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A CINEMATOGRAPHIC STUDY OF THE MASSIVE TRANSFORMATION IN Cu–Ga ALLOYS*

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The massive transformation in five Cu–Ga alloys, containing between 22.8 and 24.3 at.% Ga, has been studied cinematographically during heating and cooling in a hot-stage assembly. The rate of heating and cooling varied between 4 and 30°C/sec. The cinematographic work was supplemented by metallographic and X-ray work at room temperature.

It is concluded that under the conditions of the present study the major part of each transformation occurred by the propagation of incoherent boundaries of the massive phase in a manner expected for a diffusion-controlled process. The speed of the massive transformation was some 100 times faster than that of a diffusional process that produced equilibrium structures.

In many cases the advancing transformation front became planar, particularly in regions where plastic deformation in the parent phase produced temporary barriers to further transformation. Plastic deformation was also in part responsible for the occurrence of the ledge-type of growth in the bulk, and for slip markings observed on the surface. It is concluded that growth of the massive phase grains occurs both with and without the existence of an orientation relationship between the parent and massive phases. The growth of $(10\bar{1}1)$ twins and of other planar boundaries is reported.

ETUDE CINEMATOGRAPHIQUE DE LA TRANSFORMATION MASSIVE D'ALLIAGES Cu–Ga

Une étude cinématographique faite pendant le chauffage et le refroidissement, au moyen d'une platine chauffante, a per mis l'étude de la transformation massive de cinq alliages Cu–Ga, dont la teneur en Ga variait de 22,8 à 24,3% at. Les vitesses de chauffage et de refroidissement s'échelonnaient, de 4 à 30°C/sec. Cette étude cinématographique fût complétée par des examens au microscope et par les rayons X, à la température ambiante.

Les conclusions de cette étude sont, que les conditions présentes la majeure partie de chaque transformation se produit par la propagation des joints incohérents des phases massives, d'une façon logique pour un procédé contrôlé par la diffusion. La vitesse de la transformation massive était denviron cent fois supérieure que celle qui aurait été dûe à un processus de diffusion et aurait ainsi conduit à des structures d'équilibre.

Dans plusieurs cas, le front de propagation de la transformation devenait plan, particuliérement dans des régions où la déformation plastique de la phase mère produisait des barriéres à une transformation ultérieure. La déformation plastique était également la cause de l'apparition de lignes de glissement en surface. En conclusion, la croissance des grains de la phase massive a lieu avec ou sans l'existence d'une relation d'orientation entre la phase mère et la phase massive. La croissance de macles $(10\bar{1}1)$ et d'autres joints plans est également notée.

EINE KINEMATOGRAPHISCHE UNTERSUCHUNG DER UMWANDLUNG IN Cu–Ga–LEGIERUNGEN

Die feste Umwandlung in fünf Cu–Ga–Legierungen mit 22,8 bis 24,3 At.-% Ga wurde kinematographisch durch Heizen und Abkühlen in einer Heizstufe untersucht. Heiz- und Abkühlgeschwindigkeiten variierten zwischen 4 und 30°C/sec. Die kinematographischen Untersuchungen wurden durch metallographische und röntgenographische bei Raumtemperatur ergänzt.

Es wird gefolgert, daß bei den vorliegenden Bedingungen der größte Teil jeder Umwandlung durch die Bewegung inkohärenter Korngrenzen der festen Phase nach einem diffusionsbestimmten Prozeß erfolgt. Die Geschwindigkeit der festen Umwandlung war etwa 100 mal größer als die eines Diffusionsprozesses, der zu einer Gleichgewichtsstruktur führt.

In vielen Fällen wurde die fortschreitende Umwandlungsfront eben, besonders in Gebieten, in denen plastische Verformung in der Matrix zeitweilige Hindernisse für eine weitere Umwandlung bildete. Plastische Verformung war auch teilweise für das Auftreten leistenartigen Wachstums in der Matrix sowie von Gleitmarkierungen auf der Oberfläche verantwortlich. Es wird gefolgert, daß ein Wachsen der Phasenkörner sowohl mit als auch ohne Bestehen einer Orientierungsbeziehung zwischen Ausgangs- und fester Phase erfolgt. Ferner wird Wachsen von $(10\bar{1}1)$-Zwillingen und anderer ebener Korngrenzen beobachtet.

1. INTRODUCTION

The occurrence of a massive transformation in the b.c.c. β Cu–Ga alloys is a well-established phenomenon.[1–5] The characteristic features of this transformation are the rapid rate with which grains of the new structure form, the absence of a change in composition, and the metallographic appearance of the resultant product phase, one of massive patches or irregular grains. This latter feature has caused

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This paper is based in part upon a film *Massive Transformation in Cu–Ga Alloys* produced by the authors in 1962–63 and presented at the AIME Meeting in Cleveland, Ohio, in October 1963, as well as upon some subsequent cinematographic work. A copy of the original film may be obtained on a loan basis from the authors upon request. Both the film and the research described in this paper have been supported in part by the U.S. Atomic Energy Commission, Washington 25, D.C.

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other transformations, particularly in Fe–Ni steels[5–10] to be called massive because of the similarity of the obtained microstructures. In the Cu–Ga alloys the diverse morphological features of the "massive" microstructures have been described in detail[1–3] and have been supplemented by electron microscopy.[3,4,11] They support a possible viewpoint that the transformation process is not the same in the different alloys studied, but that it gradually changes with composition and with the rate of cooling.

In order to obtain additional information on this subject we have attempted to observe the transformation process directly, both on heating and cooling. The present paper describes a series of experiments with Cu–Ga alloys made in a hot stage and recorded cinematographically under polarized light. The movements of grain boundaries and of interfaces, and other accompanying changes as they appear on the transforming free surface, could thus be observed directly. Additional work is also reported on lattice orientations at room temperature.

The cinematographic investigation was restricted because only relatively moderate quenching and heating rates could be achieved in the hot-stage assembly. Hence, in order to prevent the equilibrium decomposition of β into $\alpha + \beta$ and $\beta + \gamma$ structures prior to the massive transformation, the composition of the alloys chosen for investigation was limited to the range near the eutectoid composition of the β phase (Fig. 1); the actual range of compositions which are susceptible to a massive transformation on cooling is known, however, to be much larger.[1,2] This is indicated in Fig. 1 by the shaded areas. Transformations can occur from the β phase to the f.c.c. α_m phase ($\beta \rightarrow \alpha_m$) in the range of 19.3–20 at.% Ga; and from the β phase to an h.c.p. ζ_m phase ($\beta \rightarrow \zeta_m$) at higher Ga contents. Only in the range of compositions falling to the right of the eutectoid point (i.e. in the hypereutectoid alloys) is the *massive transformation* clearly proceeding by the nucleation and growth of mostly incoherent high-energy boundaries.[1] In the eutectoid and hypoeutectoid alloys the morphological features of quenched alloys are considerably more complex, revealing the presence of numerous planar boundaries, heavily striated regions, and "feathery structures". Whether or not the transformation in this composition range should be called massive is open to some question.

The compositions of the presently studied alloys are shown in Fig. 1 by means of arrows on the abscissa. The phase diagram in the region of the massive transformation involves also the order–disorder reaction in

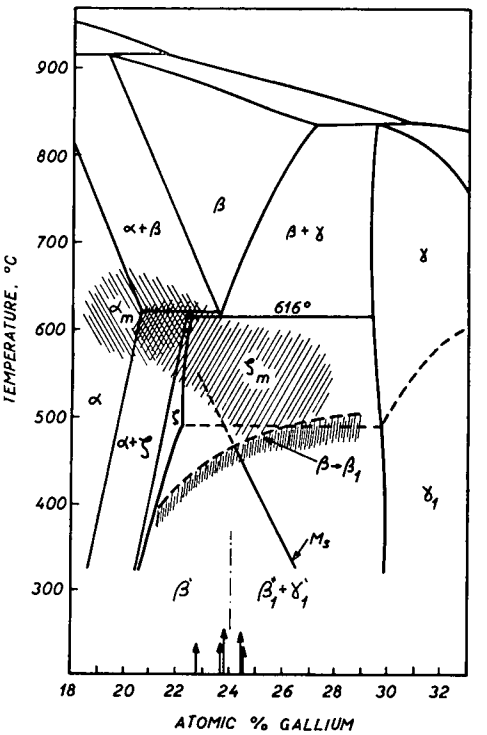


FIG. 1. Cu-rich portion of the Cu–Ga equilibrium diagram.[17] Both equilibrium phase relationships and the approximate positions of the order–disorder and martensitic structure are shown. The range of massive transformations is indicated by shaded areas and the compositions of the presently studied alloys are shown by means of arrows on the abscissa.

the β phase ($\beta \rightarrow \beta_1$), and various martensitic transformations, into both disordered ($\beta \rightarrow \beta_1$), and ordered ($\beta_1 \rightarrow \beta_1''$, $\beta_1 \rightarrow \gamma_1'$)[3,13] structures. The transformation temperatures indicated in Fig. 1 are only approximate and it appears that the $\beta \rightarrow \beta_1$ change can be considerably depressed by quenching.[14]

2. MATERIALS AND METHODS

Alloys were prepared from spectroscopically pure copper supplied by Messrs. Johnson, Matthey and Company, Ltd., and from 99.99% pure gallium supplied by the Aluminum Company of America. The details of the casting technique have been described in earlier papers. The nominal composition of the alloys was accepted when no significant change in weight had taken place during preparation. However, many compositions were confirmed by comparison of the measured lattice spacings with a previously established master curve relating lattice spacings to composition.

After casting, the alloys were deformed 10–20% by cold swaging and were heat treated in sealed quartz tubes for 20 hr at 800°C under reduced pressure of helium. This was followed by quenching in iced

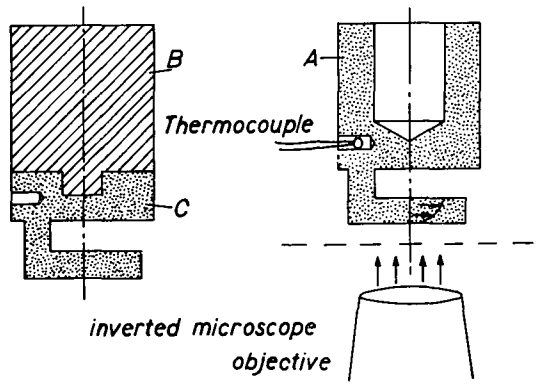


FIG. 2. Sample arrangement as used in the hot-stage assembly (schematic). The shape of the sample specimen encourages lateral heat transfer.

water. The ingots were machined in order to give the specimens a suitable shape and dimensions for use in the hot stage (see Fig. 2).

The Reichert high-temperature stage[15] used for the experiments was heated by a tantalum resistance element in a vacuum better than 10^{-4} torr, or in a helium atmosphere. The hot stage was placed above a conventional inverted microscope and the specimens were observed through a quartz window. The progress of the transformations was recorded using polarized light and a camera with a maximum film velocity of 64 frames/sec. A Xenon light source was used in order to achieve the necessary light intensity. The film material was KODAK TRI-X or PLUS-X.

The temperature was measured using a thermocouple placed in a small cavity made in the specimen or spot welded near the observation surface. During each experiment the temperature was recorded using a Speedomax-type recorder. The resulting curves showed inflections corresponding to the phase changes occurring in the specimen.

The specimen size and shape varied according to the desired cooling rate. Higher rates were obtained when the specimen shape A, shown in Fig. 2, was used and a stream of pre-cooled helium gas was directed near the top of the specimen. For a lower cooling rate, the specimen assembly consisted of two parts, the lower part being the alloy under investigation C and the upper part a copper block B mounted as shown in Fig. 2. Heating and cooling rates in the range between 120–0.2°C/sec resulted from the use of the above specimen arrangements.

Laue back-reflection photographs from individual grains were made with copper radiation collimated to 0.2 mm. In a few cases additional observations of surface contours were made using the Reichert–Nomarsky interferometer.

3. DESCRIPTION OF RESULTS

3.1 *Initial transformation temperature*

The direct visual observation of the onset of transformations in the hot stage, coupled with the temperature–time curves recorded simultaneously, permitted to establish the dependence of the initial transformation temperature upon the heating (or cooling) rate. Superheating was observed during heating, and was related to the heating rate; but no quantitative data were recorded. On cooling there was a considerable scatter between different experiments; however, the transformation temperature of the massive transformation was always lower as the cooling rate* increased within the range under investigation. There was thus observable undercooling, consistent with a growth mechanism controlled by diffusion. The results for a single sample containing 24.5 at.% Ga are plotted in Fig. 3. An approximate linear relationship between the cooling rate and the transformation temperature may be inferred. Figure 3 indicates that some degree of undercooling is required even at cooling rates amounting to a few degrees per second. The transformation temperatures for the eutectoid and hypoeutectoid alloys were also subject to undercooling.

3.2 *The general nature of interface movements*

Since all experiments involved a continuous heating and cooling of a sample, the obtained film sequences showed events corresponding to a changing range of temperatures in each case. Typical sequences of selected frames are shown in Figs. 4, 5, 6 and 7. The

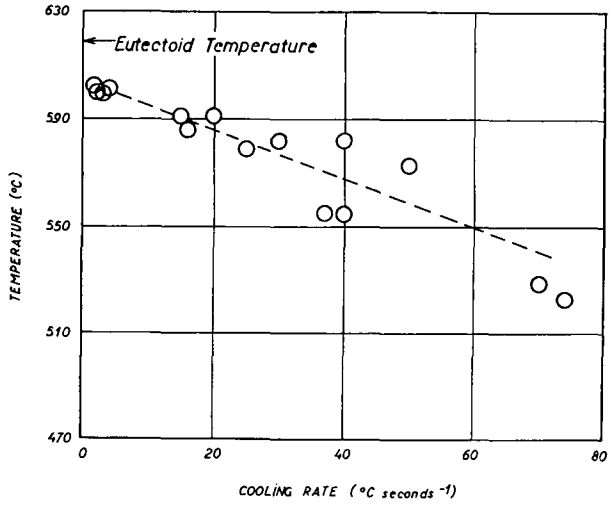


FIG. 3. Temperature of massive transformation on cooling as a function of cooling rate in a 24.5 at.% Ga alloy.

* Cooling rate was defined as the slope of the recorded temperature–time curve just before the reaction started.

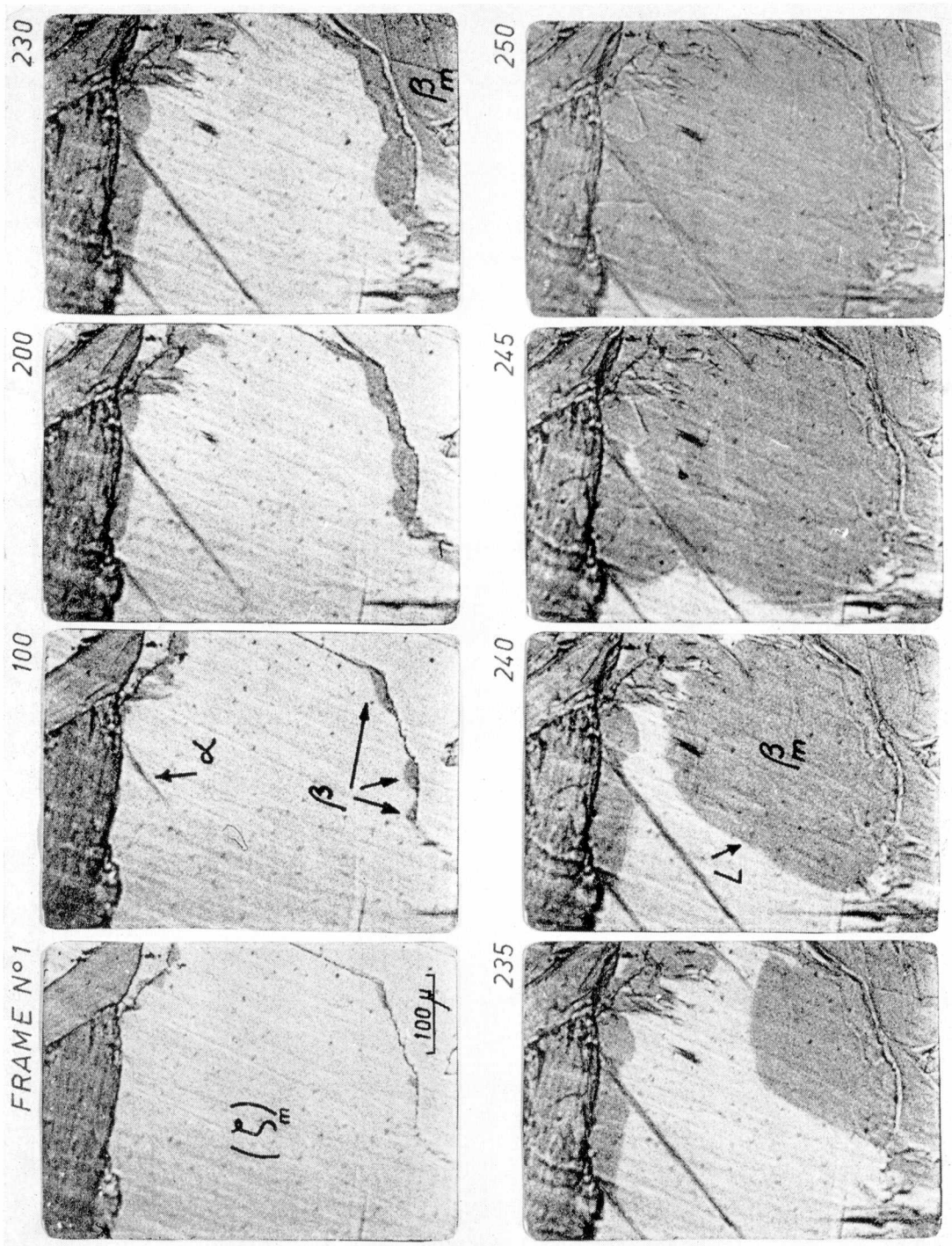


FIG. 4. A sequence of 8 non-consecutive frames obtained on heating a 22.8 at.% Ga alloy at a rate of 3–4°C/sec. ζ_m represents the original matrix α and β represent growing equilibrium phases. β_m denotes the massive b.c.c. phase. L indicates a ledge at the ζ/β_m transformation interface. Polarized light. Photographed at 24 frames/sec.

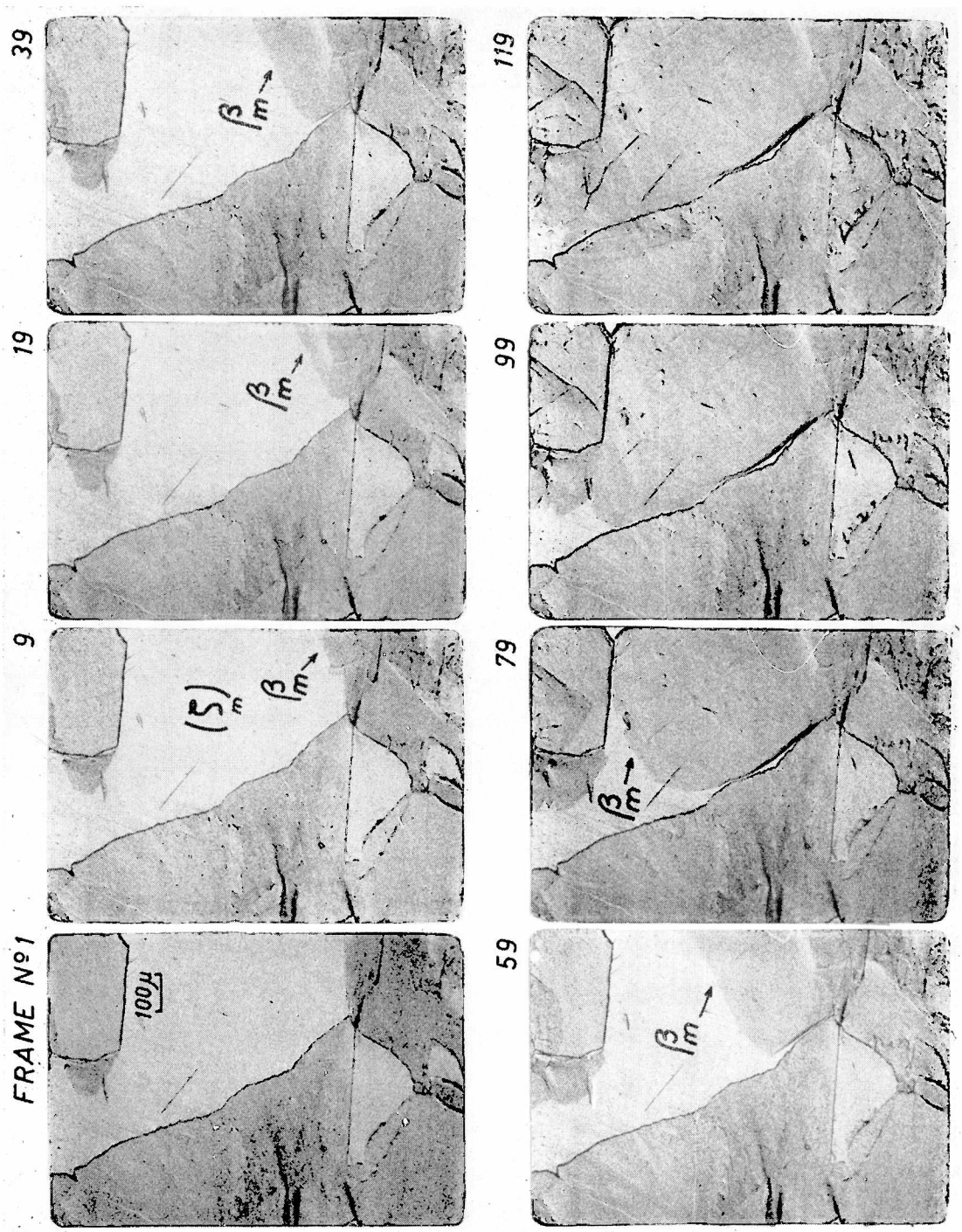


FIG. 5. A sequence of 8 non-consecutive frames obtained on heating a 23.9 at.% Ga alloy at a rate of 2–3°C/sec. β_m represents the growing massive phase. Polarized light. Photographed at 24 frames/sec.

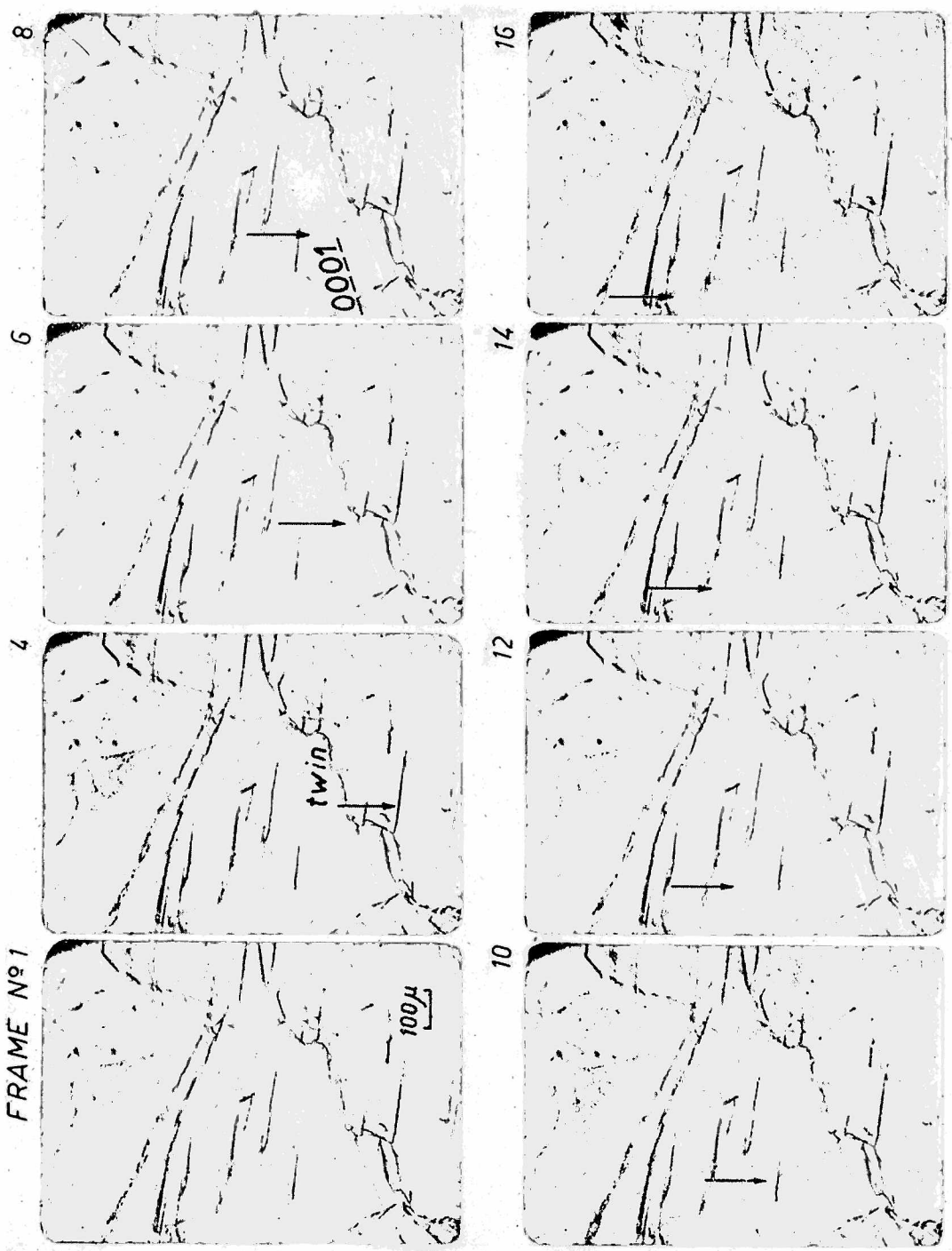


FIG. 6. Growth of a narrow (10$\bar{1}$1) twin on cooling a 23.7 at.% Ga alloy at a rate of 27°C/sec. Arrow indicated the position of the twin in each frame. Polarized light. Photographed at 24 frames/sec.

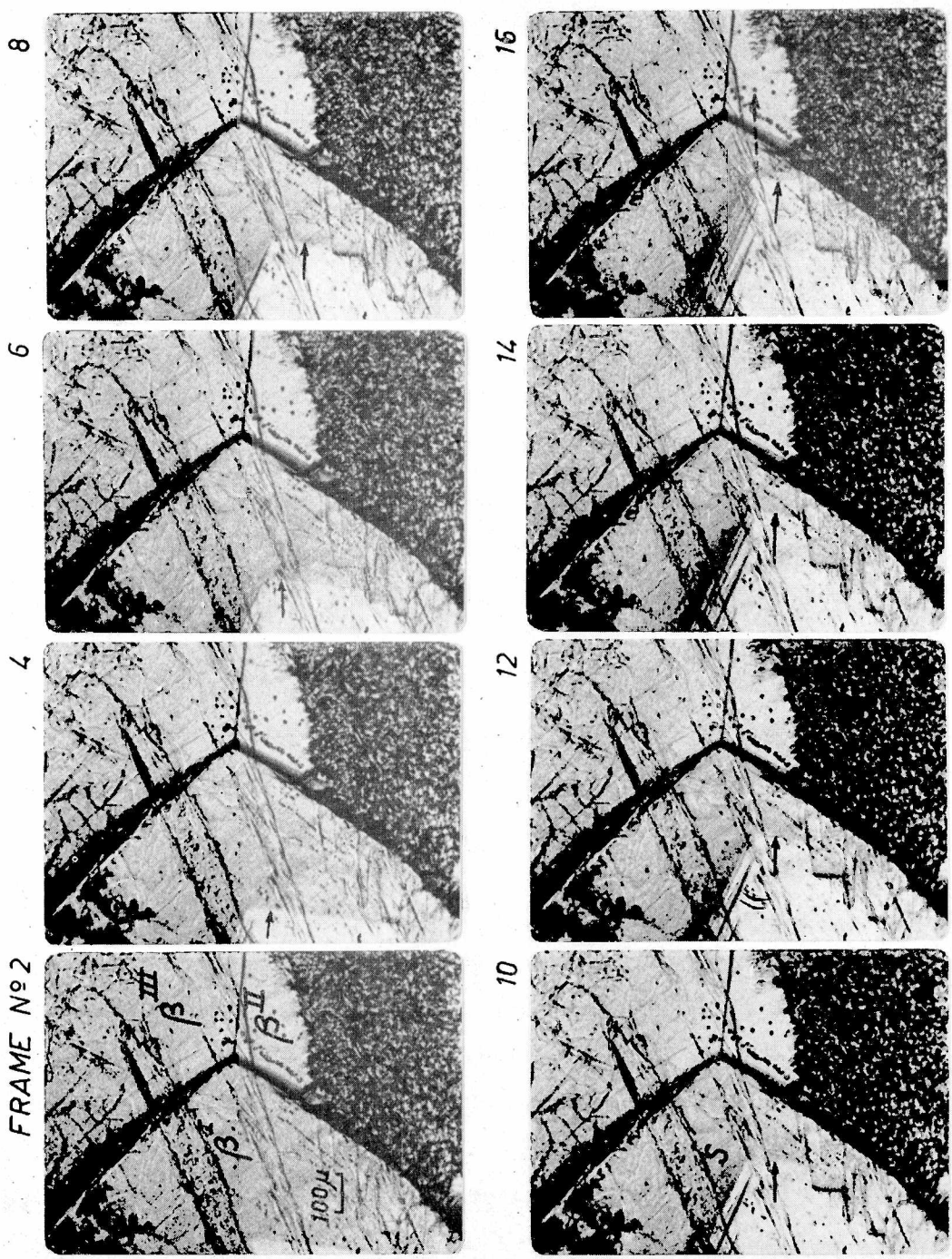


FIG. 7. A sequence of 8 non-consecutive frames showing growth on cooling of a massive ζ_m grain accompanied by surface slip, 22.8 at.% Ga alloy. Cooling rate 4°C/sec. β^{I}, β^{II} and β^{III} represent three different parent grains revealed by thermal etching. Arrows indicate critical positions of the transformation front. Black area represents cellular $\zeta + \gamma$ decomposition. Polarized light. Photographed at 24 frames/sec.

TABLE 1

Composition at.% Ga	Experiment No.	Heating or cooling rate (°C/sec)	Transf. temp. Tm	Average interface velocities along different directions (mm. sec^{-1}) a–a	b–b	Figure number	
22.8	14	3–4	618	0.40	0.35	4	Heating
23.9	18	2–3	616	0.15	0.20	5	
23.7	44	10–12	—	0.70	0.35	9	
23.7	40	27	586	0.20	—	6	Cooling
24.3	81	11	580	0.70	—	8	
22.8	17	4	590	0.50	0.25	7, 13	
23.7	73	33	—	1.00	0.70	15	

contrast between the two phases at the transformation interface depended upon a change in optical reflectivity. A good resolution of the interface was obtained only when the hexagonal grains happened to have their main symmetry axis considerably inclined with respect to the surface, thus giving maximum contrast under polarized light; many runs were wasted when the moving interface did not possess sufficient contrast to be photographed. Another complication was due to the fact that a rapid movement of an interface during the exposure time of a given frame tended to produce a gradually shadowed rather than a clear, demarcation boundary. This was particularly noticeable with the fast movement of ledges (see below). Most of the cinematographic work was done under relatively slow cooling conditions (4–30°C/sec).

The massive transformation $\beta \rightleftarrows \zeta$ has been found to be reversible on heating and cooling. The data on composition, transformation temperatures, and interface velocities for all experiments described in this and the following sections are given in Table 1. The interface velocities of the growing massive phase were estimated along certain directions from schematic traces drawn from successive frames as indicated in Fig. 8. The velocities are quoted as average values. Frame-by-frame values showed a considerable scatter. In some cases this was clearly due to interference from obstacles and particles, such as γ rosettes, that had precipitated from the β phase prior to the massive transformation. The contours of a frame-by-frame transformation sequence on cooling, in which the moving boundary is clearly affected by the presence of rosettes, are shown diagramatically in Fig. 8. The boundary involved growth of a twin-related ζ_m grain and only one-half of the twin gave contrast under polarized light. Arrows indicate the most likely directions of the moving boundary. After the transformation in the hot stage the specimen was polished and etched, revealing a large number of γ rosettes [Fig. 8(a)]. Their presence was also noted in previous investigations.[1] The outline of an actual boundary on an unpolished surface is shown in Fig. 8.(b)

Another cause of scatter in the measured velocities was due to the changing nature of the growing interfaces. Frame-by-frame traces of a heating sequence obtained in run 44 (Table 1) are shown in Fig. 9. They reveal that many of the interfaces are nearly straight and possess ledges or steps. The lateral movement of such ledges may be inferred from traces in Fig. 9; and it is clearly more rapid when compared with the average forward velocity of the advancing interface. For this reason the contours of the ledges are distinctively less sharp on the photographs (see Fig. 9). A careful examination of film strips has shown that some faint markings are sometimes left on the free surface following the passage of each successive ledge. Later studies by interferometry have shown that such markings correspond to surface shearing and slip. The apparent "size" of the ledges such as those indicated in Fig. 9 varied between 6 and 30 μ.

Ledges and less sharp boundaries are indicated by dotted lines in the traces of Fig. 9. Ledge growth appears to be a distinct feature of some of the massive transformations observed; it becomes especially pronounced with increasing undercooling.

Taking a representative heating run 44 (see Table 1, also Fig. 9) the approximate maximum and minimum values of the growth velocity in mm/sec in directions a–a and b–b are as follows:

Run 44 V_{max}	General direction of the interface a–a	b–b
V_{max}	1.0	0.7
V_{min}	0.2	0.0
$V_{average}$	0.7	0.4

Direction b–b corresponds to the penetration of the moving boundary into another parent grain. It confirms the notion proposed earlier[1] that during a massive transformation several parent grains can be

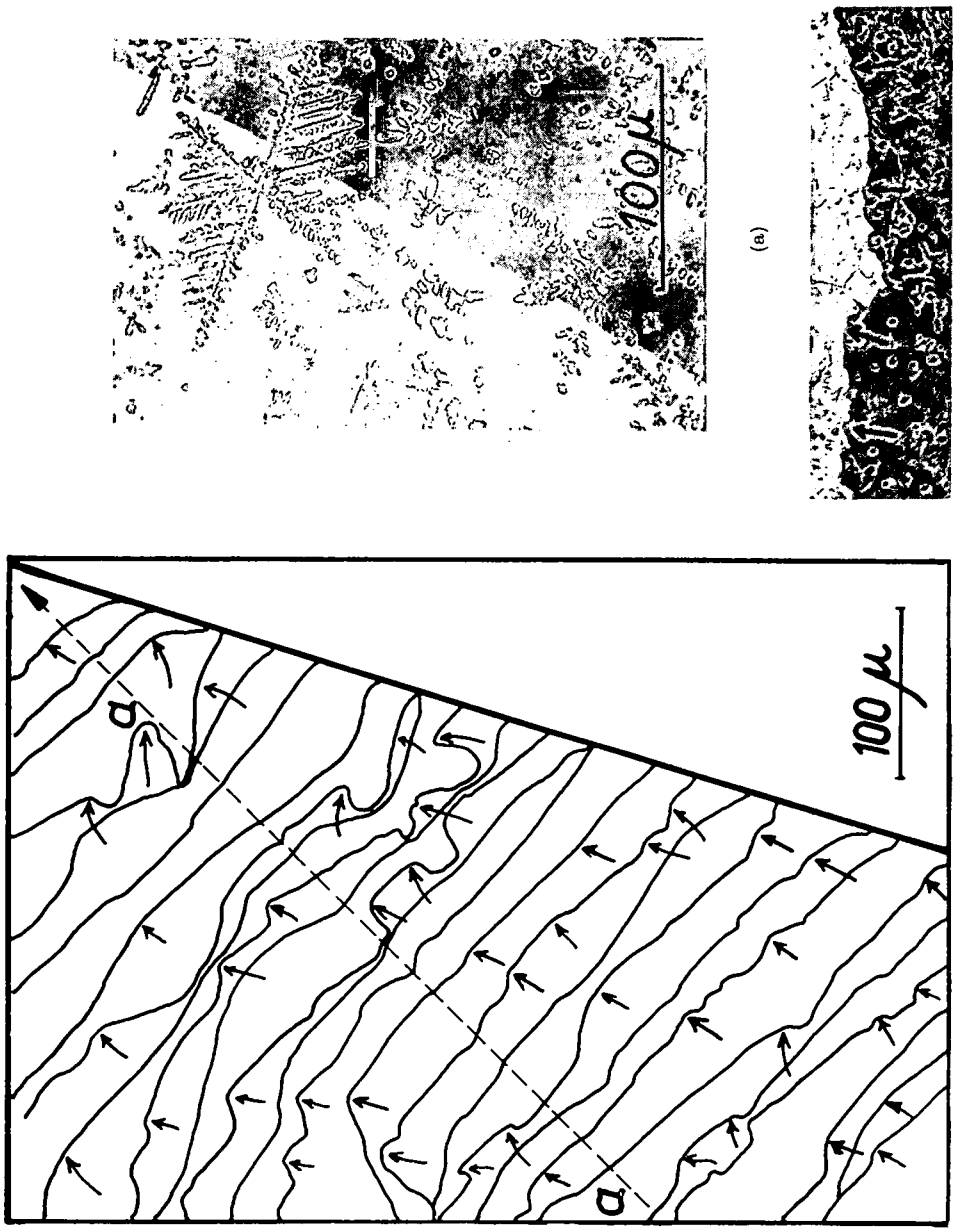


FIG. 8. Frame-by-frame traces of 26 successive contours of a moving boundary affected by interaction with γ rosettes. Only one side of the generated twinned grain has been revealed under polarized light. Photographed at 32 frames/sec.
(a) a portion of the twin boundary after polishing and etching revealing the presence of γ rosettes.
(b) A contour of an arrested boundary on one side of the twin. Unetched and unpolished. Polarized light. Magnification $\frac{1}{4}$ that of Fig. 8(a).

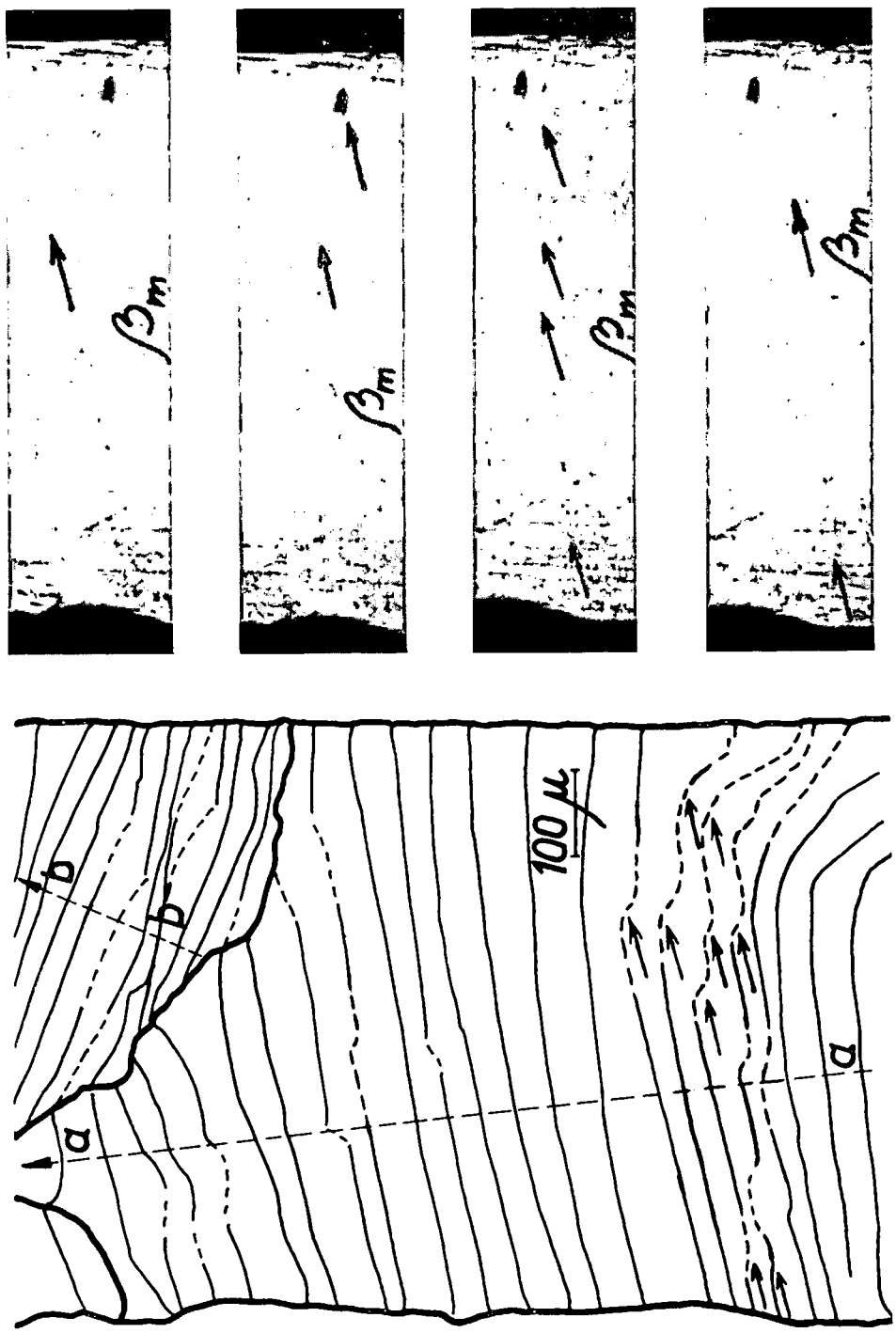


FIG. 9. Frame-by-frame traces of 30 successive contours of a moving boundary during a $\zeta \rightarrow \beta_m$ transformation on heating. Photographed at 18 frames/sec. Film strips from frames 5, 6, 7 and 8, in which the ledge growth is particularly pronounced are shown on the right.

absorbed by a single moving interface. However, the speed of movement along the b–b direction is slower than along the a–a direction. The values given in the above table correspond to an "ordinary" growth upon heating at some 10–12°/sec. Ledge-growth velocity appears to be appreciably faster. Similar observations were made during cooling runs. Here the rate of cooling could be considerably increased, and with a cooling rate exceeding 100°/sec the ledge growth could no longer be photographed. Evidence for ledge growth at high cooling rates can nevertheless be obtained from quenched and polished specimens where the contours of an advancing boundary are frequently outlined by an encounter with another growing grain. This feature will be discussed in greater detail below.

Despite the specially designed shape of the specimens, one that encouraged a lateral direction of heat transfer with respect to the viewing surface, all reported velocities are affected by the uncertainty of the angle between the actual interfaces in the bulk of the material and the plane of the observation surface. The observed velocities are projections of the actual velocities upon the observation surface, but the error is probably not substantial.

3.3 *Massive transformation on heating;* $\zeta \rightarrow \beta_m$

Figures 4 and 5 show a series of 8 non-consecutive frames each taken from the film during heating runs 14 and 18 (see Table 1). Frame 4–1 represents the 22.8 at% Ga hypoeutectoid sample consisting of the $\zeta(m)$ phase (obtained by a previous quench) at the time when the transformation has just started during heating above 618°C. Initial conditions represent decomposition into equilibrium phases: $\alpha + \beta$. Some thickening of the grain boundaries is visible, and a small amount of the equilibrium β phase (corresponding to phase diagram relationships as shown in Fig. 1) is growing slowly at grain boundaries (marked β in frame 4–100). Frame 4–100 shows the progress of this slow growth of the equilibrium β phase and also of the beginning of a faster growth of an α plate. Two α plates are fully developed in frame 4/230. The displacement velocity of the interface associated with the slow growth of the equilibrium β phase at the grain boundary is approximately 4×10^{-3} mm/sec, and of the edge growth of the α plate 4×10^{-2} mm/sec. In the lower part of frame 4–230 the appearance of the *massive* β_m transformation front may be seen, which moves rapidly and in subsequent 20 frames absorbs the remaining ζ phase. This massive transformation on heating occurs when the temperature rises above the boundary of the $\alpha + \beta$ phase field so that the transformation $\zeta \rightarrow \beta_m$ can proceed without a change of composition.

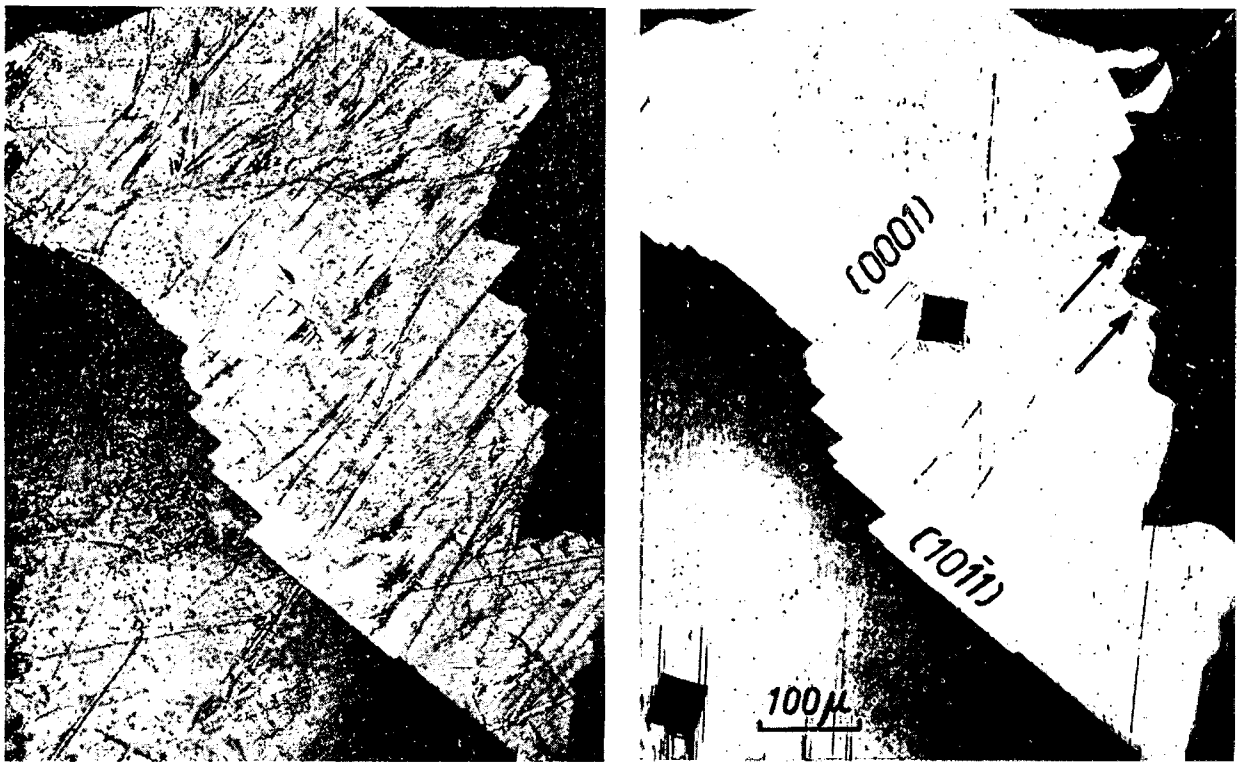
The average front velocity of the massive transformation $\zeta \rightarrow \beta_m$ is of the order of 0.35–0.40 mm/sec; it is thus some 100 times faster than the "normal" growth that requires adjustment of composition. During the transformation some of the massive interface is curved, but again a significant feature is the development of straight portions with occasional step-like twists or ledges (see for example ledge marked L in frame 4-240). In another sequence of frames shown in Fig. 5 (run 18, heating velocity 3°C/sec) no α plates are observed in agreement with the composition of the alloy (23.9 at.% Ga, approximately eutectoid). The progress of the β_m growth in a portion of the specimen is delineated in part by two fairly straight interfaces inclined to one another (see frames 5–19, 5–39 and 5–59). A large number of unsharp ledges are visible in consecutive series of different frames, but they are too faint to be reproduced. When the whole transformation sequence is viewed on a moving film, the effect to the observer is unmistakable: two sets of fast-moving ledges repeatedly sweep in directions that are at right angles to the general direction of motion of two nearly planar boundaries. We conclude therefore that the massive transformation on heating occurs by the movement of interfaces that can be both curved and planar; and, if they are planar, the likely mechanism involves movement of ledges.

3.4 *Massive transformation on cooling;* $\beta \rightarrow \zeta_m$

The data for some typical cooling runs are summarized in Table 1. An advantage with the cooling experiments was that following a run the sample could be examined at room temperature for metallographic features and for orientation relationships.

Many runs have shown the typical rapid growth of relatively random non-planar ζ_m boundaries. Sometimes, when a trace of a prior β/β boundary was outlined on the free surface by thermal growing or etching, the transformation front could be seen to cross such boundaries without hindrance. This transformation behavior was characteristic of many hypereutectoid alloys, and it corresponds to what has been previously described as a *typical massive transformation.*[1]

As mentioned earlier the β matrix prior to the transformation often contained γ rosettes in which case the advancing boundary was frequently entangled by them (Fig. 8). In addition, some γ precipitation occasionally occurred on ζ_m/ζ_m grain boundaries after transformation, and on β/ζ_m grain boundaries during transformation. This latter occurrence is of particular



(a) (b)

FIG. 10. Ledge growth in massive ζ_m phase 22.8 at.% Ga alloy. Cooling rate 15°C/sec.
(a) Unpolished surface after transformation. Polarized light.
(b) The same surface after polishing and etching. Polarized light. Microhardness indentations indicate slip traces on (0001) ζ_m plane. Arrows indicate directions of growth.

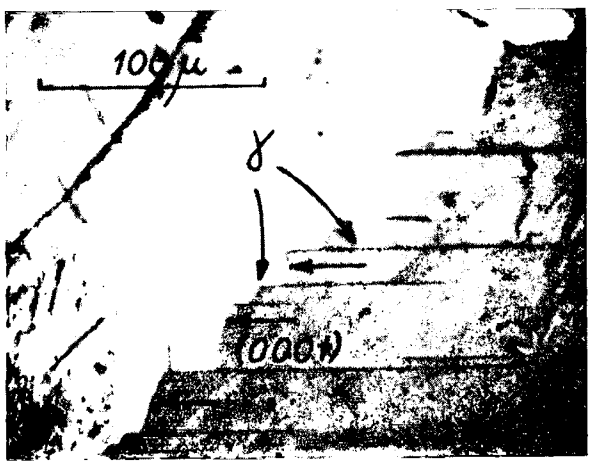
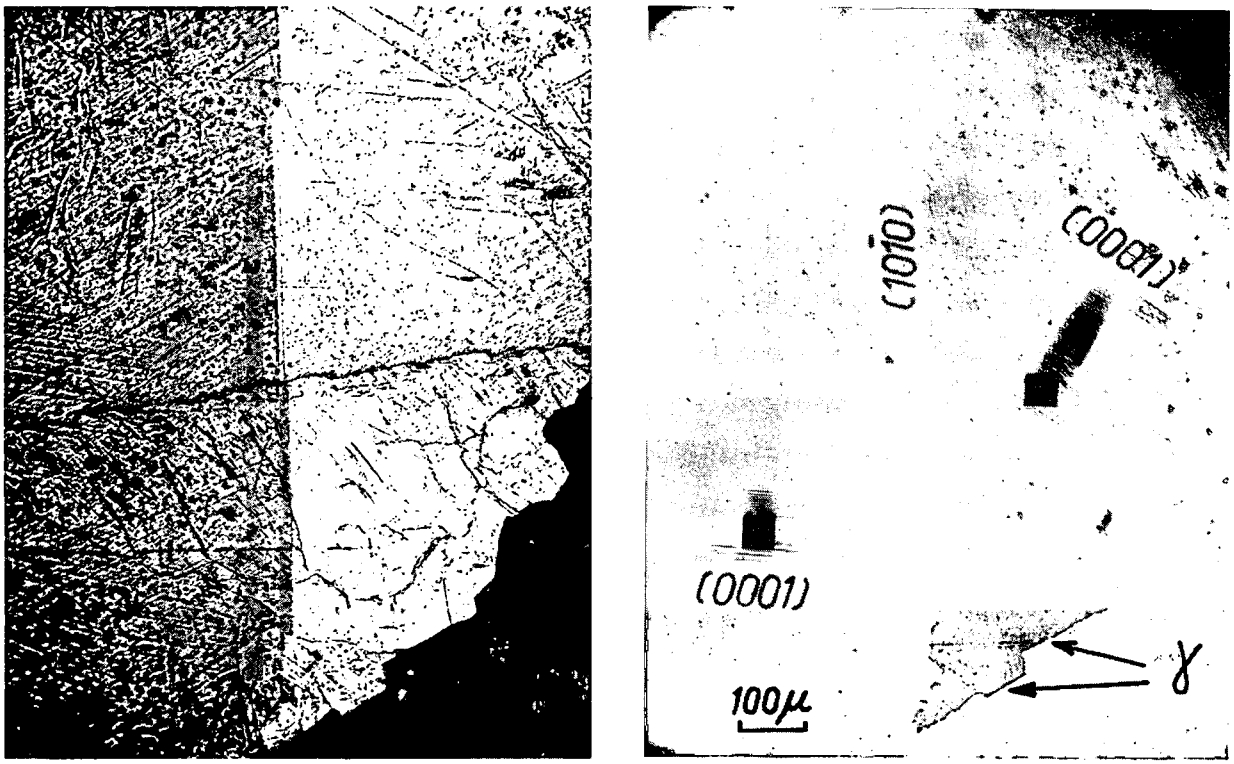


FIG. 11. Ledge growth in bulk massive ζ_m phase. 22.8 at.% Ga alloy. Cooling rate 30°C/sec. Etched after transformation. Polarized light. Arrows indicate directions of growth. γ precipitation slightly ahead of the ζ_m interface is also shown by arrows.

interest because it permitted to identify at room temperature in polished samples the momentary arrests of the transformation interface at high temperatures (see Figs. 10–13). γ precipitation was never seen on polished twin (10$\bar{1}$1) ζ_m boundaries, or on planar boundaries in which the plane on one side of the boundary was identified as prismatic (10$\bar{1}$0).*

In eutectoid alloys, and particularly in hypoeutectoid alloys between approximately 22.8 and 23.8 at. % Ga, the transformation behavior showed additional features already noted for the case of the $\zeta \rightarrow \beta_m$ transformation in the same range of composition, namely, the presence of planar boundaries, the apparent ledge growth, and fine surface relief effects. The same features were also noted in the 24.3 at. % Ga hypereutectoid alloy under faster cooling conditions. Direct viewing of film sequences indicated a continuously changing *mixture of curved and planar*

* Planar boundaries of this kind were quite frequent. Laue photographs have shown that the angle between the basal planes of the two ζ_m grains was ~33° and in a few cases, 60°. The planar boundary always involved the prismatic plane in one of the grains but apparently an irrational plane in the other grain.



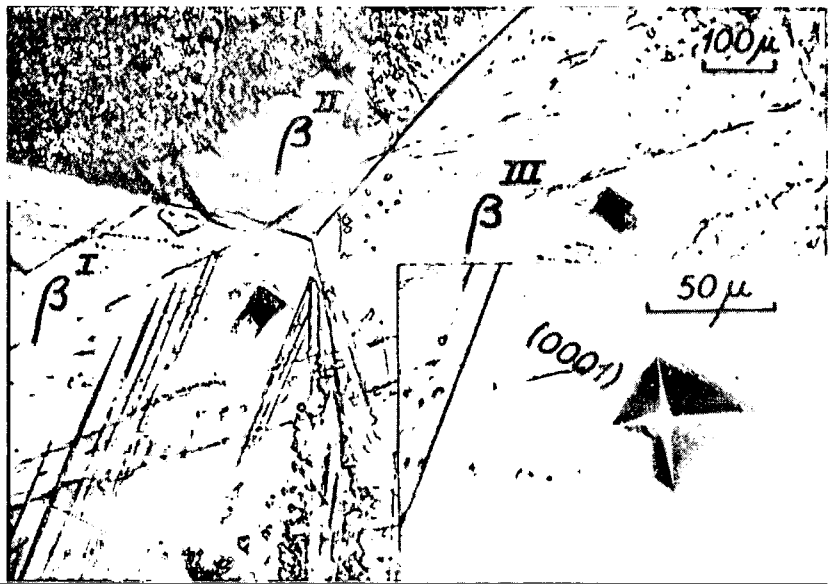
(a) (b)

FIG. 12. A planar (10$\bar{1}$0) interface in the ζ_m phase of a 22.8 at.% Ga alloy. Cooling rate 15°C/sec.
(a) Appearance of the free surface under polarized light.
(b) The same surface after polishing and etching. Microhardness indentations show traces of slip on the (0001) basal planes. γ precipitation visible on some boundaries.

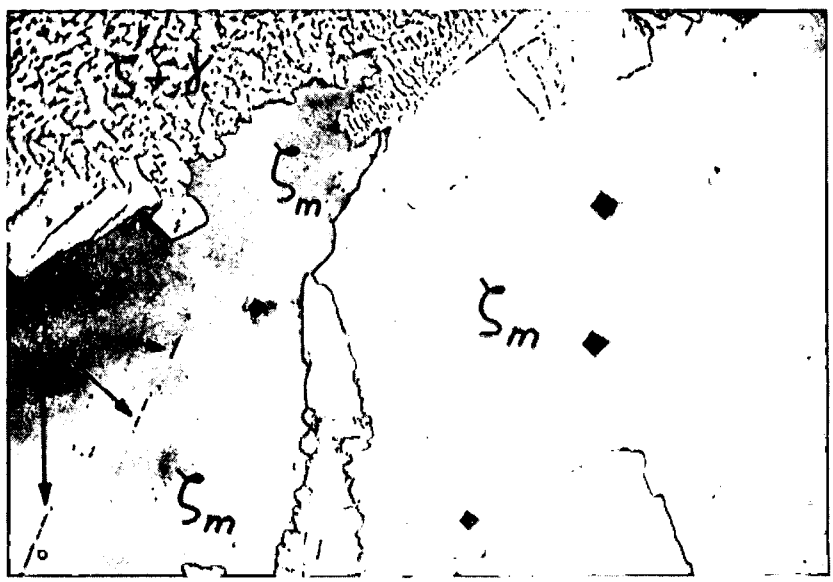
boundaries. Some of the planar boundaries were associated with surface slip (see below).

The film sequences shown in Figs. 6 and 7 illustrate some of the special features observed on cooling. In Fig. 6 the formation of a narrow (10$\bar{1}$1) twin which is a part of the growing ζ_m phase is shown. The actual interface between the disappearing (β) and growing (ζ_m) phase is not visible but its contour is outlined by slip markings on the surface. The twin boundaries on both sides of the twin are generated by the apparent forward movement of the β/ζ_m interface similarly to the behavior shown earlier in Fig. 8. However, a direct viewing of the film indicates slip or shearing along (parallel) to the β/ζ_m interface which, at least on one side of the twin, is planar and after transformation corresponds to traces of the basal (0001) plane (see Fig. 6). X-ray work and basal slip induced subsequently by microhardness indentation has confirmed this conclusion. Most likely, therefore, the rapid movement represents propagation of ledges. Once a twin-related grain is nucleated, it can extend by the subsequent advancement of the twin-related portions. However, the advancement of a twin-related grain, or a narrow twin, which has planar boundaries on one or both sides raises the question of orientation relationship. If an orientation relationship does exist between β and ζ_m when the boundaries are planar, it should be lost [the boundaries changing character from planar (semicoherent) to curved (incoherent)] when a new β grain is entered. Furthermore, if an orientation relationship exists between β and ζ_m grains and it is of the Burgers type as reported for alloys,[16,17] namely, $(110)_\beta \parallel (0001)_\zeta$ and $[11\bar{1}]_\beta \parallel [11\bar{2}0]_\zeta$, a problem arises in matching the respective close-packed planes between β and ζ_m. There is a difference of some $\sim 3°$ (depending on axial ratio) between the angle formed by two (110) planes in the b.c.c. β phase and the angle between the basal planes of two grains that are in twinned relationship. If one assumes that a perfect matching exists between a $(110)_\beta$ plane and $(0001)_\zeta$ plane on one side of the twin, a slight mismatch will occur on the other side. Perhaps this is responsible for the somewhat curved appearance of the boundary on the right side of the narrow twin in Fig. 6.

Judging by the complete absence of γ precipitation on twin (10$\bar{1}$1) boundaries, and on boundaries associated with the prismatic (10$\bar{1}$0) plane (see footnote on



(a)



(b)

FIG. 13. Surface slip following massive transformation in a 22.8 at.% Ga alloy, corresponding to film sequence shown in Fig. 7. Polarized light.
(a) Surface before polishing showing transformation slip traces and traces of slip in the ζ_m phase following microhardness indentation.
(b) The same surface after polishing and etching.

p. 172), it seems possible that these later boundaries also grow by some mechanism involving two related ζ_m subgrains (see also p. 172).

3.5 *Growth by propagation of ledges*

Detailed evidence for the formation and growth of ledges has been obtained following cooling experiments when the surface could be examined carefully, both without polishing and after polishing and etching. Typical examples of ledge growth are illustrated in Figs. 10 and 11. In both cases ledges lie along basal (0001) planes of the product phase. This has been identified by X-ray Laue patterns and by microhardness indentation. Traces of the γ phase visible along

certain (0001) planes are helpful because they permit to identify the direction of ledge growth, i.e. γ phase is seen in the grains in which ledge growth has just taken place.

Of considerable interest is the exact location of the γ precipitates at the time of ledge growth. In Fig. 11 some γ phase may be seen "on top", and a little ahead, of the advancing lateral ledge. Hence, at least in part, γ appears to have formed in the disappearing β grain along a plane that is clearly parallel to the basal plane of the growing ζ_m phase. We feel that such γ precipitation is enhanced by slip on the (110) planes of the β phase (see discussion). In Fig. 10 ledge growth is associated with the formation of a twin, and it confirms the suggestion made earlier (Fig. 6) that ledge growth accompanying the formation of a twin takes place in directions *away* from the twin boundary. We have observed this behavior in a number of other polished samples. As mentioned earlier, the sizes of the ledges vary from a few μ to more than 30 μ.

The question arises whether or not the ledge growth revealed in film sequences, both on heating and cooling, involves a close-packed plane in each case, (110) in β and (0001) in ζ_m, and whether or not this implies the existence of a definite orientation relationship between β and ζ. As will be shown in the discussion both conditions are likely to be true, but the proposed process requires the simultaneous occurrence of some slip. The important point of ledge growth is that it appears to be easily upset by encountered obstacles so that a boundary advancing by ledges may abruptly become curved, becoming a high-energy boundary along its whole length.

Figure 12 shows the appearance of a planar boundary involving the prismatic plane on one side. The planar boundary shows no γ precipitates, and in this respect it resembles a twin boundary. That it may also have formed by some ledge growth mechanism or by a growth of a duplex grain, as appears to be the case in twins, is suggested by the appearance of a thin ledge parallel to the planar boundary in Fig. 12.

3.6 *Surface relief and shearing*

The markings observed on the free surface had the appearance of slip, slip bands or surface shearing and could be removed by polishing, except in cases when some γ phase had precipitated along such markings during the transformation, or during cooling to room temperature after the transformation [see Fig. 13(b)]. Film sequences give the impression that in all cases of a momentary arrest of the advancing ζ_m boundary surface slip had occurred at the interface between the transformed and untransformed matrix; such slip appears to be associated with the exact positions, or very close proximity, to the advancing boundary. For example, the development of surface relief markings along the advancing interface may be seen in a sequence of frames in Fig. 7 corresponding to a relatively slow cooling (4°C/sec) of a 22.8 at.% Ga hypoeutectoid alloy. Prior to the tranformation the sample had been held in the β-phase field and the grain boundaries of three adjoining β grains became visible following thermal grooving and etching (see frame 7–2). On subsequent cooling a part of one grain transformed by a slow discontinuous cellular reaction $\beta \rightarrow \gamma + \zeta$ (the dark, spotty area in each frame) with an average interface velocity of 4×10^{-3} mm/sec, while the remainder transformed massively at a speed some 100 times faster. Figure 7-2 corresponds to the first appearance of a partly planar massive interface (marked by an arrow in grain β^{I}). Subsequent frames show the rapid advancement of this interface and development of shear markings at the intermittent arrest points in the upper portion of this interface. These markings do not correspond to any rational crystallographic plane within the resulting ζ_m grain. A subsequent detailed study at room temperature (Fig. 13)* has shown that the ζ_m grains after polishing and etching had the typical appearance of a massive transformation [see Fig. 13(b)]. Surface slip markings had formed while the ζ_m grain was growing into one of the three β grains (the β^{I} grain), but slip stopped near the β/β grain boundary while the ζ_m grain continued growing into the adjoining β^{II} grain, but without accompanying slip. Microhardness indentations (see insert) were made in order to confirm the direction of the basal plane in the ζ_m phase by means of induced slip. The slip markings produced at the time of transformation are not parallel to the induced slip, i.e. to the basal plane of the ζ_m. We conclude that slip at the time of transformation had occurred in the β phase and that the set of β planes undergoing slip near the free surface acted as barriers to the moving boundary, causing momentary arrests.

The appearance of surface relief markings, associated with momentary arrests of a moving boundary, has been observed in several instances of fast and slow cooling and appears to be a very general phenomenon. It is more pronounced under conditions of enhanced volumetric constraint, such as when a number of advancing ζ_m grains are about to absorb the last

* Figure 13 corresponds to the completed transformation sequence shown in Fig. 7. The microstructure in Fig. 13 represents, however, not only an enlargement but also an inverted picture of the microstructure shown in Fig. 7. In order to identify the three β grains in Fig. 7, they are indicated in Fig. 13.

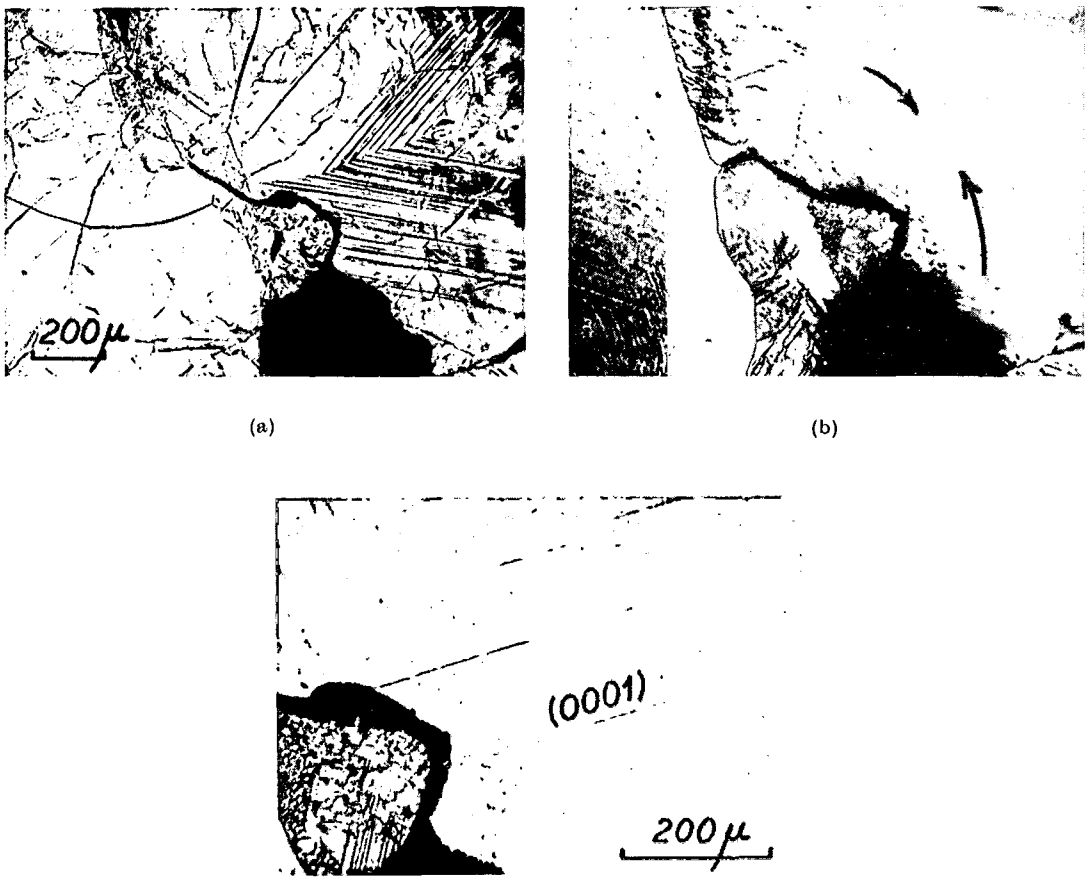


FIG. 14. Surface slip following massive transformation in a 23.9 at.% Ga alloy. Polarized light.
(a) Original free surface.
(b) Polished and etched surface. Arrows show directions of growth of two branches of the ζ_m phase.
(c) Slip in ζ_m phase revealed by deformation.

remaining portion of a disappearing β grain, or when two portions of the same boundary collide with one another after approaching from different directions. This is illustrated in Figs. 14 and 15.

In Fig. 14 two distinct sets of shear-like markings may be seen in the upper right corner of the unpolished surface. After polishing, the resulting ζ_m grain has been shown to be a single grain by X-rays, polarized light, and microhardness indentation. The general directions of movement of two advancing branches of the same ζ_m transformation front are indicated diagramatically on the micrograph showing the polished surface. Each individual shear step corresponds to a momentary arrest of that part of the moving interface which was planar. The slip trace induced by slight deformation of the resulting ζ_m grain (i.e. the 0001 basal plane) bears no relationship to the shear markings, again suggesting that slip at high temperatures has occurred in the β phase ahead of the advancing boundary and has caused momentary arrests. In Fig. 15 another occurrence of a similar phenomenon is illustrated. Surface interferometry [Fig. 15(b)] confirms that a considerable shrinkage has occurred on the surface in the region where the volumetric change accompanying the disappearance of the last portion of a β grain has caused a "pipe" to form on the surface, not unlike in a solidifying ingot. The details of surface slip markings are shown in Fig. 15(c). The markings in the left branch show a considerable angular dispersion within the ζ_m grain. In each case, however, their position constitutes a permanent record of the position of a nearly planar portion of the advancing ζ_m/β boundary. Their most likely origin is again either slip in the β phase, just ahead of the advancing boundary. Figure 15(d) shows a surface interferogram taken to reveal the shear-like nature of the surface

(a) (b)

(c) (d)

FIG. 15. Surface slip following a massive transformation in a 23.7 at.% Ga alloy, cooled at a rate of 33°C/sec. Polarized light.

(a) The direction of growth of two branches of the same ζ_m grains.
(b) A surface interferogram indicating the depression in the surface that accompanied the directional growth.
(c) Details of surface slip.
(d) Surface interferogram indicating the shear-like nature of the slip.

relief. There is no evidence that the observed surface markings represent a martensitic-like shear transformation, since no metallographic effects of any kind were observed after polishing and various depths of etching. Furthermore, a plot on a stereographic projection of a large number of *different surface traces*,* combined with Laue patterns from the corresponding ζ_m grains, has shown that if the orientation of the ζ_m grains is converted into the orientation of the prior β grains by using the Burgers relation, and the traces are assumed to be surface slip in the β phase, they can be identified in several, but not all, instances with the (110) or (112) planes of β. This supports the view that slip has occurred in the β phase at the time of the transformation and that some of the growing ζ_m grains possessed an orientation relationship with respect to the β phase, while other ζ_m grains did not.

3.7 *Substructure*

All ζ_m h.c.p. grains examined by X-rays at room temperature possessed a substructure of slightly misoriented crystallites. In rare cases the passage of transformation front would transform the whole sample into a "quasi-single" crystal. Such crystals possessed a substructure of crystallites with disorientation varying between 2 and 10° of arc. The substructure resembled the "lineage substructure" frequently observed in crystals grown from the melt, or in crystals produced by solid state transformations such as that in uranium.[18]

4. DISCUSSION

The performed experiments involved considerably lower cooling (and heating) rates than those obtained by direct quenching into a liquid medium. Hence, in all cases the massive transformation on cooling was completed before the order–disorder temperature, or the M_s temperature, was reached. Nevertheless, in the range of alloys studied, between approximately 23–25 at.% Ga, the features revealed by a polished microstructure following different cooling rates were relatively similar provided that the quenching rate was not fast enough to produce martensite.

The experiments have shown conclusively that the *massive transformation* occurs both on heating and on cooling and that it is many orders of magnitude *faster* than the "normal" growth involving long-range diffusion. The mode of growth resembles a typical recrystallization, or a grain-growth reaction; and the temperature of the transformation can be lowered or raised by a change in the cooling and heating rates. It is clear that, although the growing interface may be involved at times in directional growth and be subject to momentary arrests, the greatest part of the transformation is achieved by the propagation of curved, variable-speed, and highly flexible boundaries that have ability to absorb several grains of the parent phase. Hence, as is generally accepted, the massive transformation is a *process* whereby one alloy structure can change into another by a diffusional growth involving no change in composition. The growth is rapid because in most cases the boundary involved is highly incoherent. The amount of diffusion required may be very limited. We conclude both from observed modes of propagation, and from orientation studies, that with cooling rates between 3–30°C/sec a certain number of the growing grains possess a crystallographic orientation relationship with respect to the original parent grain boundaries. Studies of film sequences have revealed the development of special features such as *growth of twin-related crystals*, growth by means of *directional ledges*, and *surface slip*. Correlation with subsequent studies of polished and unpolished samples shows that many aspects of these phenomena can now be satisfactorily explained without further recourse to cinematography. However, the details of twin nucleation and the propagation of ledges indicate a need for a special *high-speed* cinematographic technique.

The characteristic features observed during growth are associated with the interactions between the moving transformation boundary and obstacles. These are of two kinds: *structural*, such as γ particles and imperfections, which merely cause the moving boundary to change direction, and *slip*, initiated ahead of the moving boundary in the disappearing parent phase, which appears to be responsible for momentary arrests and for the development of certain planar features in the bulk (ledges), and on the free surface (shearing). Other planar boundaries, such as $(10\bar{1}1)$ twins and boundaries associated with a prismatic $(10\bar{1}0)$ plane on one side appear to be the result of a special kind of growth as well as nucleation.

Slip in the parent phase is undoubtedly caused by the severe volumetric changes and the elastic and plastic strains that accompany a rapid passage of a structural transformation, and a thermal front. Interferometric studies have confirmed this fact by revealing numerous cases of abrupt shearing (slip) as well as other changes in the surface contours (depressions and "pipes"). In many cases slip actually appears to be taking place at the arrested interface; but, unless such a process is assisted by climb of dislocations and aided by high concentration of vacancies, it is more

* Only a single-surface trace analysis of the markings was possible for this purpose.

likely that it occurs in the adjoining parent phase just ahead of the transformation boundary. Single trace analysis of some of the surface markings produced by slip suggests that slip occurs most likely on the {110} or {112} planes in the β phase, and the method of confirming this also involves the additional assumption that a Burgers' crystallographic orientation-relationship is present. On the other hand, this orientation requires that one of the {110} planes is then nearly parallel to the (0001) basal plane (within 3–4°); yet we have found this to be the case only for twin growth of the type as shown in Fig. 5. Hence, there appear to be numerous cases where the crystallographic orientation does not hold or is not the simple one. We consider slip to be a *deformation phenomenon* occurring in the proximity of the free surface by movement of dislocations which are produced by an advancing transformation front that approaches the surface from the *inside* of the specimen, as may be expected from the cooling arrangement depicted in Fig. 2. Once a slip plane, or a slip band, becomes active, it acts as a temporary barrier to further transformation until the advancing boundary manages to envelop or bypass the plane undergoing slip; in the meantime, the process is repeated with respect to another slip plane.

The model suggested for the formation of *ledges* in the bulk material requires different conditions (see Fig. 16). Ledges in the polished phase are always found to lie along the (0001) basal plane of ζ_m, and we feel that this *requires* the existence of a prior orientation relationship between β and ζ_m. There seems to be no reason why ledge growth should not result every time slip produces a barrier to a crystallographically oriented growing, massive phase grain, particularly if heat transfer and diffusion become then more advantageous along some specific direction. If, in addition, the growing grain constitutes a portion of a twin, a further inducement for lateral growth appears to be provided by growth conditions at the tip of the twin interface. We find that in the Cu–Ga alloys twins are formed on the $(10\bar{1}1)$ plane.* The relationship between a $(10\bar{1}1)$ twin and the b.c.c. lattice at the nucleation stage is not clear, but the film sequences show that subsequently a twin-related grain can advance by the growth of the twin-related subgrains. If one of the subgrains induces some $(110)_\beta$ slip ahead of the transformation boundary, the conditions develop for a lateral growth because the forward movement of the transformation front is prevented from bursting through the parent phase plane undergoing slip particularly if, upon contact with the ζ_m phase, the $(110)_\beta$ slip plane becomes a semicoherent $(110)_\beta \parallel (0001)_{\zeta_m}$ boundary. Ledges are then generated at the tip of the growing twin and move laterally as shown in Fig. 16. In each case they are preceded by some $(110)_\beta$ slip. After the passage of several ledges, slip may stop and the advancing boundary then resumes an incoherent forward growth. Since ledge-like traces are very numerous in quenched samples, one can suppose that faster cooling, by reducing ζ_m grain size, produces more cases of existing crystallographic relationship between ζ_m and β by limiting growth across the original β/β grain boundaries. At the same time accelerated cooling enhances the likelihood of slip in the bulk of the material.

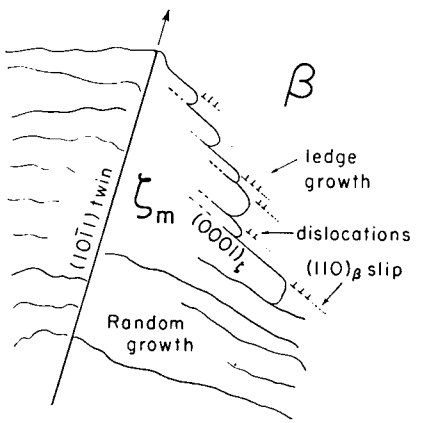


FIG. 16. Schematic model of a growing $(10\bar{1}1)$ twin accompanied by slip on $(110)\beta$ planes of the parent matrix and lateral ledge growth along (0001) ζ_m planes.

Ledges growing during the transformation on heating suggest that slip ahead of the moving boundary now takes place in an h.c.p. ζ phase and, unless other planes in addition to the basal plane become active, only one direction in the observed ledges is expected. However, at least two different directions are evident in Fig. 5, and the ledge direction indicated in Fig. 4 is not parallel to the trace of the α plate which most likely lies along an $(110)_\beta$ plane. Hence, it appears that different slip planes, in addition to the basal plane, can become active at high temperatures in this h.c.p. material. That various slip modes, different from (0001), are possible in h.c.p. alloy phases has been shown experimentally.[19]

Finally, we wish to comment upon the relationship between the massive transformation as described above and the various microstructures observed in Cu–Ga alloys upon quenching. The microstructures observed in polished and etched samples containing approximately less than 22.5 at. % Ga are considerably more complex. At the extreme end of the β phase the

* In the Cu–Ga alloys the $(10\bar{1}1)$ plane appears to be the main twin plane and not the $(10\bar{1}2)$ as supposed by Saburi and Wayman.[3] A similar twin mode has been discussed in detail for the case of an h.c.p. Cu–Ge alloy.[19]

microstructures involve the α_m phase and in the remaining range of compositions they contain areas of "blocky," "striated," "feathery," and "martensitic" structures, the nature of which is not clear. Furthermore, electron microscopy indicates the presence of stacking faults[3,4,13] and of fine duplex α/ζ areas.[4] It is clear that in this range of composition both the value of the stacking fault energy, the position of the M_s temperature, and the nature of the martensite are very important. Figure 1 suggests that, at least by extrapolation, the M_s temperature and the temperature for a massive transformation occur in the same range. Hence, it is not unlikely that a transformation product formed by a martensitic shear should also have a change to grow by diffusion. If, in addition, the martensitic product is of the lath-type[20] (also called massive martensite[16]), as in Fe–Ni alloys, involving a simple rational habit and a bunch of closely parallel martensitic plates of the same orientation, the appearance of a polished and etched sample may be highly misleading. We feel that a typical *massive transformation* is a clearly distinguishable *process* but that the appearance of the microstructure of a polished sample may be insufficient to identify the massive transformation unless some other criteria as discussed above are satisfied.

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