Morphology and Substructure of Ti–Cu Martensite and its Aged Martensite

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The morphology and substructure of Ti–Cu martensites containing 1, 2 and 5.3 wt% Cu were investigated by means of optical microscopy and transmission electron microscopy. Surface relief studies prove that the transformation of three Ti–Cu alloys during water-quenching is essentially martensitic. Detailed examinations exhibit gradual transitions in (1) the morphology, (2) the mode of the inhomogeneous shear and (3) the mode of stress accommodation, with an increase in copper content. A typical massive structure appears only in Ti–1%Cu. Above this concentration (2%Cu or more) the plate structure predominates. A transition in the operating mode of the inhomogeneous shear, from slip to twinning, occurs with increasing copper content. It occurs at a somewhat higher \( M_s \) temperature than in high purity binary titanium or zirconium alloys. A parallel transition is first observed in the mode of stress accommodation, from accommodation by movement of dislocation boundaries or by formation of dislocation tangles at low Cu, to accommodation by \( \{10\overline{1}1\} \) deformation twinning at higher Cu. A mixture of the two modes is also observed, proving a possible interchangeability of dislocation tangles and twins during the accommodation process.

Clear distinction between types of accommodation twins (stress induced twins and direct impingement twins) is given. These are compared to the transformation twins.

The rate of nucleation and growth of precipitates on lattice defects during the aging process of the martensitic structure depends on the type of defects. The phenomena observed can all be explained on the grounds of surface energy, strain energy and diffusion rate considerations. The importance of lattice defects as preferred nucleation sites decreases in the order of martensitic plate boundaries, dislocations, twin boundaries and former \( \beta \) boundaries.

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I. Introduction

Morphology and substructures of titanium and titanium alloy martensites have been reported by some authors\(^{(1)(2)}\) and recently reviewed comprehensively by Banerjee and Krishnan\(^{(3)}\) in a study of Zr–Ti alloys. Ti base alloys exhibit a transition in the operating mode of the lattice invariant deformation of the martensitic transformation, from slip to twinning. The transition occurs by increasing the alloying addition, and is mainly the result of the drop in \( M_s \) temperature down to 650 and 700°C (e.g. in Ti–Zr, Ti–Cr, Zr–Ti).

In Ti–Cu martensites, a transition from massive to acicular martensite was reported\(^{(4)}\) to exist between 4 and 6% Cu\(^{†}\), which corresponds to an \( M_s \) temperature of 700~750°C\(^{(3)}\). This transition was considered to be different from the one mentioned before; it was explained on grounds of a shift from rapid growth to rapid nucleation\(^{(4)}\), while a change in the mode of the lattice invariant deformation (reported as consisting of \( 1/3[2\overline{1}13] \) and \( 1/3[2\overline{1}00] \) dislocations) was not observed. Williams et al. reported the occurrence of twins on \( \{10\overline{1}1\} \) and \( \{10\overline{1}2\} \) planes, attributing the former twins to impingement effect only and the latter to the accommodation of transformation stresses. In the present work, on the contrary, \( \{10\overline{1}1\} \) twinning was determined to result partly from the accommodation of transformation stresses and partly from the lattice invariant deformation or the deformation of martensite by the impingement of secondary plates. The procedure described in the previous paper\(^{(6)}\) helps to distinguish between twins (or dislocations) resulting from the different origins mentioned above, by the determination of the orientation relationship and the exact variant of the habit plane in the \( bcc-hcp \) transformation, despite the absence of a retained parent

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† percent in this work indicates weight percent.
phase.

The present work deals mainly with the nature and origin of the morphology and substructure of Ti–Cu alloy martensites containing up to 5.3% Cu, in an attempt to clarify the change in this range. Precipitation on the different lattice defects was also studied and some phenomena in the martensites and aged martensites are presented and discussed.

II. Experimental Procedure

Three Ti–Cu alloys, containing 1, 2 and 5.3% Cu, were supplied by "Kobe Steel Ltd." in the cold-rolled condition. Chemical analysis indicated that the total interstitial content was about 500 ppm. Specimens were sealed in argon-filled silica tubes and received heat treatments as indicated below. The quenching was performed by breaking the tubes in cold water. Thin foil specimens for observation in the JEM 120 electron microscope were prepared by electropolishing in 5% perchloric acid + 95% acetic acid or acetic anhydride under a voltage of 40–42 volts, while the specimen was held in a specially-prepared Teflon holder(7). The electrolyte was strongly stirred and kept below −20°C in the case of acetic anhydride and at −12°C in the case of acetic acid. Specimens for optical microscopy were mechanically polished and then etched with dilute HF solutions or with a mixture of 10%HF and 90% of (20%HCl + 80%H₂O).

III. Experimental Results

The transformed structures of three Ti–Cu alloys containing 1, 2 and 5.3%Cu water-quenched from the β-phase elucidate surface relief effects on a prepolished specimen as observed in Photo. 1. Such relief effects prove the occurrence of a shape deformation during the transformation, and they were absent in other heat treatments, such as air cooling from the β phase or water quenching from the α or α+β phase. It can be concluded from these observations that the transformation during water-quenching is undoubtedly martensitic and, further, more detailed examinations exhibit gradual transitions in (1) the morphology, (2) the operating mode of the inhomogeneous shear and (3) the mode of stress accommodation, with an increase in Cu content as described below.

The morphology of the martensites obtained by water-quenching the three Ti–Cu alloys was found to exhibit, in the electron microscropic scale, the "massive" to "acicular" transition. The transition is characterized by a decrease in the amount of massive plates (arranged in groups of nearly parallel interfaces) and an increase in the amount of acicular plates, with an increase in copper content. In Ti–1%Cu, the plate boundaries are relatively curved and unclear, as seen in the electron micrograph of Photo. 2, which resemble the martensites of pure titanium(8). In Ti–2%Cu, similar structures with more definite boundaries were reported in a previous work(6), while the
Ti-5.3%Cu alloy also exhibits a tendency towards the formation of nearly parallel groups of plates, but on the much smaller scale of the secondary martensitic plates.

The optical microscope observation (Photo. 3) shows that the alloys have almost identical structures, with a gradual decrease in plate size with increasing Cu content. Primary plates decrease in width, from about 25 μ in Ti-1%Cu to about 2 μ in Ti-5.3%Cu. The interfaces of the large primary plates of the two kinds of lower-Cu alloys are quite irregular, and this fact indicates that at high temperatures the transformation is massive martensite and not usual martensite as will be discussed later.

The substructure is characterized mainly by dislocations and twins. Both kinds of the defects appear in various distributions and densities. In the lower-Cu alloy (Photo. 4), only dislocations can be observed and twins cannot be observed. This means that the lattice invariant deformation occurs by a slip-type inhomogeneous shear. On the other hand, the irregular plate boundaries indicate that the accommodation of the transformation stress is supplied by boundary movements or by dislocation tangles at low copper content. Twins increased in amount with increasing Cu content. In a previous report(6) it was shown that a considerable part of the twins in Ti-Cu martensites are transformation twins, based upon the fact that the particular variant of the \{10\bar{1}\} twins agrees with Bowles and Mackenzie's (B and M) Class A(\omega^- \omega^+) martensitic transformation.

Photograph 5 shows a possible exchangeability of twins and heavily dislocated regions. In other words, the dislocation entanglements may replace the twins (T) in the role of strain accommodation or as the lattice invariant deformation. Another phenomenon is the near-disappearance of the plate boundary where it is met by a twin at A. This happens only in
The formation of deformation twins by impingement. Note the advance of the secondary plate inside the primary one. Ti–5.3%Cu. Primary and secondary plates are indicated by P and S respectively.

the case of neighboring plates with an identical variant, as is the case with this micrograph. From the appearance of the residual faint boundary at A and B, it seems certain that the twins are formed after the transformation or on its completion.

Photograph 6 shows the formation of twins by impingement of a secondary plate on a primary one. It can be clearly observed that the primary plate is deformed by the impingement, and that the twin is a direct result of this operation. The secondary plate pierces the primary one, becomes narrower and sharper and then comes to a halt, while the compression stresses cause the formation of twins whose width appears to be similar to that of the impinging plates. The twins in Photo. 7 appear to be deformation twins as well, but in this case they form as a result of strains caused during the growth of a plate, without the effect of impingement. The twins in both cases are on \{10\overline{1}1\} planes, which is a deformation twinning plane of titanium at elevated temperatures. The method developed by the authors enables the determination of particular variant of the orientation relationship and the habit plane, and is thus most suitable for distinguishing between the different types of twins. While transformation twins must and in fact do agree with a B & M solution, and are always close to a \{110\}_{\text{bcc}} plane of the matrix phase, this is not the case with the deformation twins that can form on any \{10\overline{1}1\}_\alpha plane.

The large quantities and numerous types of lattice defects in the martensitic structure result in an extremely non-uniform and non-homogeneous precipitation on aging of a \beta-\text{quenched} Ti–Cu alloy. Photograph 8(a) shows the dislocation substructure in an as-quenched Ti–Cu alloy, confirmed by electron diffraction and dark field technique.
2\% Cu alloy, and (b) does the nucleation of precipitates on such dislocations in the alloy subsequently aged. The density of nuclei is about $10^5$ cm$^{-1}$ which is usual in other systems$^{(10)}$.

Photograph 9(a), (b), (c) show precipitation on the former $\beta$ boundaries, martensitic plate boundaries and $\{10\overline{1}1\}$ twin boundaries$^{(11)}$, respectively, all appearing in the same specimen, aged for 6 hr at 550$^\circ$C. From the micrographs it can be concluded that the main factors to enhance precipitation are the reduction in interface energy along the boundaries, strain energy in dislocations and plate-boundaries, and the high diffusion rate along the former $\beta$ boundaries, causing the coarse growth seen in Photo. 9(a).

In addition to these types of precipitates, it was observed that the center of the martensitic plate is frequently a preferred nucleation site. An example is shown in Photo. 10. It may be concluded that it results from a concentration of defects in the plate center. It is well known that in the martensite of iron alloys there is a phenomenon of regions with a high concentration of defects in the center of a martensitic plate. This is called "midrib of martensite." The precipitates may have nucleated on such defects or on substructures as can be seen from Photo. 4, but we could not find any direct evidence to support this suggestion.

The micrographs of Photo. 8–10 show precipitates inside the martensite plates. Such precipitates were varied in size and distribution, which may imply that a considerable part of them is actually nucleated heterogeneously on lattice defects within the plates, and not homogeneously.

**IV. Discussion**

We first consider the transition in transformation mode, and hence in morphology and substructure, with increase in Cu concentration. As already mentioned, there is some uncertainty regarding the nature of the transi-
tion. While many Ti alloys exhibit the transition in the mode of inhomogeneous shear (from slip to twinning)\(^{(3)}\), this has not been clearly observed in Ti–Cu, where the transition in morphology is considered to result from the differences between nucleation and growth rates of martensitic plates\(^{(4)}\).

Our results indicate that the transformation of three Ti–Cu alloys during water-quenching is undoubtedly martensitic and, further, gradual transitions occur in (1) the morphology, (2) the mode of the inhomogeneous shear and (3) the mode of stress accommodation, with an increase in copper content.

A typical “massive” (lath) structure appeared only in Ti–1\%Cu (Photo. 2). The structure very closely resembles the martensite in Zr–5\% Ti and was found to be massive martensite with a slip-type inhomogeneous shear\(^{(3)}\). Above this concentration (2\%Cu or more) the plate structure predominates. The coexistence of massive transformation products and usual martensitic structure is not unusual\(^{(12)(13)}\). In our case it is a natural consequence in view of the high critical cooling rates which are difficult to achieve in water quenching of Ti–Cu alloys. The massive transformation may occur above the M_s temperature, and the rest of the matrix is then transformed martensitically with a further drop in temperature. The appearance of surface relief (Photo. 1) proves that the massive transformation is essentially martensitic and thus the massive transformation can be regarded as a kind of martensitic transformation which may be accompanied by the rapid, thermally assisted movement of individual atoms over a small number of interatomic distances and in particular across the interface from the old to the new phase.

The transition in the mode of inhomogeneous shear does appear in the present work, although in lower concentrations than expected. A typical massive structure shows dislocations in low Cu alloys (Photo. 2) and the evidence for the operation of more than one slip system is given in Photo. 4. This could be compared with similar observations on other systems\(^{(8)}\). Above this concentration (2\%Cu or more) twinning predominates with no evidence of dislocation boundaries. The early transition can be explained on the grounds of purity level, bearing in mind that even commercial titanium, with no major β-stabilizing addition, exhibits the twin-mode of inhomogeneous shear\(^{(14)}\) because of its relatively high impurity level\(^{(8)}\).

The accommodation of the transformation stress is supplied by boundary movement or by dislocation tangles at low copper content. The irregular plate boundaries of massive structure in low copper alloys (Photo. 2 and Photo. 4) indicate that the accommodation of the transformation stress is supplied by boundary movement or by dislocation tangles. The transition in the mode of stress accommodation from slip-type to twinning occurs with an increase in copper content and the accommodation of the stress is supplied by accommodation twins on \{10\overline{1}1\} planes at higher Cu contents. The decrease in the transformation temperature can well explain this transition. It is interesting to note that this transition is essentially different from the above-mentioned transition in the mode of inhomogeneous shear. Both transitions occur at similar copper contents, but one of them concerns the shear which occurs during the transformation, while the other is a transition in the mode of accommodation following the transformation. The interchangeability of dislocation tangles and \{10\overline{1}1\} twins is clearly seen in Photo. 5 for Ti–2\%Cu, which seems to be a transition composition in this respect (it includes both modes), but it is a problem to decide whether this is the transition between inhomogeneous shear modes or the one between accommodation modes. The second possibility may be more likely, because the faint residual plate boundaries indicate that the twinning which occurred at a later stage. The fact that plate boundaries were almost extinguished after the transformation is explained by the plates being of identical crystallographic variants. Small accommodation shifts can then cause the disappearance of the low angle boundary, and the curious and interesting substructure is thus reasonably explained.

The appearance of \{10\overline{1}1\} accommodation twins along with transformation twins, in spite of \{10\overline{1}1\} planes not being a regular deformation twinning plane, was already discussed elsewhere\(^{(6)}\). The present results
show clearly that accommodation twins of two distinct types appear in the structure. Those in Photo. 7 (and probably also Photo. 5) occur as a result of the transformation stresses, but not due to a direct impingement effect. Photograph 6 shows clearly the twins that were formed as a result of impingement of secondary plates on primary ones. All the accommodation twins occur on the completion of the transformation in their specific region, while the transformation is still taking place in the nearby regions. Practically they form almost simultaneously (and at the same temperatures) with the \{1011\} transformation twins, that are characterized only by their specific variant, which can be identified in spite of the absence of the $\beta$ phase, and their more even distribution.

The rapid nucleation rates due to lattice defects and the enhanced growth rates of precipitates on grain boundaries are, of course, the expected results of the aging treatment. The precipitation was observed on all kinds of lattice defects, enabling us to compare the importance of the various factors. The fact that even twin boundaries served as nucleation sites proves that the reduction of surface energy could be sufficient for preferred nucleation. The addition of the strain energy factor, on dislocations and plate boundaries, naturally increases the rate of nucleation further. In boundaries a third factor, the increased diffusion rates, causes rapid growth as well as quick nucleation. The relative importance of the different kinds of lattice defects, in terms of the final volume of precipitate on them, decreases in the order of martensitic plate boundaries, dislocations, and twin boundaries.

V. Conclusion

(1) The morphology exhibits a transition from massive structure to plate structure with an increase in copper content. The transition is characterized by a decrease in the amount of plates with irregular boundaries and an increase in the amount of acicular plates.

(2) Gradual transition in the operating mode of the inhomogeneous shear of the martensitic transformation from shear to twinning, occurs in Ti–Cu binary alloys with increasing Cu content. The transition occurs at lower concentrations than expected, and this is explained as resulting from the relatively high impurity content.

(3) A transition in the mode of stress accommodation is first observed. Accommodation at low Cu (high transformation temperatures) is achieved by movement of dislocation boundaries or by formation of dislocation tangles. At high Cu (low temperatures) the accommodation is by \{10\overline{1}1\} twins. In the transition range mixed modes and even inter-changeability of dislocations and twins appear in the structures.

(4) Accommodation twins are of two types: the stress induced type and the direct impingement type.

(5) During aging of supersaturated martensites, preferred nucleation and growth occurs on martensitic plate boundaries, dislocations, twin boundaries and former $\beta$ boundaries (in this order of importance), and can be explained by contributions of surface energy reduction (at twin boundaries and other boundaries), strain energy reduction (at dislocations and dislocation boundaries) and increase of diffusion rates, mainly along plate boundaries and former $\beta$ boundaries.

REFERENCES