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The redistribution of alloying elements by rapid-heating solution treatment of an ($\alpha + \beta$) titanium alloy

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Thin-foil X-ray energy-dispersive chemical analysis of an ($\alpha + \beta$) titanium alloy has been used to establish the compositional profiles which develop between the α and β phases as a result of heating into the β field at a rate of 100 K sec^{-1}. The results show that α phase transforms to β via a diffusional mechanism as it is progressively enriched in β-stabilizing solutes. Complete diffusional transformation of α to β occurs 160 K above the β transus but the β phase remains chemically inhomogeneous. On subsequent quenching at a rate of 400 K sec^{-1}, β phase containing less than approximately 10 wt% Mo equivalent of β-stabilizing solutes transforms to martensite. The proposed transformation mechanisms are consistent with the results of resistivity measurements made during the heating and cooling cycles.

1. Introduction

Refinement of the microstructure of ($\alpha + \beta$) titanium alloys can be produced by the use of solution treatments involving rapid heating. The alloying elements originally partitioned between the α and β phases remain inhomogeneously distributed even after treatment entirely within the β phase field, and the degree of inhomogeneity and consequent microstructural refinement are a function of the rate of heating and cooling employed [1, 2]. In ($\alpha + \beta$) microstructures produced by isothermal heat treatment the phase fractions and compositions follow the equilibrium phase diagram, and within each phase the composition is uniform as shown schematically in Figs 1a and b (e.g. C_1^α and C_1^β at T_1, C_2^α and C_2^β at T_2 and C_0 at the β transus). When such a structure is heated rapidly the ($\alpha + \beta$) microstructure can also transform to β. However, there are two possible mechanisms by which the α phase can transform to β. It can undergo a diffusionless transformation to β of the same composition as the original α. Further heating and holding in the β phase field will result in solute redistribution and eventually produce a uniform β composition. Even with rapid heating and cooling some solute redistribution will occur near the original α/β, interface as shown schematically in Fig. 1c. In such a case the solute-lean β formed diffusionlessly from α, together with adjacent parent β phase depleted in β stabilizers ($C < C_M$), will retransform on quenching to produce α-martensite at room temperature as indicated in Fig. 1c. (If $\alpha \rightarrow \beta$ transformation is incomplete then part of the original α will remain unchanged by the heating and quenching, and martensite will be formed only in the zone where diffusion between β depleted in β stabilizers and parent β has occurred.) The sharp jump in solute content at T_3 is associated with the original α/β interface rather than with its current position.

Alternatively the ($\alpha + \beta$) $\rightarrow \beta$ transformation can occur diffusionally. In this case α only transforms to β when its composition has changed to that corresponding to the ($\alpha + \beta$)/β boundary for that temperature in the equilibrium phase diagram. Hence the microstructure contains β which grows at the expense of α, with the local position of the α/β interface corresponding in composition to C_3^β at T_3 and C_4^β when transformation to β is completed at T_4 (Fig. 1d). On subsequent quenching, solute-depleted β ($C < C_M$) will retransform to α martensitically, producing a microstructure consisting of either α and β separated by a layer of martensite of composition intermediate between that of α and β (T_3) or β and martensite (T_4). The relative widths of the α, β and martensite layers will be a function of heating rate and maximum temperature, since these parameters control the total diffusive flux which can occur: slower heating rates and higher temperatures will decrease the α and increase the width of the β and martensite regions.

Figs 1c and d illustrate that quite different microstructure/microchemical profiles will be established by the two alternative modes of transformation of α to β on rapid heating. Hence the experimental study of the microstructure and microchemistry of rapidly heated ($\alpha + \beta$) alloys can unequivocally establish the mechanism of transformation associated with any combination of heating rate and maximum temperature of heat treatment. Previous work by one of the authors [3] involving the measurement of physical property changes during rapid heating indicated the dominant role of diffusion during heating at rates of 10 to 10^3 K sec^{-1}. It was the purpose of the present work to

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directly relate the microstructure and microchemistry of these rapidly heated samples of an alloy corresponding in composition to the Soviet alloy VT23 (Ti–5.3 wt % Al–2.3 wt % Mo–4 wt % V–1 wt % Fe–1 wt % Cr) to confirm this mechanism.

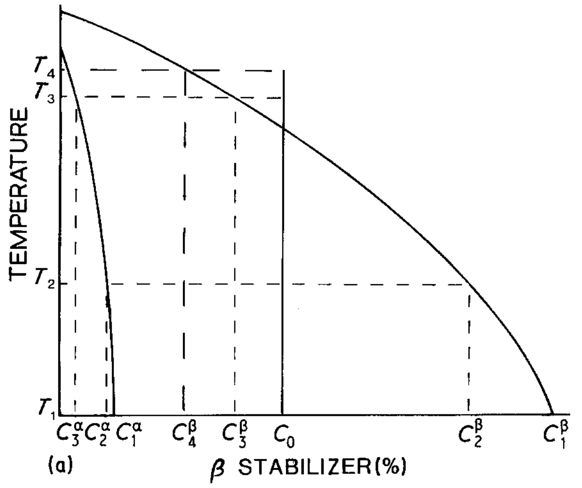
2. Experimental procedure

The material, in the form of 1.1 mm thick hot-rolled sheet, was annealed in high-purity argon in the β phase field followed by slow cooling with isothermal treatment at 1023 K (T_2) for 2 h to produce plates of α in a β matrix. Samples 1.1 mm × 10 mm × 70 mm were subsequently heat treated following two routes. One set was isothermally transformed for 0.5 h at a range of temperatures in the ($\alpha + \beta$) and β phase fields. The second set was rapidly heated at a rate of $10^2\,\mathrm{K\,sec^{-1}}$ in the same temperature range as that used for the isothermal treatments. All the samples were then quenched at a rate of approximately $4 \times 10^2\,\mathrm{K\,sec^{-1}}$ in order to suppress diffusional changes during cooling. Resistivity measurements were taken during both sets of heat treatment during the heating and cooling cycles. Thin foils were prepared by electropolishing and were examined in a JEOL 120 CX TEMSCAN transmission electron microscope equipped with a LINK 290 X-ray energy-dispersive analytical system. Chemical composition was determined using the Cliff–Lorimer method [4] incorporating correction for absorption of X-rays within the sample. The latter was necessary since, in order to obtain adequate X-ray counting statistics for the minor elements, relatively thick regions of the foils (~200 to 300 nm) were analysed. In such cases beam spreading in the sample limited the spatial resolution to 50 to 100 nm, which was adequate to establish the compositional profiles.

3. Results and discussion

Fig. 2 shows a typical example of the change in electrical resistance during rapid heating and cooling. The M_s temperature can be determined from the sharp change in resistance which occurs when β decomposes martensitically on cooling. In this way M_s was determined as a function of heat-treatment temperature for both isothermally and rapidly heated samples. The results are shown in Fig. 3. The constancy of M_s in samples isothermally treated above 1163 K indicates that this represents the β transus. At a heating rate of $10^2\,\mathrm{K\,sec^{-1}}$, M_s varied with temperature, rising to a maximum and then declining to the same value as that for isothermally treated samples heated above 1163 K above a temperature of 1323 K. This implies that β depleted below C_0 is obtained: homogeneous β is only obtained above a temperature of 1500 K. The temperature of 1323 K which corresponds to the highest M_s is the β transus for a heating rate of $10^2\,\mathrm{K\,sec^{-1}}$.

Typical microstructures associated with samples heated at $10^2\,\mathrm{K\,sec^{-1}}$ to 1213, 1243 and 1323 K, respectively, are shown in Fig. 4. Heating to 1213 K produces little obvious change in the initial ($\alpha + \beta$) structure. Plates of α in β are still observed, but an



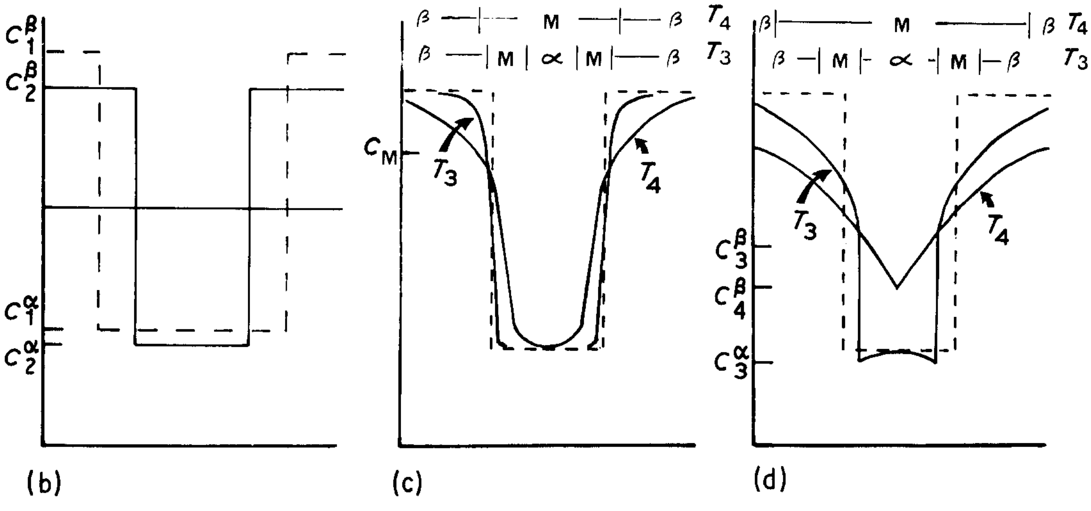


Figure 1 (a) Schematic vertical section through phase diagram for titanium aluminium alloy containing a β-stabilizing solute. (b) Equilibrium compositions across α and β phases at temperatures T_1, T_2 and above the β transus for an alloy of composition C_0 shown in Fig. 1a. (c) Microstructures and composition profiles at temperatures T_3 and T_4 above the β transus for an ($\alpha + \beta$) structure initially equilibrated at T_2 which undergoes diffusionless transformation of α to β on heating. Some interdiffusion between transformed α and initial β regions is assumed to have taken place. On quenching, β of solute content less than C_M transforms to martensite (M). (d) Microstructures and composition profiles at temperatures T_3 and T_4 for an ($\alpha + \beta$) structure initially equilibrated at T_2 which undergoes diffusional transformation of α to β. The α/β interface marks the composition limit for β stability (C_3^β and C_4^β Fig. 1a). On quenching, β of composition below C_M transforms to martensite (M).

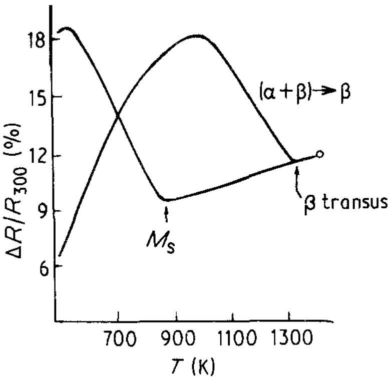


Figure 2 Electrical resistance change during rapid heating and cooling of VT23 alloy.

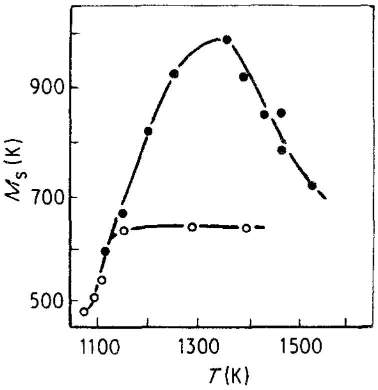


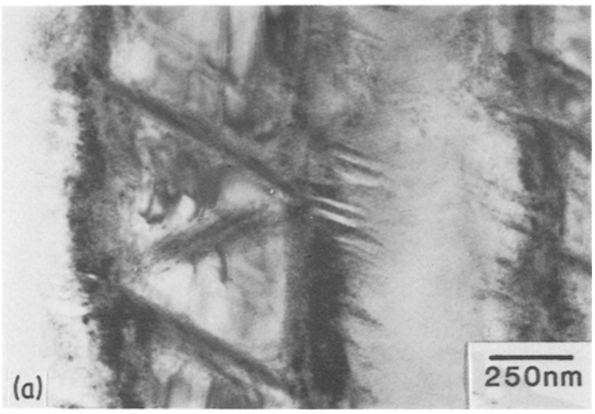
Figure 3 Effect of heat treatment temperature on the M_s under conditions of (○) isothermal treatment (●) rapid-heating treatment.

additional thin rim of martensite is seen at the α/β interfaces. At 1243 K the martensitic zone is much broader and exhibits a variable morphology, ranging from lenticular plates at the edge of the β phase through to colony or "massive" martensite at the α interface. Samples heated to 1323 K exhibit no α at all, and regions of β are separated by broad bands of martensite.

Compositional profiles were obtained for all elements present across the different zones of structure. Care was taken to ensure that the chosen plates were members of a colony of parallel plates and that they were not intersected by other plate colonies, so that the diffusional flux should be orthogonal to the plate boundaries. Since the thin foils had to be tilted to 40° inclination for analysis, the selected colonies had to be rotated in the specimen holder so that the tilt axis was orthogonal to the major axis of the sectioned plates; the analysed volume was then at a constant distance from the plate interface throughout the foil thickness. The results are presented in Figs 5, 6 and 7. Individual analysis results are shown in Fig. 5 and the best-fit profiles through the data points for aluminium, vanadium and molybdenum are shown in Fig. 6; Fig. 7 shows the β-stabilizer content expressed as a molybdenum equivalent. The molybdenum equivalent was calculated using the equation due to Zwicker [5] for determining the critical solute content for martensite formation:

$$\text{Mo equivalent} = \%\,\text{Mo} + 11.5 \times \left(\frac{\%\,\text{V}}{15} + \frac{\%\,\text{Cr}}{6.5} + \frac{\%\,\text{Fe}}{6}\right)$$

For clarity error bars are not shown: typically the error in the measured elemental concentration varies from 50% of the measured values at concentrations of less than 1 wt % to 8% of the measured value at the highest aluminium level (this approximates to 0.5 wt % at all elemental concentrations). Since relatively thick foils were employed the spatial resolution of the analysis is typically 50 to 100 nm. Thus analyses taken within 50 nm of a microstructural interface (M/α or M/β) will inevitably be an average of the compositions of the microstructural constituents on either side of that interface, and will consequently underestimate the compositional gradient across the interface. In all cases the microstructure–microchemistry relationship



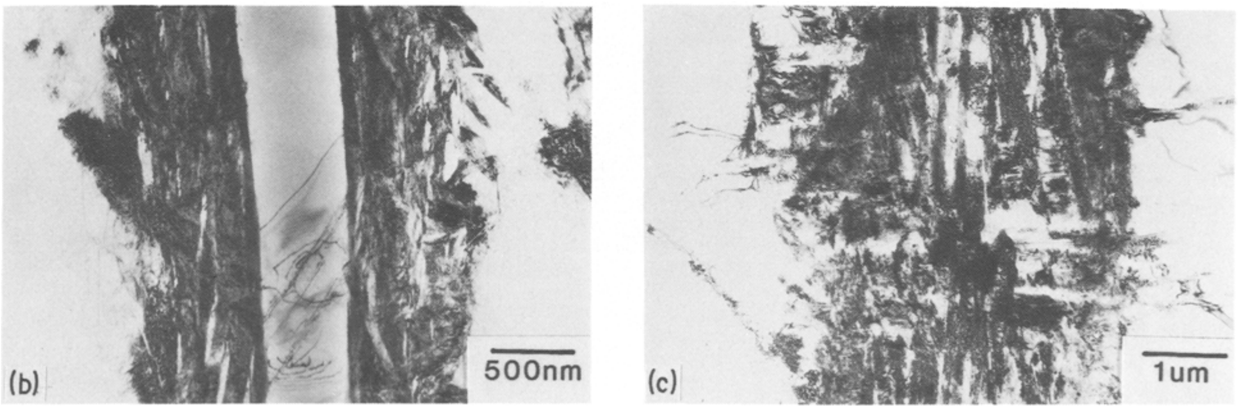


Figure 4 Typical microstructures of samples heated to (a) 1213, (b) 1243 and (c) 1323 K.

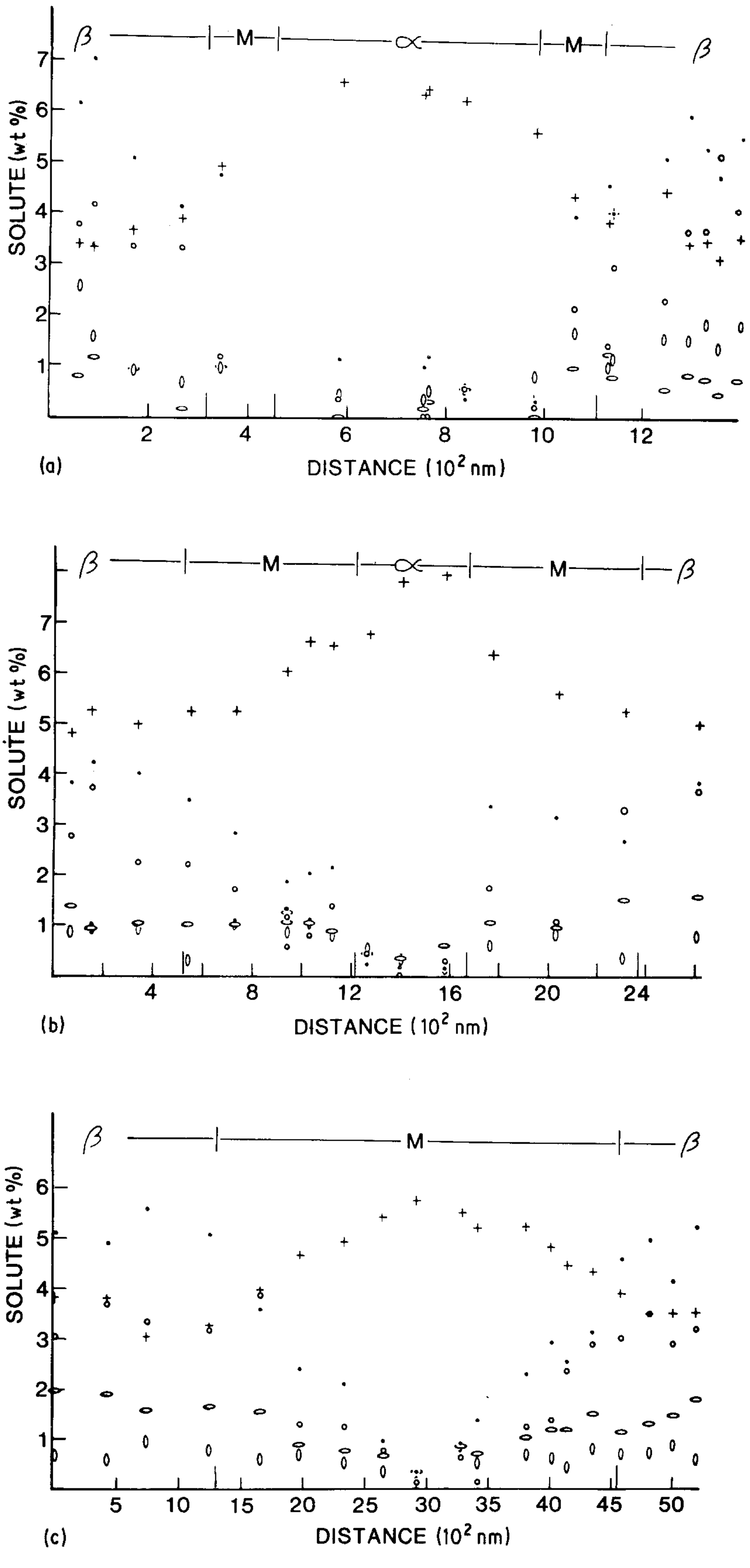


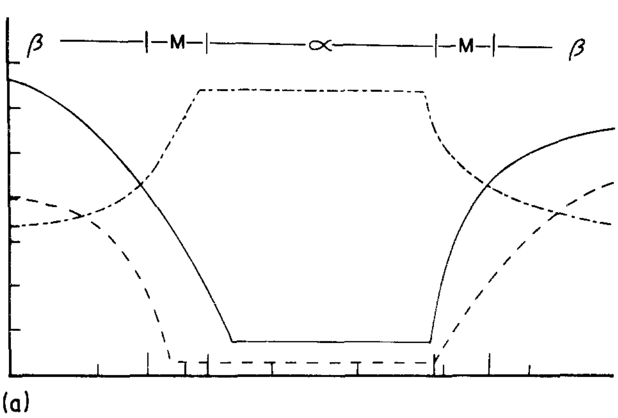
Figure 5 Individual analysis data on chemical composition profiles measured across prior α plates after rapid heating to (a) 1213, (b) 1243 and (c) 1323 K; (+) aluminium, (●) vanadium, (○) molybdenum, (⬭) iron, (0) chromium.

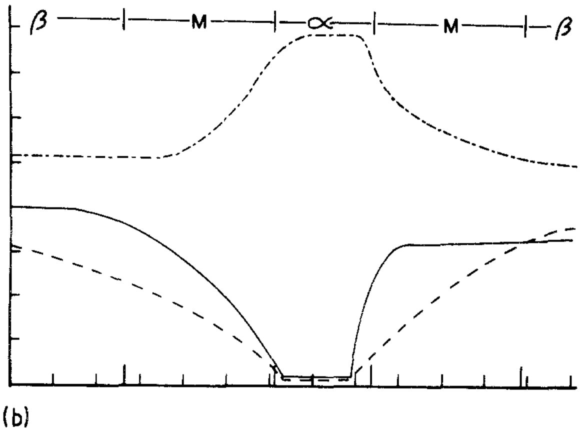
TABLE I Alloy composition at the β/martensite interface (wt %)

Temperature (K)	Element					
	Al	V	Mo	Cr	Fe	Mo equivalent
1213	4.4	4.3	2.0	1.1	0.9	8.97
1243	5.3	3.5	2.8	0.9	1.3	9.56
1323	3.8	4.6	3.3	0.8	1.5	11.13

TABLE II Composition of α at the α/martensite interface (wt %)

Temperature (K)	Element					
	Al	V	Mo	Cr	Fe	Mo equivalent
1213	6.5	1.1	0.15	0.2	0.07	1.41
1243	7.4	0.19	0.4	0.55	0.37	2.01





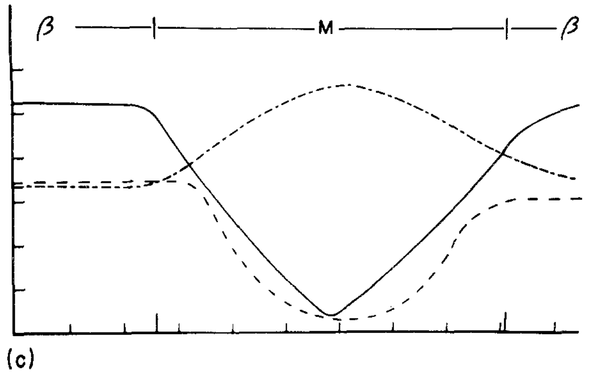


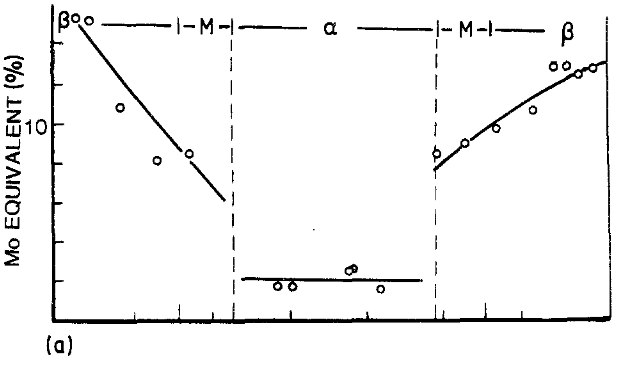
Figure 6 Best-fit relationships to the data of Fig. 5 for (a) 1213, (b) 1243 and (c) 1323 K; (–·–) aluminium, (–––) molybdenum, (—) vanadium.

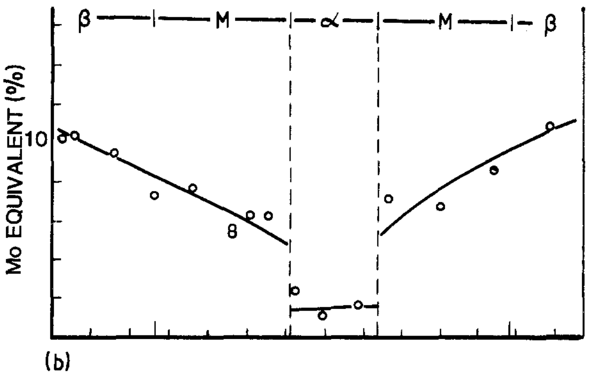
is consistent with a diffusional mode of α transformation to β upon heating, with an increasing fraction of the original α forming β at increasing heat-treatment temperature as it becomes diffusionally enriched in the β stabilizing elements vanadium, molybdenum, iron and chromium and correspondingly depleted in the α-stabilizer aluminium. On subsequent cooling some of this material is converted to martensite. It is evident that the regions of differing martensite morphology noted in the sample heated to 1243 K (Fig. 4b) correspond to different concentrations of the β-stabilizing elements. β-lean regions form the colony martensite while the most solute-rich regions form the lenticular plates. This parallels the morphological changes observed in binary alloys with increasing β-stabilizer content [6].

Average compositions at the β/martensite interface are given in Table I. In view of the large uncertainty in the measured values of the concentrations of iron and chromium no reliance can be placed upon the absolute values obtained: they are consistent with a molybdenum content of 11.5 wt % required to inhibit martensite formation at room temperature in a binary Ti–Mo alloy, and represent the composition C_M in Fig. 1.

The composition of α at the α/martensite interface should represent the composition of the α (C_3^α) at the temperature (T_3) to which the sample was heated. Averaged results are presented in Table II. The values are consistent with the schematic phase diagram shown in Fig. 1a. The β-stabilizer content on the opposite side of this interface is much higher (Fig. 6). In view of the large errors involved in the measurements it is not possible to demonstrate a decreasing concentration of β-stabilizing elements in α with increasing temperature of treatment, but the expected decrease is observed in martensite at the α/martensite interface (Fig. 7).

At a heating rate of 10^2 K sec^{-1} ($\alpha + \beta$) microstructures revert to β by a purely diffusional process. The





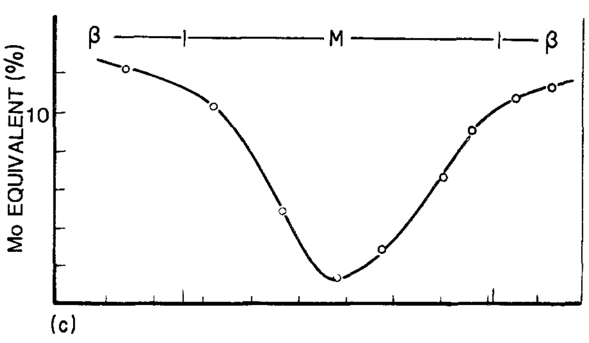


Figure 7 β-Stabilizer concentration expressed as a molybdenum equivalent [5]; (a) 1213, (b) 1243, (c) 1323 K.

material can be substantially overheated into the β phase field before complete conversion of α to β occurs, and this retransforms to fine martensite on quenching to room temperature producing a greatly refined ($\alpha' + \beta$) microstructure. Such structural refinement may be of benefit in increasing the strength and toughness of ($\alpha + \beta$) alloys and is directly relevant to the study of welding and laser heat-treatment of titanium alloys (e.g. [7]) where the heat-affected zone can experience similar heating rates and temperatures to those examined here.

4. Conclusions

($\alpha + \beta$) microstructures revert to β during heating into the β phase field at $10^2\,\mathrm{K\,sec^{-1}}$ by a purely diffusional process, and no diffusionless transformation of α to β is involved. The compositional changes which occur can be interpreted in relation to the phase diagram, and can explain the microstructural changes which result from rapid heating and quenching cycles.

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