Effects of ternary additions on the properties of gamma TiAl alloys: site preference, phase stabilisation and mechanical behaviour

R. YANG, Y. L. HAO and D. LI

Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, China

ABSTRACT
Recent experimental and theoretical results concerning the site substitution behaviour of ternary additions in \( \gamma \)-TiAl and \( \alpha_2 \)-Ti\(_3\)Al, and its relation to \((\gamma+\alpha_2)\) two-phase equilibrium and mechanical properties of the ternary alloys are summarised. The sublattice site occupancies of V, Cr, Mn, Fe, Ni, Zr, Nb, Ta, Mo, Ga and Sn in the two phases were measured using the atom location channeling enhanced microanalysis (ALCHEMI) method, and successfully interpreted using the Bragg-Williams model and bond order data obtained from electronic structure calculations. A model that relates the \((\gamma+\alpha_2)\) two-phase equilibrium to the site occupancies of alloying elements in the two phases is suggested, allowing quantitative description of the phase boundaries, prediction of phase stabilisation effects of alloying elements, and calculation of mole fractions of the constituent phases. The predictions agree well with measurements. Room temperature compression tests were conducted on alloys based on Ti-26Al-(1-2)X, Ti-51Al-2X, and Ti-46Al-(1,3,5)X. It was concluded that no simple relationship exists between the compression properties of ternary two-phase gamma alloys and those of the constituent phases.

Key words: TiAl, Ti\(_3\)Al, site occupancy, phase fraction, alloying, equilibrium, compression, strength

1. INTRODUCTION

There has been intense activity directed at understanding the effects of alloying and microstructure on the properties of TiAl-based alloys in the last decade. The additions of V, Cr or Mn were reported to improve the ductility of two-phase TiAl alloys, as reviewed by Huang and Hall [1] and by Kim [2]. Theoretical considerations by Morinaga et al. [3] suggested that V, Cr and Mn effectively improve the ductility of the \( \gamma \) phase only when they substitute for Al, in agreement with experimental results [4-6]. More recent first principles studies [7, 8] showed that the site preference of alloying elements is a basic parameter in describing properties such as twin-boundary energy and dislocation mobility of the alloyed crystal. Experimentally measured site occupancies of alloying elements in TiAl are not entirely consistent ([4,5,9-11] for example). It is not clear to what extent alloy composition influences the site occupancies of ternary additions, so a systematic study is necessary.

The optimum volume fraction of the \( \alpha_2 \) phase, for balanced properties of a two-phase alloy, is about 0.05 to 0.15 [2]. Given the composition of a target alloy, it is often difficult to know \textit{a priori} the equilibrium volume fraction of the second phase, due to incomplete phase equilibrium data for ternary and more complex alloy systems. Ochiai \textit{et al.} [12] were the first to relate the site preference of alloying elements to phase diagrams. They used the direction of the solubility lobe of the intermetallic phases to classify the substitution behaviour of alloying additions in Ni-based compounds. Nandy \textit{et al.} [13] used this approach to predict the site preference of alloying additions in TiAl. Given the measured site occupancies of alloying elements in the individual phases, however, we can estimate the equilibrium between the two phases. Such an approach complements conventional phase equilibrium studies by virtue of its simplicity.

In this paper, we summarise our recent measurement and interpretation of site occupancies of alloying elements in both TiAl and Ti\(_3\)Al. A model that relates the phase fractions to the sublattice site occupancies of alloying elements is presented, its predictions compared with experiments. Simple mechanical tests were conducted on some of the alloys, and the implication of the results will be discussed.

\footnote{Fax: 86 24 2389 1320; e-mail: ryang@pub.sy.ln.cn or ryang@imr.ac.cn.}
2. EXPERIMENTAL

Alloys used in this work are all ~50g buttons prepared in an arc furnace with magnetic agitation under argon protection. Wet chemical analysis shows that typical departure from nominal composition for Al is <0.2 at.%. Heat treatment was done using ingots sealed in quartz tubes filled with argon. The TiAl alloys used for site occupancy measurements were homogenised at 1173K for 240h and then quenched in ice water. The Ti$_2$Al alloys were homogenised at 1423K for 0.5h in the single β phase field, and then equilibrated at 973K for 200h followed by air cooling to room temperature. Dual-phase alloys used for measuring volume fractions were homogenised at 1473K for 1h, and annealed at 1173K for 240h.

Disc specimens for electron microscopy were prepared by twin jet electropolishing in the conventional way. The specimens were examined in a Philips EM420 microscope equipped with an EDAX 9100 analyser. The ALCHEMI method was used to measure the site occupancies of ternary elements in the host compounds. Channelling experiments were conducted using the planar method [14]. An accelerating voltage of 100kV was used in order to minimise the delocalisation effects [11, 15]. Other experimental details and procedures of error analysis have been described elsewhere [16, 17].

Volume fractions of the constituent phases were measured by optical and electron microscopy. Compression tests were conducted at room temperature using cylinders 3mm in diameter and 5mm in length spark-machined from the heat-treated ingots. The samples were compressed at a strain rate of 5x10$^3$ s$^{-1}$.

3. RESULTS AND DISCUSSION

3.1. SITE OCCUPANCIES OF ALLOYING ELEMENTS

3.1.1. Composition dependence of site occupancies in TiAl

A tiny amount of precipitates such as β, Ti(Cr,Al)$_2$ and FeTiAl$_2$ are present in some of the alloys, and many alloys also contain some α$_2$ phase [16]. Fig. 1 presents the results of Ti site occupancy on the TiAl lattice of ternary additions obtained in this work. Clearly, the site occupancies of Fe and Nb do not change much with alloy composition, but the occupancies of V, Cr and Mn change considerably with alloy composition. The tendency to occupy the Ti site increases in the order of Mn, Cr and V. Since the experimental error of this analysis, estimated at about ±10% [17], is much less than the fluctuation in site occupancies for alloys containing Mn, Cr or V, the composition dependence of site occupancies in these alloy systems is judged to be genuine, which we believe partially accounts for the discrepancies among reported measurements.

![Fig. 1 Experimentally measured fractions of Ti sites occupied by ternary atoms X (X= Nb, V, Cr, Mn or Fe ) for TiAl alloys with a range of compositions. Alloys No. 1 through 7 correspond to compositions of Ti-46Al-1X, Ti-46Al-3X, Ti-46Al-5X, Ti-50Al-2X, Ti-51Al-2X, Ti-51Al-5X and Ti-53Al-5X.](image1.png)

![Fig. 2 The fractions of Ti sites occupied by ternary atoms in TiAl alloys with the compositions of Ti-51Al-2X (X= Ta, Zr, Nb, Mo, V, Cr, Mn, Fe, Ni, Sn or Ga ).](image2.png)
3.1.2. Site occupancies in alloys with fixed Al contents

The Ti site occupancies of alloying elements in TiAl and Ti₃Al, shown in Figs. 2 and 3, respectively, were measured using alloys of Ti-51Al-2X and Ti-26Al-(1~2)X. The errors in Fig.3 are larger than those for the TiAl phase (Fig.2), because there does not exist a lattice plane consisting of alternate planes of pure Ti and pure Al atoms for the D₀₁₉ structure of Ti₃Al. Measurements using the axial channelling method show improved accuracy[17]. It is clear, however, that the investigated elements occupy exclusively either Ti or Al sites in Ti₃Al, different from those in TiAl. A general tendency can be seen from Figs.2 and 3 that, with increasing atomic number, elements in the same row of the periodic table increasingly prefer the Al sites; elements in the same group show increasing tendency to occupy the Ti sites.

3.1.3. Interpretation of measured site occupancies

Following Ochiai et al.[12], the site preference of X can be determined by the difference in bond energy (ΔH) between the two cases of X substituting for Ti and for Al. If [d(ΔH)/dCₓ]Cₓ=0 < 0, the ternary addition X will occupy Ti sites. An analysis has been made in [16] and the theoretical results are given in Fig.4. It can be seen that the predicted relative site preference of ternary additions in TiAl agrees with measurements (except for Mn).

3.2. ESTIMATION OF PHASE FRACTIONS USING SITE OCCUPANCIES

3.2.1. A model for phase fraction calculation based on site occupancies

The following relation has been derived [18] between the mole fraction of the α₂ phase (mₐ₂) and the site occupancies (pₐ₂ and pₓₐ₁) for alloy Ti-cAl-xX:

\[(b-a)(1-r)(m_{α₂})^2 + [(b-a)r - r p_{A_{1}} + x p_{A_{1}}^2 - (b-c)(1-r)]m_{α₂} - (b-c)r + r p_{A_{1}} = 0\]

where r is the interphase partition ratio of X between the γ and α₂ phase, and a and b are the Al contents at the boundaries of the (γ+α₂) two-phase field in binary Ti-Al.

3.2.2. Phase stabilisation effects of alloying elements

Some systematic measurements of the site occupancies of alloying additions in both the γ and α₂ phase are summarised in Table 1. Different alloys with x=0.02 (0.015 for Cr in the α₂) were used for the two phases in
Table 1. Summary of experimental data of site occupancies, partition ratio, and stabilising effects of alloying elements.

<table>
<thead>
<tr>
<th>Alloy (at.%)</th>
<th>( \rho_{\alpha} )</th>
<th>( \rho_{\gamma} )</th>
<th>( r ) [19]</th>
<th>Stabilising effect [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-26Al-2Nb</td>
<td>0</td>
<td>0</td>
<td>1.08</td>
<td>( \alpha_2 ) stabiliser</td>
</tr>
<tr>
<td>Ti-50Al-2Nb</td>
<td>0</td>
<td>0</td>
<td></td>
<td>Neutral or slight ( \gamma ) stabiliser</td>
</tr>
<tr>
<td>Ti-26Al-1.5Cr</td>
<td>0</td>
<td>0.52</td>
<td>0.88</td>
<td>( \alpha_2 ) stabiliser</td>
</tr>
<tr>
<td>Ti-50Al-2Cr</td>
<td>0</td>
<td>0.22</td>
<td></td>
<td>Strong ( \gamma ) stabiliser</td>
</tr>
<tr>
<td>(Ti$<em>{52}$Al$</em>{48}$)$<em>{0.99}$Ta$</em>{0.01}$ [19]</td>
<td>0.08</td>
<td>0.17</td>
<td>0.83</td>
<td>( \alpha_2 ) stabiliser</td>
</tr>
<tr>
<td>(Ti$<em>{52}$Al$</em>{48}$)$<em>{0.99}$W$</em>{0.01}$ [19]</td>
<td>0.17</td>
<td>0.61</td>
<td>0.72</td>
<td>( \alpha_2 ) stabiliser</td>
</tr>
<tr>
<td>(Ti$<em>{52}$Al$</em>{48}$)$<em>{0.99}$Mo$</em>{0.01}$ [19]</td>
<td>0.13</td>
<td>0.66</td>
<td>0.66</td>
<td>Moderate ( \gamma ) stabiliser</td>
</tr>
<tr>
<td>Ti-26Al-2Ga</td>
<td>0.94</td>
<td>1</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>Ti-50Al-2Ga</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 Predicted mole fractions of the \( \gamma \) phase in some two-phase Ti-Al-X alloys.

The equation given in 3.2.1 can be used to predict the mole fractions of the constituent phases in two-phase gamma alloys. To estimate the accuracy of such predictions, the volume fractions of the \( \alpha_2 \) phase in some ternary Ti-46Al-X alloys have been measured by means of optical and transmission electron microscopy [17]. The measurements are compared with predicted volume fractions of the \( \alpha_2 \) phase (converted from calculated mole fractions) in Table 2, the last column of which lists the difference between experimental and theoretical values. The difference is thought to be mainly due to experimental error. The measured volume fractions of the \( \alpha_2 \) phase represent underestimates, for the following two reasons: 1) Lamellar grains occasionally contain large volume fractions of the \( \alpha_2 \) phase, and these \( \alpha_2 \) particles have not been taken into account in measurement.
Table 2. Comparison between experimentally measured \( f_{a_2/lam} \) and predicted \( f_{a_2} \) volume percentage of the \( a_2 \) phase for some ternary Ti-46Al-X alloys. \( f_{a_2/lam} \) and \( f_{a_2/eq} \) denote the volume percentage of the \( a_2 \) phase in lamellar grains, the volume percentage of the equiaxed \( \gamma \) grains, and the volume percentage of faceted \( a_2 \) precipitates in \( \gamma \) grains, respectively.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Experimentally measured volume fractions</th>
<th>Predicted</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( f_{a_2/lam} ) (%)</td>
<td>( f_{a_2/eq} ) (%)</td>
<td>( f_{a_2} ) (%)</td>
</tr>
<tr>
<td>Ti-46Al</td>
<td>21.4</td>
<td>1.0</td>
<td>21.3</td>
</tr>
<tr>
<td>Ti-46Al-1Ta</td>
<td>20.8</td>
<td>3.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Ti-46Al-3Ta</td>
<td>20.2</td>
<td>6.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Ti-46Al-1Nb</td>
<td>20.1</td>
<td>1.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Ti-46Al-3Nb</td>
<td>21.5</td>
<td>9.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Ti-46Al-1V</td>
<td>20.5</td>
<td>3.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Ti-46Al-3V</td>
<td>20.8</td>
<td>4.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Ti-46Al-5V</td>
<td>21.1</td>
<td>8.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Ti-46Al-1Cr</td>
<td>17.8</td>
<td>10.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Ti-46Al-1Mn</td>
<td>16.1</td>
<td>18.6</td>
<td>6.2</td>
</tr>
<tr>
<td>Ti-46Al-3Mn</td>
<td>15.1</td>
<td>62.4</td>
<td>6.8</td>
</tr>
<tr>
<td>Ti-46Al-1Ga</td>
<td>14.5</td>
<td>42.6</td>
<td>4.9</td>
</tr>
</tbody>
</table>

2) Some \( a_2 \) plates in the lamellae are so thin that their thickness cannot be measured. This portion of the \( a_2 \) phase has therefore been ignored. The difference between measured and predicted volume fraction of the \( a_2 \) phase for binary Ti-46Al alloy, 5.6%, can be regarded as an estimate of the experimental error. If this factor is taken into consideration, the error of prediction for most alloys listed in Table 2 will be less than 3%.

3.3. COMPRESSION PROPERTIES OF DUAL-PHASE GAMMA ALLOYS AND THEIR CONSTITUENT PHASES

Room temperature compression tests were conducted on Ti-26Al-(1–2)X and Ti-51Al-2X alloys, to survey the effects of alloying on compression ratio and yield strength of the \( a_2 \) and \( \gamma \) phase, respectively. The results are presented in Figs. 6 and 7. The amplitudes of the "fracture strength" are apparent values and are listed only for completeness. Interestingly, it can be observed from Fig.6 that the two elements (Ga and Sn) which substitute for Al, decrease the compression ratio of the \( a_2 \) phase, while most elements (except V) which substitute for Ti improve the compression deformability of the \( a_2 \) phase. For the \( \gamma \) phase, Morinaga et al. [3] suggested that V, Cr and Mn effectively improve the ductility of the \( \gamma \) phase only when they substitute for Al. In our compression

Fig. 6 The room temperature compression results for Ti-26Al-(1–2)X alloys: (a) compression ratio, and (b) 0.2% yield strength and fracture strength.
Fig. 7 The room temperature compression results for Ti-51Al-2X alloys: (a) compression ratio, and (b) 0.2% yield strength and fracture strength.

Fig. 8 The room temperature compression ratio (a) and 0.2% yield strength (b) for alloys based on Ti-46Al. Alloys No. 1 through 4 correspond to compositions of Ti-46Al, Ti-46Al-1X, Ti-46Al-3X and Ti-46Al-5X, respectively.

measurements shown in Fig. 7a, it can be seen that the investigated elements (apart from Cr, V and Ta) decrease the compressive deformability of the γ phase regardless of their site preference.

Fig. 8 summarises our compression tests of two-phase alloys based on Ti-46Al. These alloys were subject to the same heat treatment, but they have quite different microstructure. Since the properties of dual-phase gamma alloys are very sensitive to microstructure [2], there is no simple relationship between the properties of the two-phase alloys and the properties of their constituent phases. It can be seen from Fig. 8a, however, that the alloying additions most helpful to improving the deformability of dual-phase gamma alloys are Cr, Nb, and Mn, in agreement with previous reports.

4. CONCLUSIONS

(1) The site occupancies of some alloying elements in TiAl and Ti₃Al were measured using the ALCHEMI method. In TiAl, Zr and Nb occupy Ti sites; Fe, Ni, Ga and Sn occupy Al sites. The site substitution behaviour of V, Cr and Mn changes with composition, depending on the Ti/Al ratio. With increasing atomic number, elements in the same period show increasing tendency to substitute for Al, while elements in the same group of the periodic table show increasing tendency to substitute for Ti. In Ti₃Al alloys, V, Cr, Mn, Zr, Nb, Mo and Ta
occupy Ti sites, while Ga and Sn occupy Al sites. The experimental site occupancy data are successfully interpreted using the Bragg-Williams model.

(2) A model that relates the \((\gamma+\alpha_2)\) two-phase equilibrium in ternary Ti-Al-X alloys to the substitution behaviour of alloying elements in the two ordered phases has been suggested. Predictions of the stabilising effects on the \(\gamma\) or \(\alpha_2\) phase of Nb, Ta, Cr, Mo, W etc. are made using measured site occupancy data, and are compared with independent phase stabilisation results. Good agreement has been reached. In particular, the variation in the stabilising effect of Cr is explained by the strong composition dependence (especially on Ti/Al ratio) of the site occupancy of Cr in the \(\gamma\) phase. Phase fractions measured using a variety of ternary Ti-Al-X alloys agree with predictions of the model.

(3) The room temperature compression properties of a series of ternary two-phase gamma alloys and their constituent phases were measured. No simple relationship was observed between the compressive properties of dual-phase alloys and those of the individual \(\alpha_2\) and \(\gamma\) phases.

LITERATURE

15. S. J. PENNYCOOK, Ultramicroscopy, 1988, 26, 239.