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The Structure of an α/β Brass

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A detailed examination of the structure of an α/β brass is described. In the annealed state ordinary etching methods reveal small angular crystals of the α phase embedded in large crystals of β. Careful electrolytic polishing and etching show that the large β crystals are in reality colonies of much smaller grains. This is confirmed by X-ray methods which show that the misorientation of the subgrains in any one colony is of the order of a few degrees and diminishes with the time of annealing. The angles on the α crystals occur at the boundaries of the β subgrains. The β substructure is also present in the alloy when extruded hot and finished by cold working. The effect of annealing on the form of the α and β crystals is described, and the reasons for the formation of the β substructure are discussed.

1. Introductory

The microstructures of annealed α/β brasses are well known, and often contain curiously shaped α crystals whose boundaries involve numerous sharp changes in direction. Such changes in direction are to be expected where an α crystal exists at the junction of two β crystals, but the number of sharp angles on an α crystal is usually greater than the number of β crystals with which it is in contact, and no satisfactory reason for this has previously been advanced. In the course of work on the effect of thermal cycles on the structure of an α/β brass, it was necessary to examine in detail the structure in the as-provided state, and also the effect of annealing at 500° C. This work revealed several points of interest which are described in the present paper, and which show how the shapes of the α crystals are related to a substructure within the β crystals.

The brass used was provided by the kindness of the British Non-Ferrous Metals Research Association, and High Duty Alloys Limited of Slough. It was prepared from specially pure metals, and contained 42·1 % zinc by weight. After preliminary homogenization, the brass had been extruded at 800° C. to 0·395 in. diameter, and was then cooled in air and reduced cold to 0·375 in. diameter. Chemical analysis showed the rod to be of uniform composition and free from segregation. At 800° C. a brass of this composition consists of the homogeneous β phase with a random body-centred cubic structure. On cooling under equilibrium conditions the α phase begins to precipitate at about 640° C., and at 500° C. the alloy consists of about 30 % α : 70 % β. On further cooling, the order $\rightleftharpoons$ disorder transformation takes place at about 454° C.

2. Experimental

Lengths of about $\frac{1}{2}$ in. were cut from the rods by means of a fine circular saw. Care was taken to avoid distortion of the alloy, and all portions gripped in the vice were discarded. After sealing in evacuated hard-glass capsules, the specimens were annealed at 500 ± 3° C. in furnaces controlled by Foster Temperature Regulators, and were then quenched in iced water, and sectioned longitudinally by a circular saw.

In the earlier work the specimens were prepared by hand grinding on graded emery papers, and were polished with a cream of the Brasso type. They were then etched with aqueous acid ferric chloride, in order to obtain a strong contrast between the α and β phases (see Figs. 2–4). Etching with aqueous ammonia and hydrogen peroxide was also used in order to distinguish between the orientations of different crystals of the α phase. In the later work it was necessary to reveal finer details, and the specimens were ground by hand to 000 emery, and then polished electrolytically using aqueous orthophosphoric acid (2 volumes acid to 1–2 volumes distilled water) to which about 1 % of copper sulphate was added to reduce gassing. This technique showed that what have previously been regarded as large crystals of the β phase are in reality colonies of much smaller crystals which differ only slightly in orientation. This effect was established by three methods which may be summarized as follows:

(A) After polishing, the specimen is rinsed in very dilute phosphoric acid when a sensitive grain-contrast etch is obtained which is clear although not readily reproducible (see Figs. 8, 9).

(B) After polishing at a p.d. of 1·5–1·7 V., and a current density of 50–70 mA. cm.$^{-2}$ the voltage is gradually reduced to 0·6–0·8 V. for from $\frac{1}{2}$ to 3 min., when a sensitive relief etch is obtained. This method was suggested to us by Mr E. C. W. Perryman, to whom we must express our thanks.

(C) After polishing electrolytically, the specimen and cathode are lifted bodily from the electrolyte and plunged into distilled water whilst the current is switched off. This produces a pitting etch which reveals the substructure (Fig. 6).

3. The microstructure of the original extruded material

The original extruded material showed a large-scale Widmannstätten structure. The large β grains were about 1·5 mm. diameter (see Fig. 2); their boundaries were usually outlined by necklaces of α crystals. The Widmannstätten pattern of α shows families of needle-like cross-sections in parallel array. Discussion (Marzke, 1933; cf. Mehl & Marzke, 1931) has taken place as to whether the 'α needles' represent the intersection of the surface with plate-like or needle-like crystals. We have examined specimens in which two sections were cut at right-angles, and polished and examined along their common edge. Previous results were confirmed in that needles in one section always corresponded to 'dots' in the other. Furthermore, it was apparent that the needles are often arranged in rows, more closely spaced within than between the rows. It was found that a row of parallel needles originated from the branching of a single dendrite from an intergranular α grain, thus forming an array like the teeth on the back of a comb. The characteristic spacing in the rows differs from that between, since the latter is that characteristic of the backs of the combs, while the former is characteristic of the branching process, which presumably took place at a lower temperature in the continuous cooling after the extrusion. In extreme cases, the teeth of the comb may actually touch, giving rise to 'composite plates', and it is presumably this which led to earlier confusion between needles and plates.

Fig. 5 shows a family of dark etching needles in oblique section, originating from the grain at the left, and interlacing with the light etching family in longitudinal section. Several small crystals can be seen showing more than one orientation, usually in a twinned form.

The electrolytic methods (A–C), referred to above, showed that the β colonies in the as-extruded material possessed a substructure related to the directions of the α needles. Where the plane of the section was nearly parallel to the axis of the α needles, the boundaries of the β substructure were elongated in the direction of the needles and were very difficult to reveal. In sections perpendicular to the direction of the needles the β-substructure boundaries were more nearly equiaxed and more readily shown. A back-reflexion X-ray diffraction photograph from the electrolytically polished surface, using a 0·5 × 60 mm. collimator and a 5° oscillation, showed only blurred arcs for both phases owing to the effect of the cold work, and consequently the substructure could not be examined in this way.

Careful tests were made to ensure that the substructure was genuine and not due to the polishing or etching technique. Specimens on whose surfaces the substructure had been revealed were given a slight electrolytic repolish and re-etching, the α crystals being used as a means of identifying the area examined. Except with very light repolishes, the α crystals changed in shape, and the patterns of the β subboundaries altered completely, showing that the surface had been lowered by an amount of the same order as the size of the subgrains. With a very light repolish, the α crystals were attacked less readily than the β phase, so that if the full line in Fig. 1 represented the original surface, the broken line might represent the surface after a very light repolish. When viewed microscopically the curvature of the surface at X produced a ghost or shadow round the α crystals, and the original patterns of the β-subgrain boundaries persisted. These experiments proved the β substructure to be genuine and this was confirmed by the X-ray work described below.

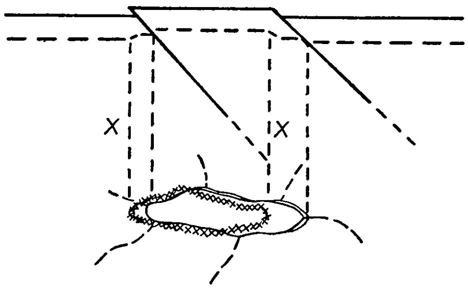

Fig. 1.

4. The effects of annealing at 500° C.

The effects of annealing at 500° C. may be considered under three headings: (1) The growth of the β colonies. (2) The changes in the α crystals. (3) The development of the β substructure.

(1) *The growth of the β colonies*

On annealing at 500° C. the β colonies grow rapidly until after 13 hr. they are of the order 2–3 mm., the longer dimensions being in the direction of rolling. Comparatively little further growth occurs when the annealing is extended to 35 days.

(2) *The changes in the α crystals*

On annealing at 500° C. the Widmannstätten structure is rapidly destroyed, and necklaces of twinned α crystals are formed in the boundaries between the β colonies. Fig. 3 shows the structure after 13 hr., at which stage only a few needles remain and the α necklaces are beginning to break up. The destruction of the needles thus takes place in a time of the same order as that of the rapid growth of the β colonies.

On further annealing there is a slow progressive change in which the α crystals become fewer and larger, and more nearly equiaxed, whilst the necklaces in the boundaries of the β colonies are destroyed. Fig. 4 shows the structure after 35 days, and the curiously irregular shapes of the α crystals are apparent.

(3) *The development of the β substructure*

During the early stages of annealing at 500° C., where some needles still persist, the substructure is always revealed less clearly in sections where the needles are nearly parallel to the polished surface than in sections nearly perpendicular to the surface. Fig. 7

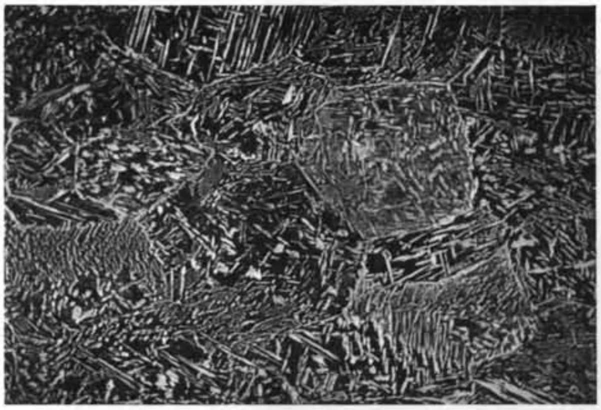

Fig. 2. Initial alloy. Etched with aqueous acid ferric chloride. × 25.

Fig. 3. Alloy annealed 13 hr. at 500° C. Etched with aqueous acid ferric chloride. × 25.

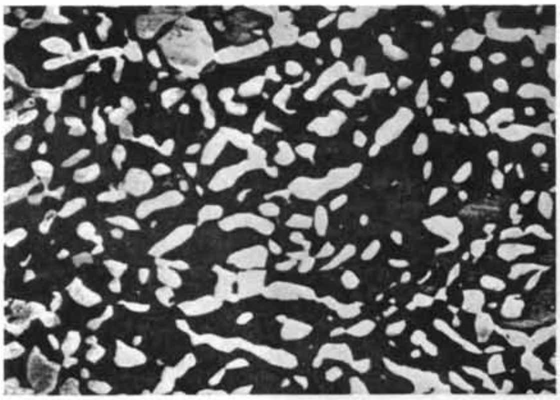

Fig. 4. Alloy annealed 35 days at 500° C. Etched with aqueous acid ferric chloride. × 25.

Fig. 5. Initial alloy. Etched with ammoniacal hydrogen peroxide. × 150.

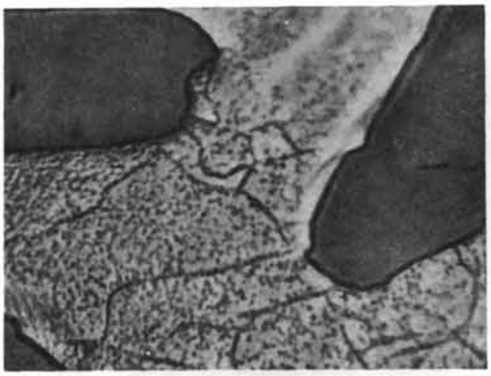

Fig. 6. Initial alloy. Electropolished and etched by method (*B*). × 800.

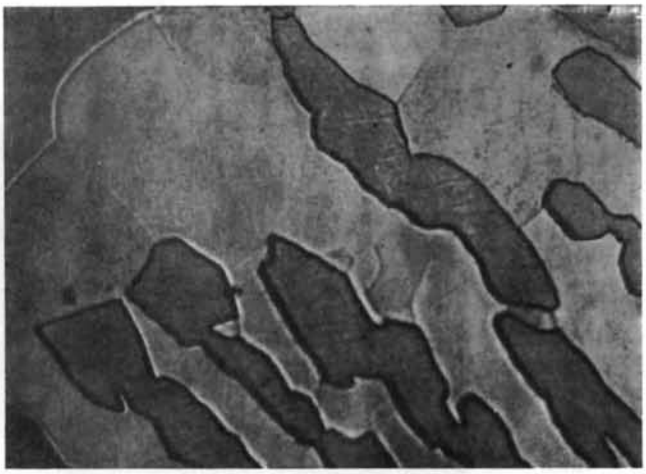

Fig. 7. Alloy annealed 13 hr. at 500° C. Electro-polished and etched by method (*B*) followed by method (*C*). × 1200.

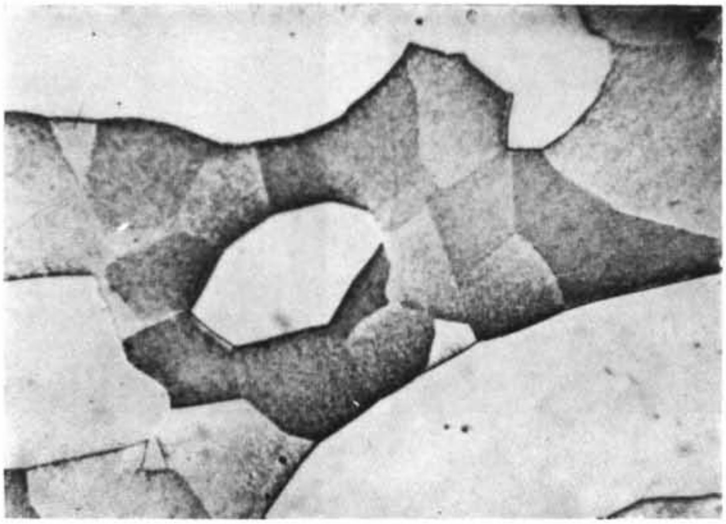

Fig. 8. Alloy annealed 5 days at 500° C. Electro-polished and etched by method (*A*). × 50).

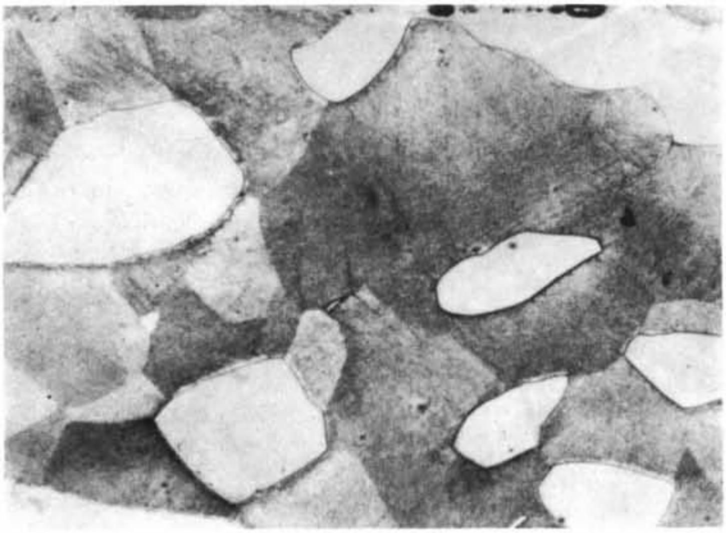

Fig. 9. Alloy annealed 11 days at 500° C. Electro-polished and etched by method (*A*). × 330.

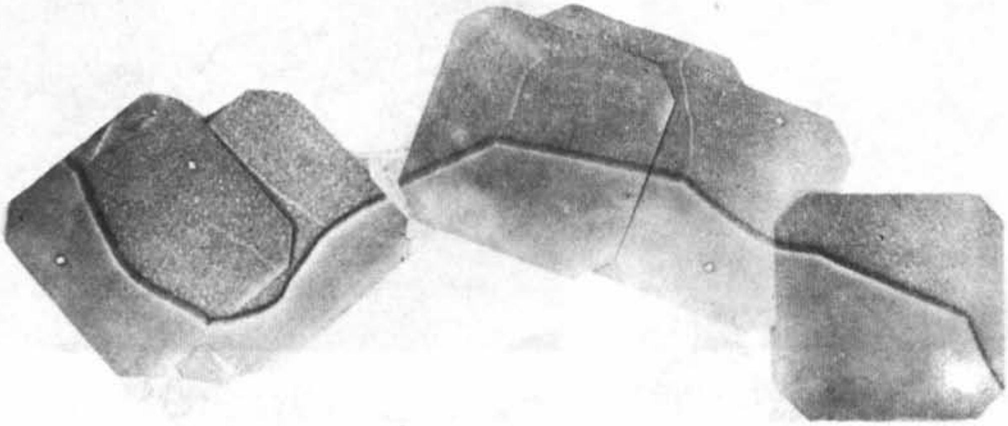

Fig. 10. Alloy annealed 5 days at 500° C. Electron micrograph by the British Non-Ferrous Metals Research Association. Original × 8800; reproduction × 3500.

shows a section of the latter type in an alloy annealed for 13 hr. at 500° C., and this shows clearly that many of the sharp angles of the α crystals coincide with the boundary between two of the β subgrains. Figs. 8 and 9 show alloys annealed for 5 and 11 days respectively, and when allowance is made for the different magnifications it is clear that the size of the β subgrain is increasing with the time of annealing.

In view of the difficulty of the etching technique, two of the specimens were kindly examined by Dr P. B. Hirsch and Mr P. Gay, using an X-ray diffraction method which is being described elsewhere. The results showed that the β colonies gave rise to groups of spots arranged along short arcs of the back-reflexion diffraction rings. In the specimens annealed for 11 days at 500° C., the X-ray data indicated a subgrain size of the order of 0·07 mm. in agreement with the microscopical results, whilst the total spread of orientation in the colony examined was 3°. In a specimen annealed for 35 days at 500° C. the corresponding values were 0·1 mm. and 0·9° respectively, so that the effect of annealing is to produce a β colony which is more nearly a perfect crystal.

To examine the matter further a specimen annealed for 5 days at 500° C. was examined by electron microscopy by the British Non-Ferrous Metals Research Association, and we must thank Prof. A. G. Quarrell for his kindness in this connexion. Fig. 10 shows a composite electron micrograph of the boundary between two α crystals and one β colony, and there is a striking correlation between the changes in direction of the surface of the α crystals and the boundaries of the β subgrains.

5. Discussion

It may be objected that the observed substructures are surface structures resulting from strains in grinding the specimen, and are not genuine structures characteristic of the interior. This seems improbable because of (1) their clear relation to the angles of the α crystals, and (2) of the fact that repeated electrolytic polishing and etching gave no indication that the substructure was becoming fainter. We have also carried out experiments in which specimens were annealed at 800° C., and then cooled at different rates to 500° C., and annealed at this temperature. A specimen quenched from 800° C. showed no substructure. Specimens in which the α crystals had been precipitated above 500° C. showed very faint indefinite substructure whilst X-ray methods gave single spots for the large α crystals, indicating that these were sensibly single crystals. Angular α crystals were, however, produced, and we think that the corners on these indicate the presence of β subboundaries although the orientation differences are too small to be definitely detected by either X-ray or etching methods. These experiments suggest clearly that the substructures are not surface effects due to straining in grinding, because if such effects existed they would be present in all the specimens, and a substructure should have been present in all cases.

The present work shows, therefore, that the α/β brass annealed at 500° C. consists of α crystals embedded in β colonies which consist of subgrains whose size is substantially greater than that of the usual 'mosaic' structures. At high temperatures the β subgrains unite to form nearly perfect crystals, but at 500° C. they are anchored by the α crystals and persist for prolonged periods, although, since continued annealing produces larger subgrains in more perfect alignment, the final structure would presumably be one with perfect crystals of the β phase. The boundaries of the subgrains are intimately related to the shapes of the α crystals, and this is remarkable in view of the small difference in orientation of the β subgrains.

The correspondence between the shapes of the α crystals and the β subgrain boundaries makes it unlikely that the substructure is connected with the order$\rightleftharpoons$disorder transformation at 454° C. We think that the formation of the substructure is related to the volume change and hence the stresses resulting from the $\beta \rightarrow \alpha$ transformation, and that a distinction must be made between the substructure in the extruded material and that in the annealed state. In the extruded material the shapes of the α crystals are clearly related to those of the β subgrains, which suggests that the latter results from stresses produced during the precipitation of the α phase, and are not hot-working substructures. The fact that in the extruded material the β-substructure boundaries did not always register exactly with the corners of the α crystals suggests that the final cold work merely distorted a substructure which was initially present.

The operation of these precipitation stresses may also be seen in the branching of the original α dendrites to form comb-like arrays of parallel needles. The original needles grow lengthwise until the stresses reach such a value that the free energy of precipitation is insufficient to compensate for further internal stress. At this point precipitation occurs more readily by branching, and this continues in the same needle-like form in a new crystallographic direction, and at a new characteristic spacing. It is suggested that the substructure is another manifestation of the internal stresses of precipitation.

In the annealed alloys, the substructure has a slightly different etching behaviour, being more readily revealed, and quite equiaxed in shape. It is possible that it arises by growth of the original substructure. Alternatively, it may be caused by polygonization of the β after the small amount of cold deformation it received.

References

MARZKE, O. T. (1933). *Trans. Amer. Inst. Min. (Metall.) Engrs*, **104**, 64.

MEHL, R. F. & MARZKE, O. T. (1931). *Trans. Amer. Inst. Min. (Metall.) Engrs*, **93**, **123**.