

The $\beta \rightleftharpoons \alpha$ transformation in dilute Ti-Mo alloys

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An investigation has been made of the various phase transformations which occur when dilute Ti-Mo (0.5 and 1.0 wt % Mo) alloys are cooled from the β phase field and are subsequently tempered in the $\alpha + \beta$ phase field. The morphology of the decomposition products varied with cooling rate and can be correlated with the competition between the formation of α' by martensitic and by diffusional processes. On isothermal transformation below the M_s , or upon tempering, β phase precipitates grow heterogeneously from the supersaturated α' plates formed by shear. The precipitate habit plane is irrational and corresponds to the $\{334\}$ β plane.

1. Introduction

In certain "near α " titanium alloys a small volume fraction of the bcc phase can be retained between martensitic (α') plates on quenching from the β -phase field [1]. Alloys containing small amounts of molybdenum are of particular interest in this context and a recent investigation of dilute Ti-Mo-Si [2] alloys has shown that the retention of β is associated with solute diffusion to the periphery of the α' plates during cooling. The present work represents a further study of the specific effect of molybdenum in relation to β retention in two binary Ti-Mo alloys containing 0.5 and 1 wt % Mo respectively; in addition to the examination of structure after quenching from the β -field, a study has been made of β precipitation occurring when α' is tempered.

2. Experimental procedure

The alloys (nominal composition 0.5 and 1.0 wt % Mo) were prepared by arc melting small "ingots" as described previously [1]. The ingots were rolled at 600°C to sheet of various thickness in the range 0.05 to 2.5 mm and the surface layers were removed to a depth of 0.01 mm. Heat-treatment was carried out in sealed silica capsules containing argon, the specimens being wrapped in molybdenum foil. Solution treatment was carried out at 1100°C for 10 min producing a β grain size of 0.7 mm. Five different cooling

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treatments were employed after solution treatment.

1. Water quenching, the silica capsule being broken on contact with the water to ensure a rapid quench.

2. Water quenching, the silica capsule being left unbroken. This treatment preserved the pre-polished surfaces of the specimens so that any surface tilts could be observed.

3. Air cooling the silica capsule in still air.

4. Furnace cooling. This provided a slow cooling rate so that equilibrium could be approached.

5. Direct transfer of the capsule to a furnace at 750°C followed by isothermal transformation for periods up to 25 min.

Additionally, selected specimens from 1, 2 and 3 were tempered in the temperature range 450 to 750°C to produce β phase precipitation within supersaturated α' plates.

The specimens were examined using light and electron metallography: special care was taken to produce foils containing large uniformly thin regions so that low magnification micrographs ($\times 1500$) could be obtained from large areas to correlate the gross features observed by light metallography with the detailed structure visible in the electron microscope.

3. Experimental results

Specimens of both the 0.5 and 1.0 wt % Mo

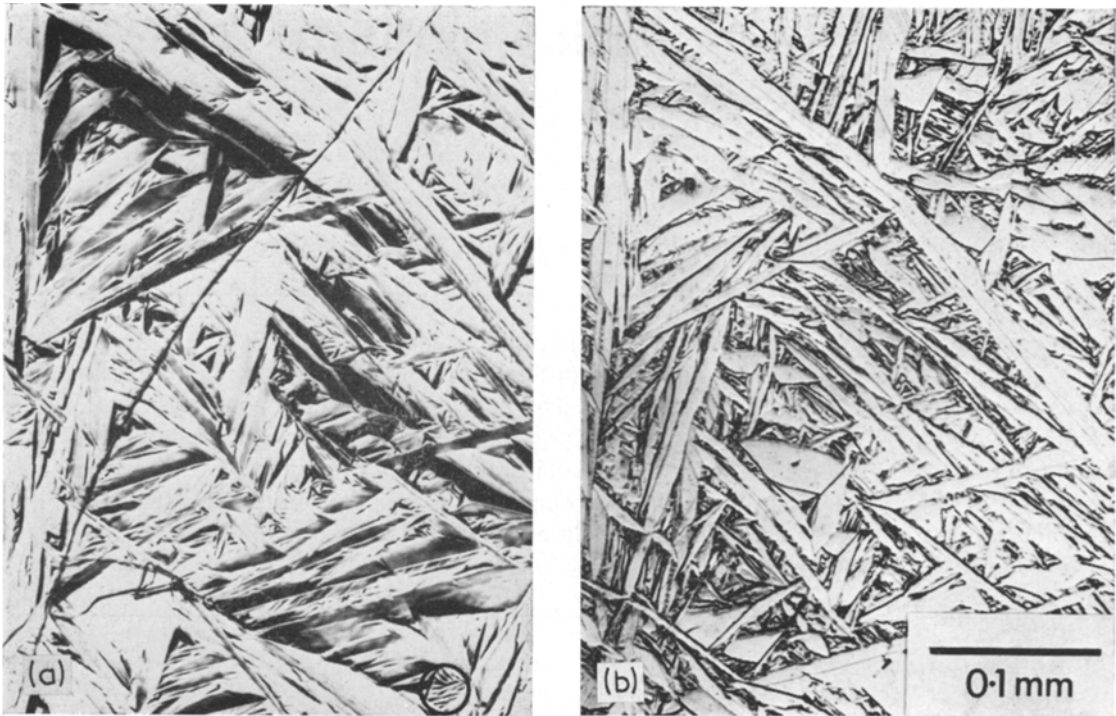


Figure 1 (a) Ti 1 wt % Mo 1100°C/10 min water quenched without breaking the silica capsule. Surface tilts on a pre-polished surface. The circled area shows a colony structure ($\times 250$). (b) The same area as in (a) but after grinding 10 μm from the surface showing that the surface tilts are associated with the bulk transformation product.

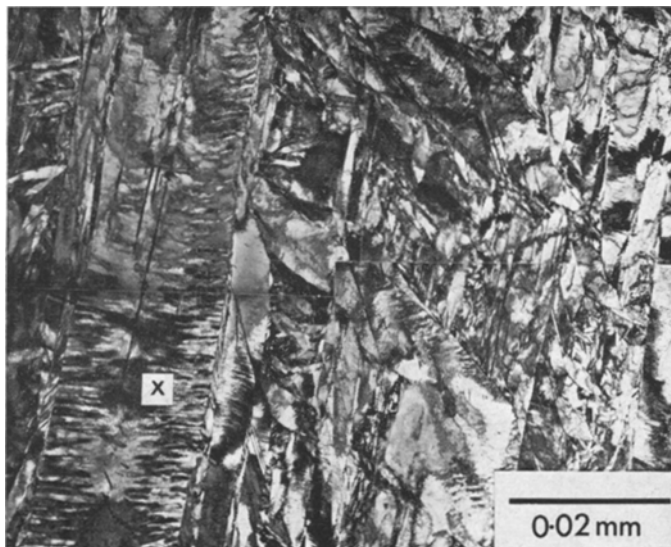


Figure 2 Ti 1 wt % Mo 1100°C/10 min water quenched with the silica capsule broken on contact with the water. A composite electron micrograph showing the large primary α' plates which contain sub-boundaries (e.g. at X) and the fine secondary plates ($\times 1000$).

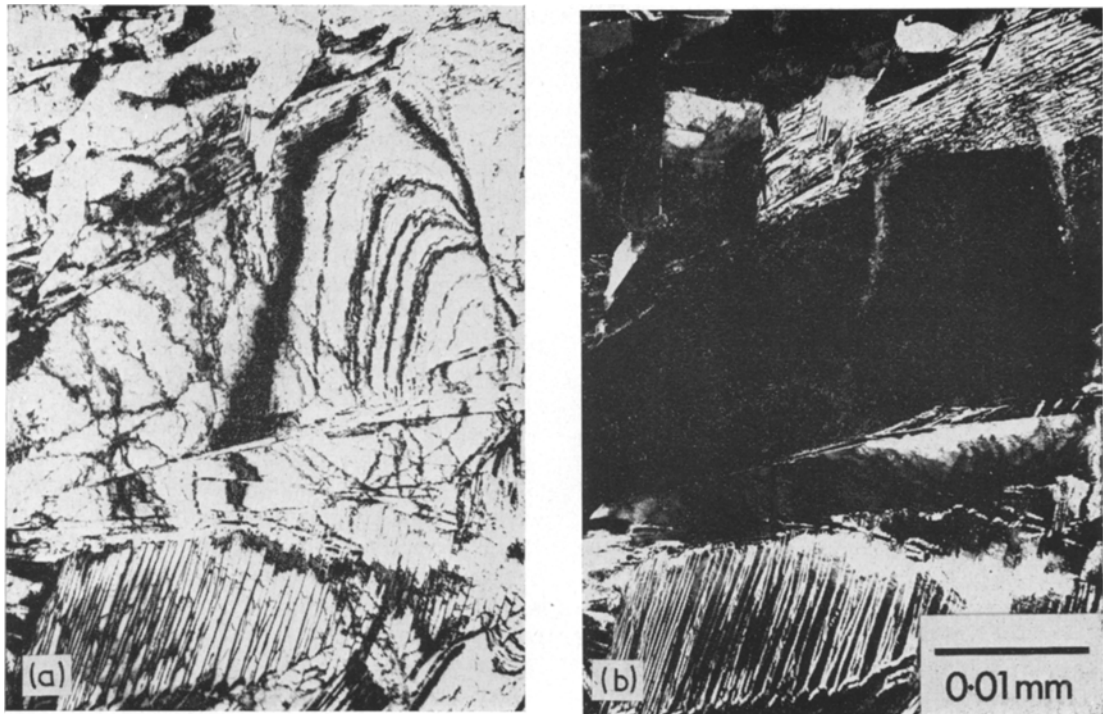


Figure 3 (a) Ti 1 wt % Mo 1100°C/10 min water quenched without breaking the silica capsule. Bright field electron micrograph showing large primary α' plates together with secondary plates, some of which form colonies of plates of parallel orientation. (b) The same area as in (a). Dark field micrograph taken using a β reflection which was extremely close to several α' reflections. The retained β phase can be seen most easily in the boundaries between the colony plates.

alloys which had been water quenched (with or without the silica being broken) exhibited large parallel-sided primary α' plates approximately 10^{-3} cm in thickness, some of which completely spanned the prior β grains (Fig. 1a). The partitioned regions between these plates contained many smaller, secondary plates, a small proportion of which formed colonies of parallel plates (e.g. the circled area in Fig. 1a). The number of primary plates was lower and the number of colonies higher in the 0.5% Mo alloy. The primary plates exhibited highly uniform surface tilts (as revealed by interferometry). The surfaces of the partitioned regions were so highly disrupted that interferometry was not possible, except where large secondary plates or the colony product was observed. The former exhibited uniform surface tilts while the latter exhibited irregular tilting similar to that observed in pure titanium [3]. Repeated grinding, polishing and etching showed that the surface tilts were associated with the

bulk transformation product and not any surface artefact (Fig. 1b). In a number of cases plates could be followed to a depth of over 70 μ m from the surface.

Electron microscopical examination of specimens water quenched (with the capsules broken) (Fig. 2) showed that the plates contained a high density of dislocations and infrequent $\{10\bar{1}1\}$ twins. Many plates were also approximately $\{10\bar{1}1\}$ twin related as observed in previous work [1]. Additionally, the large primary plates contained a regular series of sub-boundaries lying approximately normal to the broad face of the plate (e.g. X in Fig. 2) but not extending to the centre of the plate which exhibited only random dislocation arrays. Only trace amounts of retained β phase could be identified in these specimens, associated with the boundaries between adjacent plates of the colony product. However, a greater amount of β phase was observed in the specimens quenched without breaking the silica capsules; again the β phase

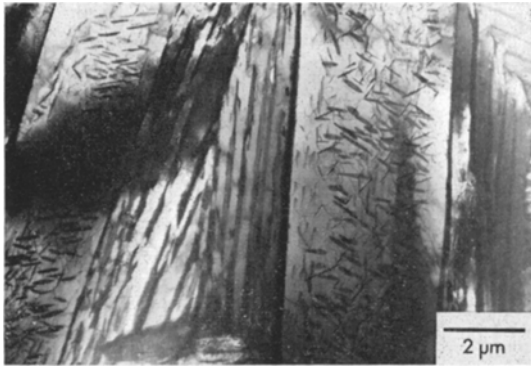


Figure 4 Ti 1 wt % Mo 1100°C/10 min, directly cooled to 750°C and isothermally transformed for 15 min. The large primary α' plate contains heterogeneously nucleated β precipitates ($\times 5000$).

was most readily detected in association with the colony product (Fig. 3a and b).

The air-cooled specimens also exhibited the large primary plates with uniform surface tilts and high internal dislocation density. There was much less evidence of sub-boundary formation within the primary plates than in the corresponding water-quenched specimens. Both the 0.5 and 1.0 wt % Mo specimens contained fewer of these plates than the corresponding water-quenched specimens. Also, the partitioned regions almost exclusively contained colonies of parallel plates which exhibited irregular tilts and a low dislocation density; as in the water-quenched condition the $\frac{1}{2}$ wt % Mo alloy contained more colony product than the 1 wt % alloy. Layers of β phase were observed around all the α' plates but no β precipitation was observed within the plates. Examination of the α'/β interfaces in the colony regions showed that the β layers are associated with dislocation arrays which ranged from complex networks to simple arrays of straight $[0001]$ edge dislocations spaced approximately 250 Å apart.

Specimens transferred directly to a furnace at 750°C exhibited complete transformation after the shortest period of isothermal treatment (5 min). The 0.5 wt % Mo alloy exhibited only a few large primary plates, the remainder of the structure being the colony product; the 1 wt % Mo alloy contained more primary plates (constituting about 10% of the structure) and the partitioned regions contained the colony product. Additionally, extensive heterogeneous precipitation of plate-shaped β particles was observed within the primary plates (particle

density $\sim 10^{14} \text{ cm}^{-3}$) indicating that when first formed, the α' plates are supersaturated in molybdenum (Fig. 4). Precipitate-free zones, approximately 5000 Å in width, were observed adjacent to the primary α' plate boundaries. No β precipitation was observed within the colony plates which were themselves between 0.5 and 1 μm in width, a value similar to that found in the air-cooled specimens; these plates were separated by β layers. In both the air-cooled and isothermally transformed specimens a few primary plates were observed to have broken up into colonies of parallel plates without any detectable change in orientation or habit plane. (In general the colony plates exhibited similar variants to the primary plates.)

Water-quenched and air-cooled specimens were aged at temperatures in the range 450 to 750°C for times up to 100 h. Substantial heterogeneous precipitation of β phase occurred within the α' plates except for those forming the colony product, but no significant age-hardening response was detectable using hardness testing. Water-quenched specimens aged at 750°C exhibited precipitate sizes and densities similar to those found in the isothermally transformed samples: however, the precipitate free zones at α' plates boundaries were only one third as wide as those observed in the isothermally transformed specimens. In all cases the precipitates were related to the α' plates in which they formed by a variant of the normal Burgers relationship:

$$(0001) \alpha' // (011) \beta \\ [2\bar{1}\bar{1}0] \alpha' \sim // [1\bar{1}1] \beta.$$

Single surface trace analysis of twenty-four β precipitate particles showed that the precipitate habit plane lies normal to the $(0001) \alpha'$ plane. The mean value of the angle between the habit plane normal and the $(1\bar{3}20) \alpha'$ normal is 5° in the direction of the adjacent $(0\bar{1}10) \alpha'$ normal (with a deviation of $\pm 3^\circ$ from the mean); this corresponds approximately to a habit plane with indices of $(1\bar{4}30) \alpha'$. A stereographic projection of both α' and β planes related by the observed orientation relationship shows that six crystallographically different β planes lie parallel to the $\{1\bar{4}30\} \alpha'$ planes. In order that the particular bcc plane of the α'/β interface could be established foils containing regions of α' with a $[1\bar{2}10]$ normal were examined. β precipitates whose habit plane was close to parallel to the

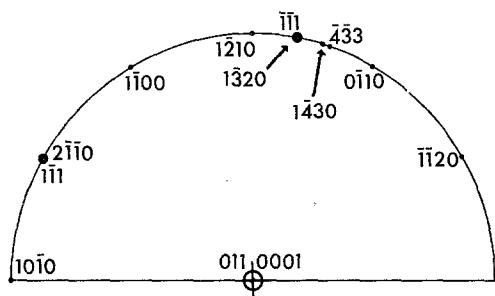


Figure 5 A stereographic projection showing α' and β phases related by the Burgers relationship. The projection shows the close correspondence between the observed $(1\bar{4}30)$ α' habit plane of β particles grown diffusively in the α' and the $(\bar{4}\bar{3}3)$ β plane.

foil surface produced a $[\bar{1}\bar{1}1]$ β zone diffraction pattern (with (011) $\beta // (0001)$ α') when the foil was tilted about the $[0001]$ α' axis by approximately 8° . The specific variant of the orientation relationship for these β particles is thus:

$$(011) \beta // (0001) \alpha' \\ [1\bar{1}1] \beta \approx // [2\bar{1}\bar{1}0] \alpha'$$

The specific variant of the habit plane is $(1\bar{4}30)$ α' . From this information the indices of the habit plane, in terms of the β phase, can be uniquely determined to be close to $(\bar{4}\bar{3}3)$ β (Fig. 5). This is the specific habit plane which would normally be associated with an α' martensite crystal formed in β with the same variant of the orientation relationship, i.e. the crystallography of the β precipitates grown diffusively in α' is the same as that associated with α' crystals grown martensitically in β phase.

The furnace-cooled specimens showed a thin layer of α at prior β grain boundaries and the structure within the prior β grains consisted of a lamellar mixture of α and β phases (Fig. 6) of low dislocation density which exhibited slight surface rumpling but no uniformity of tilt. The α phase predominated in the structure and its plate thickness was approximately 3000 to 5000 Å.

4. Discussion

The phase transformations reported in this work involve both shear (martensitic) and diffusional growth mechanisms. The large primary α' plates are clearly the first transformation product to form on cooling these alloys from the β field since they partition the β grains, and subsequent transformation infills the partitioned



Figure 6 Ti 1 wt % Mo 1100°C/10 min furnace cooled. Light micrograph showing α phase outlining the prior β grain boundaries and a lamellar mixture of α and β phases within the grains ($\times 800$).

regions. The fact that the primary plates exhibit uniform surface tilts, high internal dislocation density and orientation relationships between adjacent plates consistent with the Burgers relationship indicates that the plates are formed by a martensitic reaction. The observations that no detectable solute segregation occurs in the primary plates on water quenching and the fact that heterogeneous β phase precipitation takes place within the plates on tempering are consistent with this interpretation.

The primary plates formed in the air cooled and isothermally transformed specimens again exhibit the characteristics noted above including β precipitation within the plates on tempering, the precipitate size and density being similar to that observed in quenched and tempered specimens. This necessarily implies that these plates, when initially formed, have a similar degree of solute supersaturation to that of the water-quenched samples and are also the products of a martensitic reaction. There is, however, a change in the dislocation interaction accompanying the growth of the plates since the subboundaries within the plates are not observed in air-cooled specimens. The observations show that the critical cooling rate necessary to reach the M_s temperature prior to any diffusional transformation is low. This is quite understandable if the M_s lies well above the "nose" of the TTT curve for completely diffusional transformation, as shown schematically in Fig. 7. There are conflicting data in the literature concerning the actual M_s temperature for dilute Ti-Mo alloys. Delazaro [4], using a metallo-

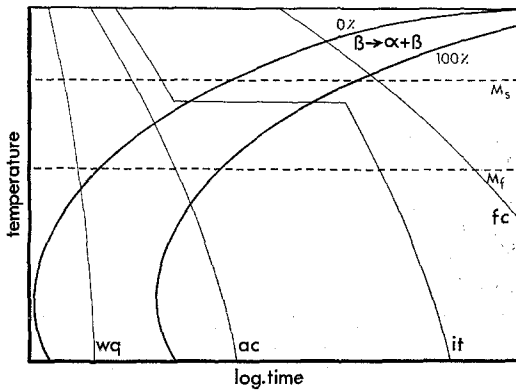


Figure 7 A schematic TTT curve for a dilute Ti-Mo alloy with the cooling curves for water-quenched (w.q.), air-cooled (a.c.), isothermally transformed (i.t.) and furnace-cooled (f.c.) specimens superimposed. It can be seen that the w.q. specimen transforms completely martensitically while the f.c. specimen is transformed diffusively. Both a.c. and i.t. specimens begin to transform by shear but diffusional decomposition provides a competing α' growth mechanism.

graphic technique, reported an M_s of 690°C for a 1 wt % Mo alloy and a C-curve for isothermal transformation above the M_s . Duwez [5], however, reported an M_s of 820°C for a 2.3 wt % Mo alloy on the basis of thermal analysis data. This value is in reasonable agreement with the results of Huang *et al* [6]. The exact value of M_s can be expected to vary with the interstitial content but must, in any case, lie above 750°C in the alloys employed in this study.

It was noted that the precipitate-free zones in the primary plates of the specimens air cooled and tempered and also of the specimens isothermally transformed were wider than those in the corresponding water-quenched and tempered specimens. Additionally, the primary plates were bounded by thin layers of retained β phase. Since no β retention occurs in association with the primary plates in water-quenched samples, this necessarily implies that some molybdenum segregation occurred during the growth of the plates in air-cooled and in isothermally transformed specimens. Since the plates exhibit uniform surface tilts and are formed over the majority of their thickness fully supersaturated in molybdenum, this suggests that during a later stage in their formation the growth mechanism changes from a martensitic mode to one involving diffusion. Molybdenum is rejected ahead of the growing plates pro-

ducing the retained β layers and increasing the size of the precipitate-free zones within the plates as a result of solute depletion. Since these diffusion assisted regions constitute, at most, 10% of the total plate thickness of $\sim 10\ \mu\text{m}$ the plates still exhibit uniform surface tilts as observed in the light microscope. Additional evidence for a change in growth mechanism during the transformation is afforded by the observation that some primary plates break up into colony structures.

In the colony product regions, the presence of β layers between the α' plates clearly demonstrates that diffusion occurs during their growth. Additionally, the α'/β morphology appears microstructurally similar to the diffusively formed product in the furnace-cooled specimens with the exception that the latter does not exhibit surface tilting. In air-cooled specimens the colony regions exhibit extensive surface tilting, the sense of the tilt being the same for each plate in the colony. The tilting is much less regular than in the primary plates and is similar to that observed in unalloyed titanium [3] or in massive martensite in iron-nickel alloys [7]. In such martensites, the lack of complete regularity in the tilting does not necessarily imply that the transformation is not martensitic. For example, it has been suggested [8] that the shape strain of a martensitic transformation may induce plastic flow in either the parent or product crystals: this is most likely to occur if, as in dilute titanium alloys, the transformation occurs at high temperatures where the yield strengths of the α and β phases are low.

However, diffusion following the initial growth of the shear plates could also relieve the shape strain and would result in a low dislocation density in the colonies which is observed in practice. Since it is well established that the α' formed in β by shear or diffusion both exhibit the same orientation relationship and habit plane (and in this work the converse β precipitation in α has been shown to exhibit exactly similar crystallographic relationships), it is possible that the transition from shear to diffusional growth is not sharply defined and the relative contributions of shear and diffusion to the growth of α' plates change continuously with cooling rate (slow cooling rates increasing the diffusional contribution), and also with alloy composition. Decreasing the solute content is known to raise the M_s and to move the "nose" of the diffusion-controlled C-curve nearer to the zero time axis

and to higher temperatures so that the competition between the two growth modes will increase.

In this context, it is of interest to note that Jepson *et al* [9] observed a continuous decrease in the transformation temperature of unalloyed titanium with increase in cooling rate. No discontinuity, such as would be expected to mark the transition between diffusional and shear transformation could be detected in the thermal analysis data. At high cooling rates, however, surface "rumpling" occurred. These results imply that there is a diffusional contribution to the transformation which decreases with increase in cooling rate. The results of these workers suggest that the transition between the diffusional growth mode and the martensite reaction is not abrupt and that the massive martensite observed in unalloyed titanium may have a diffusional growth component. Only when sufficient solute is added to move the C-curve to the right, and to sufficiently low temperatures that the rate of diffusional α' growth falls significantly below that for martensite growth, will a clear delineation between the two growth modes be obtained.

Finally, the present results may be considered in relation to the microstructures observed in other titanium alloys, quenched from the β phase field, when β retention is not observed. In these systems, a morphological transition occurs between a "massive" martensite (consisting of colonies of parallel plates separated by sub-boundaries) and a conventional platelike martensite, as the solute content is raised and the M_s is lowered. It has been suggested [1] that the massive martensite forms when slip occurs in the β phase ahead of the α' plate to reduce the shape strain. This is followed by the growth of more α' plates next to the first and exhibiting parallel orientation. When solid solution strengthening and the lowering of the M_s sufficiently strengthen the β phase to prevent slip, normal plate-like martensite is obtained.

In the light of the present results, there exists the strong possibility that in very dilute alloys which form "massive" martensite, diffusion also contributes to the reduction of the shape strain during water quenching from the β phase field. It should, however, be noted that the experimental evidence does not permit the "massive" martensite observed in other alloys to be identified with the colony product obtained in the present work; one difficulty is that the "massive"

martensite is assumed to form at higher temperatures than the plate-like martensite, whereas in the present work, the colony product forms at lower temperatures than the plate-like morphology. Further work is required to determine the roles of accommodation slip and diffusion in the formation of "massive" martensite and to determine the relationship between the formation of the colony product and the C-curve for diffusional transformation.

Although the detailed interpretation is not yet clear, it is of interest to note that molybdenum which is very effective as a solid solution strengthener is also particularly effective in producing plate-like martensite, as evidenced by the fact that even at the $\frac{1}{2}\%$ Mo level very little massive martensite forms on water quenching. A further point of interest is that for a given cooling rate there is less colony product and β -phase retention in the Ti- $\frac{1}{2}\%$ Mo and Ti-1% Mo alloys than in corresponding alloys containing additionally 1 wt % Si [2]. In the latter alloys, very similar surface tilting was observed in the colonies and it is suggested that the silicon addition increases the rate of diffusional decomposition of β .

5. Conclusions

1. In Ti-0.5% Mo and Ti-1.0% Mo alloys, both shear and diffusional mechanisms occur during rapid cooling from the β range. Primary α' plates form predominantly by shear, while in the colonies of α' secondary plates there is a greater contribution of diffusional transformation.

2. Retained β phase can form as a result of the diffusional component of the $\beta \leftarrow \alpha'$ transformation.

3. β precipitation occurs within α' plates on tempering with a $\{334\}$ β habit plane and also in α' plates formed by isothermal transformation of β .

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