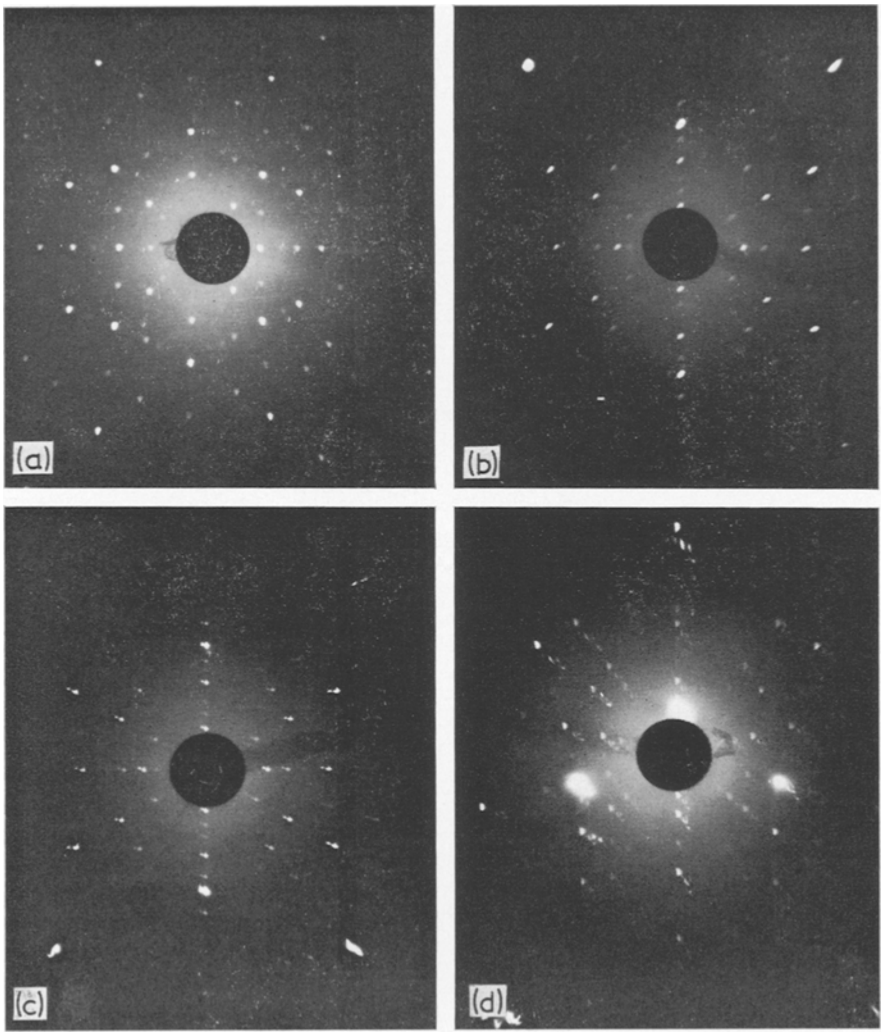

Figure 9 Laue back-reflection X-ray photographs of single crystals of alloy A grown at different velocities. (a) 1.1 mm sec^{-1}, (b) 5.4 mm sec^{-1}, (c) 8.5 mm sec^{-1}, (d) 12.0 mm sec^{-1}.

In the schematic arrangement shown in Fig. 11, as the specimen is moved to the left through the temperature gradient, the T_0 temperature region moves to the right along its length. The T_i temperature, at the transformation interface between β and ζ_m, will also become displaced, always lagging some distance behind T_0. The interface velocity v corresponds to the rate of displacement of T_i. During a massive transformation which resulted in the formation of a single crystal, it may be expected that the value of ΔT was just sufficient to provide a driving free energy for an incoherent growth of a single interface. Any additional nucleation was inhibited by lack of additional driving free energy. A larger degree of undercooling than ΔT would have promoted additional nucleation. Any smaller amount than ΔT would have provided insufficient driving free energy for the propagation of even a single incoherent transformation interface at a rate commensurate with the rate of cooling.

To appreciate the specific balance between velocity and undercooling during single crystal growth, it is of interest to consider what would happen if the interface velocity at any given temperature were less than, or greater than, the rate of progress of T_0, which corresponds to the cooling rate. For an undercooling which resulted in a velocity greater than the rate of

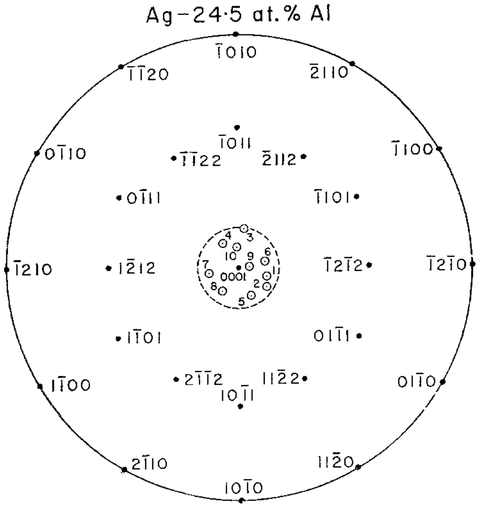

Figure 10 Representation of the orientation of alloy A single crystals on a standard (0001) stereographic projection. The (0001) plane is parallel to the sample surface and includes the cooling direction.

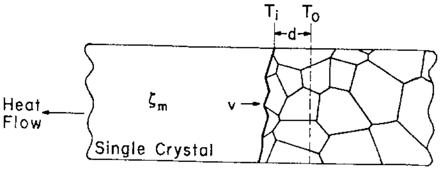

Figure 11 Schematic illustration of the displacement, *d*, between the interface temperature, T_i, and the T_0 temperature. *v* is the average interface velocity.

displacement of T_0, the interface would tend "to overrun T_0". However, this could not happen because as the interface approached T_0 the undercooling would decrease, resulting in a decrease of velocity. If an undercooling were selected which resulted in a velocity lower than the cooling rate, then the interface would lag behind T_0 as the cooling progressed. In a massive transformation this would result in an increase of ΔT giving rise to an increase in the velocity. The interaction of these factors leads to a condition whereby, for each cooling rate, there is a particular combination of undercooling and interface velocity that will enable a single interface to traverse the specimen. Consistent with this view is the observation that, although during single crystal growth the specimen is undergoing a continuous cooling, the interface temperature, T_i, is constant, as indicated by the same value of the thermal arrest temperature measured at different positions on the specimen. Therefore, the imposed cooling rate determines the velocity of the interface and the required undercooling.

Furthermore, the metallographic observations indicate that the interface velocity during successful single crystal growth must be near the maximum value possible for the imposed cooling conditions. The main evidence for this comes from the numerous examples of growth competition between grains in the neck region which resulted in only one β/ζ_m interface emerging from the neck. Additional evidence is derived from the observations of breakdowns of single crystal growth. In cases where an advancing single interface encountered a stray grain already formed by nucleation ahead of it, one of two sequences of events occurred. The main transformation front would either by-pass the stray grain, indicating that it had a slower growth rate, or the stray grain would outrun the main transformation front and curtail its progress, indicating that the stray grain was more mobile. Thus, during a successful single crystal run the interface velocity must have a value which is high enough to prevent any nucleation and growth of grains ahead of it.

These considerations may be viewed in a more explicit manner by noting that the distance, *d*, between the moving interface and the position of T_0 (Fig. 11) is given by

$$d = \Delta T/(\mathrm{d}T/\mathrm{d}x) = \Delta T(\mathrm{d}x/\mathrm{d}T) \qquad (2)$$

where ($\mathrm{d}T/\mathrm{d}x$) is the thermal gradient along the length of the specimen. The volume of material, Ω, between T_0 and the interface (i.e. the undercooled β phase) may be expressed as

$$\Omega = Ad = A\Delta T(\mathrm{d}x/\mathrm{d}T) = A\Delta Tv/\dot{T} \qquad (3)$$

where A is the cross-sectional area of the specimen, v is the interface velocity $\mathrm{d}x/\mathrm{d}t$ and $\dot{T}$ is the cooling rate $\mathrm{d}T/\mathrm{d}t$. Under steady state growth conditions, away from the neck, Ω will be constant. Also, for a given value of ΔT and $\dot{T}$ with constant A, the time, τ, during which the undercooled β phase will exist before transformation by a single reaction interface, is inversely proportional to v and is given by

$$\tau = d/v\,. \qquad (4)$$

Therefore, under steady state conditions the interface with the highest velocity will offer the greatest opportunity for single crystal growth by allowing the least time for the nucleation of new grains.

3.4. Nucleation time of the massive phase

Previous [10] and present experimental work have shown that there exists a well-defined relationship between the transformation temperature of a massive transformation and the rate of cooling. In the single crystal experiments the transformation temperature corresponds to the temperature at the interface, T_i, measured during the passage of a single transformation front under given thermal conditions. In the continuous cooling experiments [11] the transformation temperature corresponds to the thermal arrest temperature observed on an oscillographically recorded cooling curve. In both cases it is possible to estimate, therefore, the amount of time a specimen spends between T_0 and the transformation temperature. During continuous cooling this time, t, consists of two parts: t_n, the time required to nucleate the massive phase, and t_g, the time taken to grow a certain minimum amount. A detailed study of these relative times, based on an assessment of various cooling experiments, has shown that, for the high interface velocities obtained during a massive transformation, t_g is practically negligible compared with t_n (i.e. $t_n \gg t_g$), and that $t \simeq t_n$. This is the experimental basis of a theory describing nucleation during continuous cooling [11].

In the present case it was found that with an increasing cooling rate the success of growing a single crystal gradually diminished until no single crystals were produced when the cooling rate exceeded a certain value. At low undercoolings it was possible to grow successfully a single crystal in about four out of every five attempts. As the amount of undercooling increased, the degree of success decreased. For crystals grown at rates in excess of 1 cm $\sec^{-1}$, about twenty attempts were necessary in order to grow one single crystal.

It is possible to propose an explanation of this observed difficulty in producing single crystals by the $\beta \rightarrow \zeta_m$ reaction at high undercoolings and high cooling rates in terms of the nucleation of the ζ_m phase. During single crystal growth the time τ, during which the undercooled β phase can exist before the transformation temperature reaches it, is given by $\tau = d/v$. If τ becomes much greater than t_n, the time for nucleation of the ζ_m phase under the imposed cooling conditions, then new grains of ζ_m will form in the undercooled β phase before it has transformed by the passage of a single β/ζ_m reaction interface, i.e. the propagation of a single β/ζ_m interface will be hindered by the formation of additional ζ_m grains ahead of it.

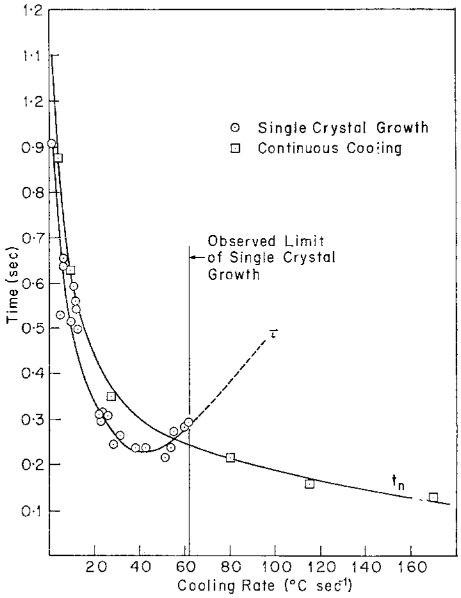

Figure 12 Dependence of the τ and t_n times for the $\beta \rightarrow \zeta_m$ reaction upon cooling rate. Continuous cooling data reproduced from reference [11].

In Fig. 12 the time for commencing conversion of β into ζ_m, either by the passage of a single β/ζ_m reaction front (i.e. $\tau = d/v$), or by nucleation of new ζ_m grains in a continuous cooling process (i.e. $t \simeq t_n \simeq \Delta T/\dot{T}$) [11], is plotted as a function of the measured cooling rate. Up to a cooling rate of about 55° C $\sec^{-1}$ τ is less than t_n. Single crystal growth should be possible, and in fact was observed, for this range of cooling rate. Above a cooling rate of about 55° C $\sec^{-1}$ τ is larger than t_n and single crystal growth should become difficult. This increased difficulty was observed as predicted because, as indicated by the vertical line in Fig. 12, the maximum cooling rate at which a single crystal was still produced was about 62° C $\sec^{-1}$.

3.5. Nature of the interphase boundary

In many respects, the observations of single crystal growth during a massive transformation suggest that there is an evident similarity between the reactions that occur at the massive reaction interface and those that occur at the liquid-solid interface during solidification. The numerous examples of parent-phase grain-boundary crossing during single crystal growth, and the lack of any obvious crystallographic orientation relationship between the parent and product phases, are results which one would expect if the massive reaction interface had some amorphous features. Indeed, a single crystal of the Ag-Al ζ_m phase produced during the $\beta \rightarrow \zeta_m$ massive transformation (solsol process) has features not unlike those found following the cooling from the melt procedure (liquisol process) characteristic of the Czochralski technique. The observation of the development of a mosaic substructure in the ζ_m phase at increasing growth velocities compares closely with the striation substructure found in single crystals produced during controlled solidification.

It has been suggested [12] that as a massive transformation gets under way and reaches its characteristic interface velocity, the interphase region in which the structural transformation is accomplished may become widened and diffuse. Across such transformation boundaries there will be a gradual breakdown of the parent crystal structure, followed by the rearrangement of atoms into the product (massive) structure. This concept of a widened interphase region may be also considered in terms of the kinetic features likely to exist at a rapidly moving boundary.

For the case of a mobile liquid model of a crystal-liquid interface, Nason and Tiller [13] propose that the breakdown of the crystal structure at the interface may occur progressively, over several atomic layers, estimated between 3 a_0 and 7 a_0. The same possibility has been also considered for the case of massive transformations; where the existence of a severely disturbed region extending over several atomic layers has been proposed [12].

4. Summary and conclusions

1. Single crystals of the close-packed hexagonal ζ phase can be grown successfully in the solid state in the Ag-Al system from the high temperature β phase, utilizing the massive transformation. Such crystals are grown at speeds between 0.01 and 1.2 cm sec^{-1} by the passage of a single transformation interface through the specimen.

2. The success of producing single crystals by a massive transformation is related to the fact that in the Ag-Al system the massive transformation, $\beta \rightarrow \zeta_m$, can occur at the congruent composition, where other possible reactions, associated with solute partitioning, are absent. Nevertheless, single crystals can also be grown in alloys near the congruent composition, in which case the massive transformation takes precedence over equilibrium phase separation in the narrow two-phase field.

3. As the velocity of the transformation interface is increased through increased undercooling the resulting single crystals become less perfect and exhibit a structure with small misorientations.

4. The occurrence of single crystal growth is sensitively related to the relationship between undercooling and the transformation interface velocity. In a successful run the velocity of the interface is near the maximum value possible for the imposed cooling conditions. Under such conditions any nucleation and growth of grains ahead of the main transformation interface is inhibited.

5. The present experiments suggest that single crystals can be produced only if the nucleation time of the massive transformation, at a given cooling rate, is larger than the time during which the undercooled β phase can exist at the same cooling rate, before it is swept by a passage of a single transformation front. For the Ag-Al alloys the maximum undercooling possible, that still allows growth of single crystals, is about 20°C.

6. An evident similarity appears to exist between the structural features of crystals resulting from a solid state massive transformation and from solidification of liquid metals.

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