

The effect of an addition of molybdenum on the quenched and aged structure of a Ti-1 wt % Si alloy

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Titanium-1% silicon alloys with the addition of 0.5 and 1 wt % Mo, when water quenched from the β field, contain small regions of the β -phase lying between the martensitic crystals indicating that some diffusional changes occur during quenching. On ageing the 1% Mo alloy at 650°C titanium silicide precipitation occurs together with spheroidization of the β -phase.

1. Introduction

Small additions of silicon (up to ~0.5 wt %) have been found advantageous in developing good creep properties in certain "near- α " titanium alloys. Results have recently been reported on the structure and strength of various alloys from the Ti-Al-Zr-Mo-Si system, ranging from binary alloys, e.g. Ti-1 wt % Si, to a Ti-5 wt % Zr-6 wt % Al-0.5 wt % Si-0.5 wt % Mo composition [1, 2]. In this latter alloy (similar in composition to the commercial IMI 685 creep-resistant alloy) it was observed that small regions of β -phase were present between the martensite crystals (α'), after quenching from the β -phase field. Ageing for 1 week at 550°C did not affect these β regions. The orientation relationship between the α' - and β -phases was a variant of the Burgers relationship.

$$(0001)_{\alpha} // (011)_{\beta} [1\bar{2}10]_{\alpha} // [11\bar{1}]_{\beta}$$

The existence of thin platelets of β -phase between martensite crystals has also been reported by Seagle and Bomberger [3] in a Ti-6 Al-5 Sn-2 Zr-0.8 Mo-0.25 Si alloy after cooling from the β range. Such regions of β -phase may be important in relation to creep properties, and, as part of further work in this area, a structural investigation has been made of two Ti-Mo-Si alloys containing 1 wt % Si and 0.5 and 1.0 wt % Mo respectively.

2. Experimental procedure

The two alloys were made as 30 g "ingots" by

arc melting, using high purity silicon, molybdenum and sponge titanium as the basis materials [1]; the compositions of the alloys were taken as calculated from the weights of the components used in melting. The ingots were wrapped in molybdenum foil and were solution-treated in argon-filled silica capsules for 24 h at 1200°C and water quenched, the capsules being broken on contact with the water to ensure a rapid quench. Specimens were sliced from the ingots for electron microscopy and hardness measurements. Some specimens were sealed in evacuated pyrex capsules and aged at 550 and 650°C for times up to 50 h.

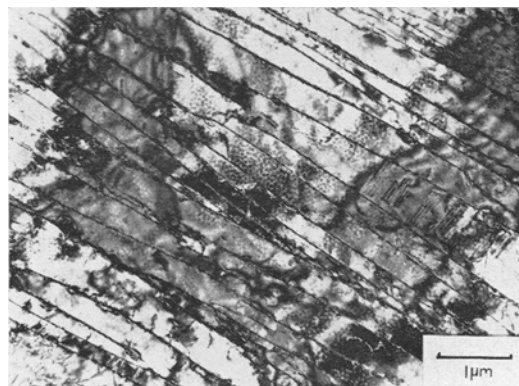


Figure 1 Ti-0.5Mo-1 Si: water quenched from 1200°C. A colony of massive martensite containing dislocations and stacking faults.

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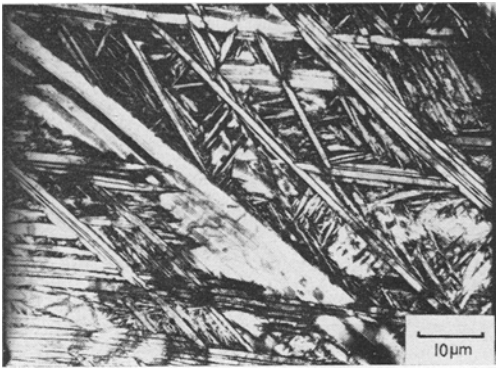


Figure 2 Ti-1 Mo-1 Si: water quenched from 1200°C. The microstructure contains both colonies of parallel plates and plates surrounded by crystals of different orientation.

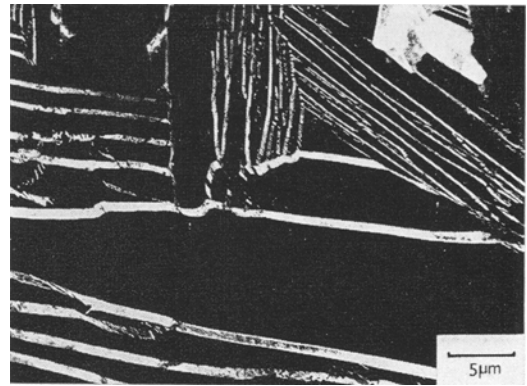


Figure 3 Ti-0.5 Mo-1 Si: water quenched from 1200°C. Dark field micrograph obtained using a β -phase reflection and showing at least three different α' variants which are all surrounded by a single variant of the β -phase.

3. Results

The martensitic structure in the as-quenched Ti-0.5Mo-1 Si alloy is predominantly of the massive type consisting of colonies of parallel plates separated by small angle boundaries (Fig. 1): in the Ti-1 Mo-1 Si alloy the structure contained a greater proportion of relatively large plate-like crystals, together with some massive colonies (Fig. 2). (In both alloys the transformation was accompanied by surface tilts seen on prepolished samples.) It appeared from electron microscopy that the large plates of the type observed by light microscopy are often made up of a number of parallel plates, separated by sub-boundaries and representing a morphology intermediate between the massive colonies and the single crystal martensite plates. Dislocations and stacking faults were observed in both alloys, while in the alloy with higher molybdenum content, internal twinning of the plate-type martensite was occasionally observed. Single surface trace analysis was carried out to determine the plane of the sub-boundaries in the massive colonies (which in mixed structures ran parallel to the conventional martensite habit planes). Using Burgers α/β orientation relationship it was found that in all cases the sub-boundary traces lay within 5° of the expected trace for a $\{334\}_\beta$ habit plane.

In both alloys it was found that the sub-boundaries in the massive colonies and the martensite plate boundaries contained a thin discontinuous layer of a second phase identified as β by selected-area diffraction and dark-field microscopy. Fig. 3 shows a high resolution dark-field micrograph of the Ti-0.5 Mo-1 Si alloy

obtained using a β reflection. It can be seen that the β had the same orientation throughout an area containing more than one α' variant. Selected-area diffraction patterns confirmed the α'/β orientation relationship to be a variant of the Burgers relationship.

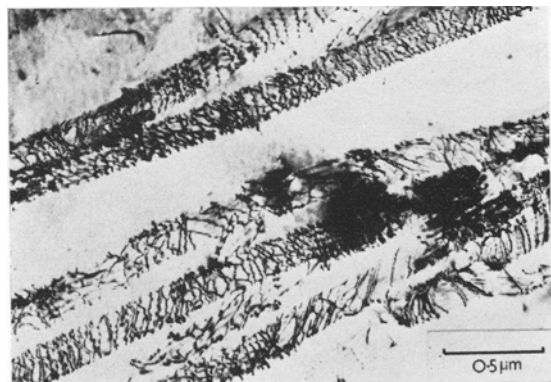


Figure 4 Ti-0.5 Mo-1 Si: water quenched from 1200°C. Bright field micrograph of the boundaries between the martensite plates in a massive colony $g = 0002\alpha'$.

Fig. 4 shows the dislocation networks at the interfaces of the α' plates in a massive colony imaged using an α' reflection. The presence of the β layers in the boundaries clearly complicates the observed dislocation contrast (e.g. the $(0002)_{\alpha'}$ reflection is extremely close to a $\{110\}_\beta$ reflection) and as a result exact visibility criteria could not be established. The dislocations showed strongest contrast under the $(0002)_{\alpha'}$ reflection and either weaker or zero

contrast under $\{11\bar{2}0\}$ or $\{10\bar{1}0\}_{\alpha'}$. This suggests that the networks contain both $\frac{1}{3}\langle 11\bar{2}3 \rangle$ and $[0001]$ dislocations but in view of the complications noted above this result cannot be considered conclusive.

It is clearly of interest to establish whether or not the β layers are enriched in molybdenum. Electron microscope microprobe analysis (EMMA) offered a possible method of chemical analysis with a spatial resolution of the order of 10^3 Å. Unfortunately, the maximum thickness of the β layers is of the order of 10^2 Å so that a sample volume of foil containing a β layer consists predominantly of α' and as a result of this any difference in molybdenum contents between the α' and β was not detectable by this technique.

Negligible hardening was obtained on ageing both of the alloys at 550 and 650 °C. Electron microscopical observations of a specimen of the Ti-1 Mo-1 Si alloy in the overaged condition (50 h at 650 °C) showed that the β layers form discrete particles undergoing spheroidizing (Fig. 5). As a consequence of the break up of the sub-boundaries in the massive colonies, some merging of the α' plates occurs (Fig. 6). The structure also contained heterogeneously nucleated precipitate particles which had nucleated preferentially on the sub-boundaries (Fig. 6). The diffraction patterns from this precipitate were indexed as corresponding to Ti_5Si_3 . Silicide precipitates also nucleated on dislocations in the α' phase and exhibited the same orientation rela-

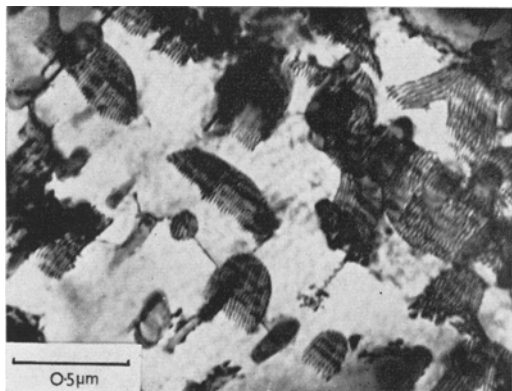


Figure 5 Ti-1 Mo-1 Si: aged for 50 h at 650 °C. The spheroidizing β -phase exhibits a striped contrast due to the presence of interfacial dislocations while the incoherent silicide precipitates appear as featureless ellipsoidal particles.

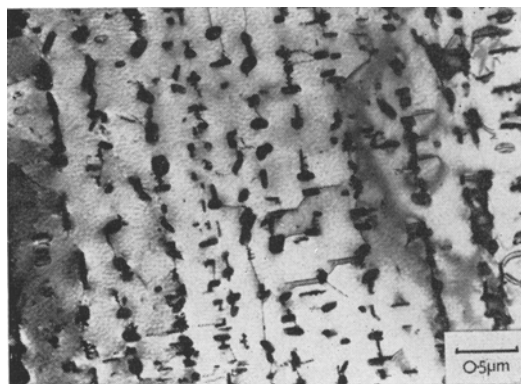


Figure 6 Ti-0.5 Mo-Si: aged for 50 h at 650 °C. A former massive colony has coalesced into a single α grain containing bands of spheroidized β and silicide precipitates nucleated at the positions of the original α' plate boundaries.

tionships to the matrix as that previously reported [1] namely:

$$\begin{aligned} (01\bar{1}0)_{\alpha'} // (01\bar{1}0) Ti_5Si_3 \\ (2\bar{1}\bar{1}0)_{\alpha'} // (2\bar{1}\bar{1}\bar{1}) Ti_5Si_3 \end{aligned}$$

The orientation relationship for the silicide particles nucleated at the sub-boundaries was not established but is different from the above.

4. Discussion

In binary titanium-silicon alloys a transition in morphology occurs from the massive type martensite to plate type, with increasing solute content; the binary Ti-1 Si alloy shows a mixed structure containing both types of martensite morphology [2]. The structure of both of the Ti-Mo-Si alloys is also of the mixed type, and the greater proportion of plate martensite in the 1% Mo alloy is consistent with the greater solute content.

The trace analysis indicates that the habit plane in these alloys is close to $\{334\}_{\beta}$ which is consistent with the fact that $\{334\}_{\beta}$ is the commonly observed habit plane in titanium alloys of low solute content. Williams *et al* [4] have previously observed $\frac{1}{3}\langle 11\bar{2}3 \rangle$ dislocations in the massive martensite boundaries in Ti-Cu alloys: in the present alloys these dislocations have also been identified in conjunction with $[0001]$ dislocations and retained β -phase.

The fact that the β regions lying between several variants of α' (Fig. 3) have the same orientation implies that this β was retained from the parent grain, although it seems unlikely that

the presence of only 0.5 or 1 wt% Mo will lower the M_f below room temperature. The M_s temperature is probably above 800°C and it is reported that ~12 wt% Mo is required for complete retention of β in Ti-Mo alloys [5]. β layers, similar to those observed in the present work, can be retained in binary Ti-0.5 Mo and Ti-1 Mo alloys [6], implying some enrichment of β in molybdenum during quenching. It may be inferred that similar effects operate in the Ti-0.5 Mo-1 Si and Ti-1 Mo-1 Si alloys, involving segregation of molybdenum and of silicon into the β . The fact that retained β layers are not observed in quenched binary Ti-Si alloys does not rule out the possibility of some silicon segregation, but it indicates that silicon is less potent than molybdenum in bringing about β retention.

In the ternary alloys, assuming a diffusion distance of ~2000 Å (i.e. half the width of an α' plate in a massive colony) and an effective diffusion time of 0.1 to 1 sec an effective diffusion coefficient of $\sim 5 \times 10^{-9}$ to 10^{-10} cm² sec⁻¹ is required. Considering molybdenum diffusion rather than that of silicon, since molybdenum is the slower diffusing species, reported values for the diffusion coefficient at 800°C are $\sim 10^{-10}$ cm² sec⁻¹ in the β phase and $\sim 10^{-13}$ cm² sec⁻¹ in the α phase [7, 8]. If molybdenum segregation occurs in the β ahead of the advancing α' plates then substantial molybdenum enrichment of the β can occur during quenching by normal bulk diffusion. However, if diffusion in α' is rate-limiting, then significant enhancement of the diffusion rate is required. Bokshtein *et al* [9] in a study of micro-inhomogeneity in titanium alloys reported that in Ti-Ni alloys diffusion is enhanced by a factor of 10^3 to 10^4 during cooling and that this is associated with the occurrence of the crystallographic transformation. In the present case diffusion enhancement of this order in the α' -phase would be sufficient to permit molybdenum segregation.

It is of interest to note that Williams and Hickman [10] studying Ti 7.7 wt% Mo and 7.7 wt% Mo 0.14 wt% Si alloys did not observe β layers or retained β of any form, after water

quenching from the β -phase field: the M_s and M_f temperatures of these alloys would be expected to be lower than those of the present alloys due to the higher molybdenum content. This implies that a high M_s and enrichment of the β in molybdenum are required for β layer formation.

5. Conclusions

1. The addition of 0.5 and 1 wt% Mo to a Ti-1% Si alloy results in the retention of a thin discontinuous layer of β -phase between the α' crystals when the alloys are quenched from the β range; this β is enriched in molybdenum.
2. On ageing the Ti-1 Mo-1 Si alloy at 650°C, Ti₅Si₃ precipitation occurs together with spheroidization of the β -phase.

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