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On the Decomposition of the Beta Phase in Titanium Alloys

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A systematic analysis is made of the possible free energy diagrams for a binary titanium alloy consisting of a metastable beta phase, which tends to form either the alpha or the omega phase, or both. The predictions based on each of the possible free energy diagram configurations are compared with the available experimental data. Arguments are developed to show that it should be possible to nucleate an omega phase having an initial solute content less than the metastable equilibrium value and not necessarily a higher solute concentration, as suggested by other investigators. It is further shown that the observed precipitation of a solute-lean beta phase in certain binary and ternary beta alloys cannot be explained in terms of an ordinary miscibility gap resulting from a preference for bonds between like atoms rather than bonds between unlike atoms. An explanation is suggested on the basis of an early model proposed by M. K. McQuillan in which the electronic structure of the titanium atom can change with temperature leading to two possible types of bonding behaviour.

1. Introduction

Several investigations dealing with the formation of the alpha and the omega phase from the metastable beta phase in titanium and zirconium base alloys have made reference to free energy diagrams or equilibrium phase diagrams [1-4], but the diagrams have been used mainly to rationalise the results obtained, rather than to predict further possible properties of the systems. In this paper a systematic analysis is made of the free energy diagrams for a binary titanium alloy consisting of a metastable beta phase that tends to form either the alpha or the omega phase or both. The predictions based on each of the possible free energy diagram configurations are compared with the available experimental data.

2. Hypothetical Free Energy Composition Relationships

Experimental observations relevant to the decomposition of the beta phase make it possible to limit the number of free energy curve configurations that must be considered in a thermodynamic analysis of the metastable constitution of alloys based on Ti and Zr. The most important observation is that the omega phase forms spontaneously on quenching in low-solute alloys, and that ageing is necessary to produce omega if the solute content is increased [2, 3, 5]. Furthermore it is found that there exists a maximum solute content above which omega has not been found under any circumstances [3, 4]. These facts taken together prove that the minimum in the free energy curve for the omega phase must be on the solute-lean side of a minimum in the free energy curve for the beta phase. It is also observed that the omega phase is a metastable phase and that an aggregate of the omega and the beta phase has a tendency to transform, as a result of ageing, to form a mixture of the alpha and the beta phases [3, 6]. This fact indicates that the common tangent to the alpha and the beta phase curves has a lower position than the common tangent to the omega and the beta phase curves, as shown in fig. 1a.

When making use of these restrictions in constructing the free energy diagram only two variables are left, namely, the shape of the beta

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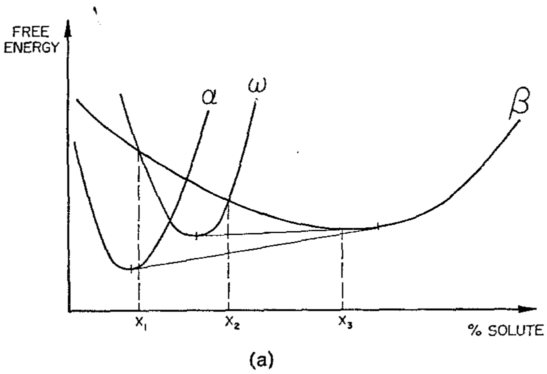
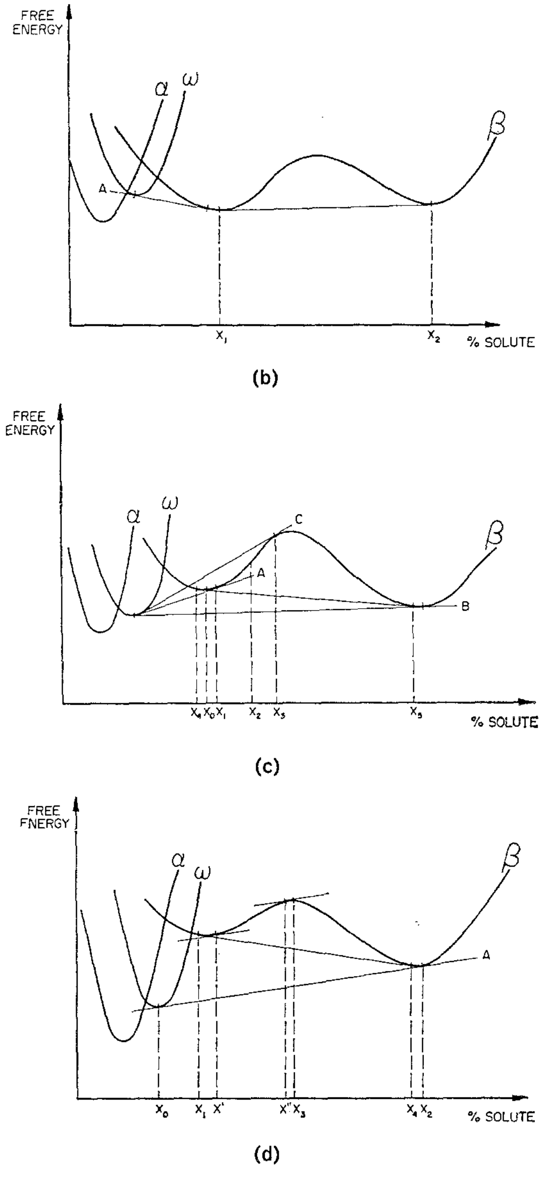
phase free energy curve and the relative position and shape of the omega phase free energy curve with respect to that of the beta phase. Since the beta phase may exist over a wide range of composition its free energy curve can have either a single minimum or two minima, the latter alternative being typical for a system exhibiting a misciblity gap. The first alternative with a single minimum in the beta curve is shown in fig. 1a. In this case the relative position of the omega curve is immaterial as long as its minimum is on the titanium-rich side of the beta curve minimum. It is immediately seen that this free energy diagram rationalises some common features of the omega phase occurrence. There is a certain region $x_1 < x < x_2$ within which it would be possible to form the omega phase on quenching, without any change in the composition of the beta phase. Furthermore, there is an upper limit, x_3, to the solute content of the beta phase beyond which the omega phase cannot form under any conditions. However, the free energy diagram does not make any provision for a phase separation reaction in the beta phase prior to the formation of the omega, as suggested by several investigators [5, 7].

The occurrence of a phase separation in the beta phase means that the free energy curve must have two minima. The omega curve can then be positioned in three different ways with respect to the beta free energy curve as shown in figs. 1b, c and d. For the configuration shown in fig. 1b the common tangent *A* to the omega and beta curves touches on the titanium-rich side of the beta curve minimum. This means that a phase separation in the beta phase can occur only in a composition range $x_1 < x < x_2$ over which the omega phase cannot form so that the situation governing the formation of the omega phase is identical in figs. 1a and b.



(a)



(b)

(c)

(d)

Figure 1 (a, b, c, d) Hypothetical free energy-composition curves for titanium binary alloys.

In fig. 1c one common tangent *A* to the omega and the beta phase curves meets the beta curve at a point x_1 between the titanium-rich minimum x_0 and the adjacent inflection point x_2. A second common tangent *B* can be drawn between the omega curve and the titanium-lean minimum of the beta curve, but this tangent indicates an unlikely decomposition situation since the driving force for omega nucleation is nonexistent in a certain composition range, $x_1 < x < x_3$, where x_3 is defined by the common tangent *C*. All compositions between the two common tangent points x_4 and x_5 on the beta curve have a tendency to decompose into two beta phases. In the composition range $x_4 < x < x_1$ the special situation arises where it is thermodynamically possible to have two reactions going on simultaneously, one in which omega precipitates and another in which a titanium-lean beta phase precipitates. The dominant reaction is determined by the relative rates of nucleation and growth. If the solute content is slightly higher than x_1 it is theoretically possible for the precipitation of a solute-rich beta phase to proceed for a long enough time to reduce the matrix composition below x_1, following which the omega phase can nucleate in the solute-depleted matrix.

The third situation in which the beta phase curve has two minima is shown in fig. 1d, where the common tangent A to the omega and the beta curves meets the beta curve at the point x_2, which is close to the titanium-lean minimum. No other common tangent is possible between the beta and the omega curves. If the solute content of the beta phase is between x_0 and x_2, the omega phase can form and if the solute content is in the range $x_1 < x < x_4$ where x_1 and x_4 are the points of common tangency on the beta curve, there is the possibility of the precipitation of a second beta phase. This beta phase will be titanium-lean, if $x_1 < x < x_3$ and titanium-rich, if $x_3 < x < x_4$ where x_3 is the maximum between x_1 and x_4.

3. Discussion

The four free energy situations presented in fig. 1 reflect the fact that the omega phase has an equilibrium solute content lower than the solute content corresponding to a minimum in the beta phase free energy curve. They also show that a maximum solute content exists for the beta phase, above which the omega phase should not form under any conditions. Furthermore the omega phase is shown as metastable with respect to the alpha phase.

The three situations illustrated in figs. 1a, b and c all predict that a nucleus of the omega phase should have a lower solute content than the equilibrium value if the classical tangent construction for the maximum driving force is used [8]. In situation 1d the nucleus of the omega phase can have a solute content higher than the equilibrium value only over the narrow composition range $x' < x < x''$. The tangents to the beta curve at compositions x' and x'' are parallel to the common tangent A to the omega and the beta curves. For other compositions in case 1d the appropriate geometric construction [8] shows that the nucleus is lower in solute content than the equilibrium value.

It is tempting to use here the results reported by Hickman [9] that the omega phase in Ti-V alloys forms with a solute content considerably higher than the equilibrium value because this information would rule out the first three free energy curves 1a, 1b and 1c, at least with respect to the Ti-V system. Unfortunately, a close examination reveals that the method employed by Hickman to determine the solute content of the omega phase can involve errors large enough to cast doubt on any conclusions that are drawn from the calculations. From the equations

$$x_\omega = \frac{x_a}{V} - \frac{1-V}{V} x_\beta \qquad (1)$$

where x_ω is the solute content of the omega phase, x_β is the solute content of the beta phase, x_a the average solute content of the alloy, and V the volume fraction of the omega phase, it is seen that the error in the omega phase solute content, due to an error in x_β alone, ranges from three times the absolute error in x_β when the volume fraction V is 0.25 to one third of the absolute error in x_β when the volume fraction V is 0.75. If the error in x_β has a systematic part Δx_β that is negative, then equation 1 shows that Δx_ω is positive so that x_ω will be larger than its true value.

Two systematic errors must be considered with respect to the analysis made by Hickman. When the omega phase forms by a nucleation and growth process, and has a solute content that is lower than that of the matrix, it is necessary for an omega phase particle to be surrounded by a layer that has a higher solute content than the rest of the matrix. According to the data given by Hickman [9], if local interfacial equilibrium exists during the ageing of a 19% vanadium alloy at 350°C, then the solute content of the beta matrix at the interface should reach a value of about 40% vanadium. Even if the enriched regions represent a significant volume fraction of the matrix they will probably give rise to a diffuse X-ray diffraction intensity because of their relatively small dimensions; this diffuse scattering occurs in addition to the more clearly defined diffraction lines from the rest of the matrix. It is therefore evident that the intensity distribution of the X-ray reflections from the beta phase prohibits the calculation of a representative average for the matrix solute content. The calculation would result in a value for the solute concentration of the beta phase that is too low; thus in this case the systematic error ΔX_β is negative.

A second systematic error arises in the calculation by Hickman of the effect on the lattice parameters of the elastic interaction between the omega phase and the matrix. For the purposes of these calculations Hickman evaluated the specific volume of the omega phase, but it is difficult to see how this quantity can be determined for a given vanadium content in the omega phase since omega particles never have been isolated in a strain free condition. Although it has not been specified in the paper by Hickman, it appears that the specific volume of the omega phase was calculated from the measured lattice parameters; however, these parameters must be influenced by the elastic strain present in the matrix and consequently they do not give the true specific volume of the omega phase. A calculation of the correction in the lattice parameter of the beta phase that neglects the elastic contraction of the omega phase results in a value for the solute content of the beta phase that is too low, and a corresponding omega phase solute content that is too high. It is important to realise that it is virtually impossible to determine whether a change in the lattice parameters of the omega phase is due to a change in composition, or to a change in the strain conditions in and around the omega particles. A numerical example can be taken from the data given by Hickman for the Ti-25V alloy for 1 h at 250°C. Hickman reported 30 vol % omega phase with a solute content of 23 % vanadium, from which it follows that the beta phase has a solute content of 26 %.

The following equation was used by Hickman for calculating the fractional correction $\Delta a/a$ of the beta phase lattice parameter

$$\frac{\Delta a}{a} = \frac{2}{3}\,\frac{1-2\mu}{1-\mu}\cdot\frac{v_\beta - v_\omega}{3v_\beta}\cdot V \qquad (2)$$

where μ = Poisson's ratio, v_β = specific volume of β-phase, and v_ω = specific volume of ω-phase.

Equation 2 yields a value of $\Delta a/a$ equal to $-\,0.0013$ for a Poisson's ratio equal to $\frac{1}{3}$. If the solute content of the omega phase is assumed to be identical to the equilibrium value of 14 %, the solute content of the beta phase must be 30 % in which case the fractional correction $\Delta a/a$ amounts to $-\,0.0019$. The difference of 0.0006 between the two corrections for the lattice parameter of the beta phase changes the solute content of the beta phase by about 1 % [10]. According to equation 1 the solute content of the omega phase changes by 3 % when, as in this case, the volume fraction of omega phase is 30 %. The resulting change from 23 to 20 % for the omega solute content is only one third of the reduction needed to reach the equilibrium value of 14 % that was used in the calculation. This calculation must be considered as indicating a lower limit of the effect of strain on the evaluation of the omega phase solute content since the experimental lattice parameters for the omega phase containing 14 % solute have been used. It can be argued that some elastic contraction is also present at this solute content, in which case the effect would be even larger than the above estimate. This second systematic error Δx_β is again negative so that the two errors add up and the error Δx_ω in the omega phase solute content is positive.

If the simultaneous contributions of the two systematic errors are considered, then it is questionable whether ageing will lead to a change in the solute content of the omega phase in the manner described by Hickman.

Experimental evidence for the simultaneous precipitation of a solute-rich beta phase together with the omega phase has not been reported; however, such a situation is suggested for compositions between x_4 and x_1 of the free energy diagram in fig. 1c. A re-examination of the X-ray data given by Hickman in his investigation of the ageing behaviour of Ti-V alloys [9] leads to the conclusion that such a simultaneous precipitation can occur.

Hickman reports that at low ageing temperatures (200 to 250°C) the intensity of the omega phase reflections increased with ageing time, while the intensity of the sharp beta-phase reflections decreased and broad diffuse reflections were observed at higher and lower angles Hickman attributes the low-angle broad reflections to the omega phase, and the high-angle reflections to the beta phase enriched in vanadum From the way in which the composition of the omega phase is determined it appears that Hickman has assumed that the enrichment in vanadium of certain regions is due to the rejection of vanadium when the matrix transforms to the omega phase. The localised rejection of solute to the beta phase should lead to a decreasing solute concentration with increasing distance from the omega/beta interface; thus only a broadening of the X-ray reflections, and not a splitting of the peaks, should occur. Instead it is probable that the splitting observed by Hickman is an indication of the precipitation of a solute-rich beta phase occurring simultaneously with the precipitation of the omega phase.

Hickman has employed the Warren-Averbach technique to analyse the broadening of beta phase reflections in a titanium-25% vanadium alloy aged for 300 h at 350°C. The results indicate that the matrix consists of coherently reflecting domains with a size of about 40 Å. Hickman suggests that the matrix has been broken up into misoriented domains between the omega particles, since 40 Å is of the same order as the interparticle spacing in the alloy. The results are also consistent with the presence of domains identical to the solute-rich beta particles previously discussed.

It has been suggested [5, 7] that the precipitation of a titanium-rich region precedes the formation of the omega phase. If titanium-rich regions form at the ageing temperature then the omega phase could form in these regions on quenching to a lower temperature, but the available experimental evidence [3] does not support this model. Alternatively, after sufficient time at the ageing temperature, the titanium-rich regions could act as nucleation and growth sites for the omega phase. This mechanism has not been observed experimentally for the formation of the omega phase, but has been reported recently with respect to the formation of the alpha phase [11], for which the same thermodynamic arguments hold. Other workers [12] have not been able to relate the beta phase precipitates in the Ti-V-Cr system directly to the formation of the alpha phase and have concluded that the precipitates are titanium-lean. On the other hand the precipitation of beta particles tentatively identified as titanium-rich has been found in a binary Ti-Cr alloy [13].

The existence of a miscibility gap in a binary system means that bonds like atoms are preferred to bonds between unlike atoms, which usually implies that the free energy curve representing a miscibility gap is fairly symmetric around the 50% composition line. If the titanium-rich minimum of the free energy curve is somewhere in the range 10 to 20 at. % solute it would be expected that the titanium-lean minimum is at least beyond 50 at. % solute. A phase separation process leading to titanium-rich beta phase precipitates has been observed in a binary alloy containing 15% Cr [13] and in ternary alloys containing 20% V as the beta stabilising agent in one case and 6 to 10% Mo in the other [11]. These results provide a strong indication that both the minima in the free energy curve are well below 50 at. % solute. This conclusion is based on the fact that the alloy composition must be between the maximum x_3 and the solute-rich x_4 in the free energy curve in fig. 1d for solute-lean precipitates to occur.

The theory proposed by M. K. McQuillan [14] involving a change in the electronic structure of the titanium atom with temperature provides a basis for explaining the shift of the minima of the free energy curve towards the titanium-rich compositions. Such a shift is a consequence of the tendency for titanium atoms to favour nearest neighbours having the same electronic configuration. The anomalous resistivity behaviour reported for titanium-chromium alloys [15] is consistent with such a change in electronic structure. This would imply that a binary titanium alloy in effect is a three-component system consisting of two variants of the titanium atoms and a solute. The description of this complex behaviour requires that consideration be given to the combination of the free energy situation shown in fig. 1d with any one of figs. 1a, b or c. This would mean that even in binary titanium systems where there is no tendency to form an ordinary miscibility gap, e.g. in the Ti-Fe system, the formation of a titanium-rich phase or cluster could influence the formation of the omega and the alpha phase.

4. Conclusions

(1) It has been shown that only four different free energy situations must be considered to describe the precipitation of the omega phase from the metastable beta phase in titanium-base alloys.

(2) From a consideration of the available experimental data it has been shown that the simultaneous precipitation of a solute-rich beta phase and the omega phase can occur in titanium-vanadium alloys.

(3) Arguments have been developed to show that it should be possible to nucleate the omega phase with a solute content that is less than the metastable equilibrium value.

(4) Systematic errors are shown to exist in the determination of the omega phase solute content

such that this solute content need not change in the manner proposed by Hickman.

(5) On the basis of thermodynamic arguments it has been shown that the precipitation of a solute-lean beta phase in certain binary and ternary alloys cannot be explained by an ordinary miscibility gap. An explanation has been suggested on the basis of a model originally proposed by M. K. McQuillan, wherein two different kinds of titanium atoms exist with different electronic structures.

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