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## Segregation of Tungsten to Interfaces in Lamellar TiAl

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### Objective/Scope

There has been a great interest in recent years in lamellar TiAl, which is prepared by heat treating an alloy with a composition near Ti - (47-49) Al in the  $\alpha$ -region (usually near 1400°C) and then cooling it to room temperature. During the cool down,  $\gamma$ -lamellae form along the basal planes of hcp- $\alpha$ . The  $\gamma$ -phase has the L1<sub>0</sub> structure and the stoichiometry of TiAl. The remaining  $\alpha$ -phase becomes ordered Ti<sub>3</sub>Al ( $\alpha_2$ -DO19). The final microstructure consists of lamellae of these two phases. Two types of interfaces exist in this lamellar structure. One set is between Ti<sub>3</sub>Al and TiAl ( $\alpha_2/\gamma$ ) and the other is between two lamellae of TiAl ( $\gamma/\gamma$ ). The orientations of these interfaces have been determined that the former interfaces consist of  $1/6\langle 112 \rangle$  or  $1/3\langle 112 \rangle$  misfit dislocations while the latter, which are twin-related, contain  $1/6[11\bar{2}]$  type twinning dislocations or geometrically necessary dislocations [1].

The engineering interest in this material stems from the fact that it is lightweight and also has good creep properties [2-5]. As a result of the promising results reported in the literature, efforts have been made to improve the creep resistance of the material and to understand the mechanism by which creep occurs. This research has focused on both structural refinement and stability and alloying additions to the material, and all of these have provided significant improvements [6-8]. One element that has received particular attention is tungsten [7,9-12]. This element has been found to increase creep resistance [7,9], oxidation resistance [13] and strength [14] and to also stabilize the lamellar structure during creep [9]. It has been proposed that one way in which tungsten provides this effect is through segregation to the interfaces between the lamellae, and Table I summarizes the segregation results that have been presented in the literature. This segregation could pin the dislocations whose motion allows creep to occur, and also affect the interfacial energy in such a way as to inhibit the coarsening of the lamellae.

In this note, we use a straightforward model to show that the segregation of tungsten observed experimentally is consistent to what would be expected for segregation of this solute to dislocations. This result lends credence to a model in which tungsten improves creep resistance by segregating to the core of interfacial dislocations and inhibiting their motion.

<b>Table I</b> <b>Values for Tungsten Segregation in TiAl</b>			
Interface : Condition	Alloy Composition	Tungsten Composition at Interface	Reference
$\gamma/\alpha_2$ : Crept 3 hours at 1073 K	Ti-46.5Al-2Cr-3Nb- 0.2 W	0.5 +/- 0.1	11
$\gamma/\alpha_2$ Ledge : Crept 3 hours at 1073 K	Ti-46.5Al-2Cr-3Nb- 0.2 W	0.6 +/- 0.1	11
$\gamma/\alpha_2$ : Crept at 1088 K	Ti - 47Al - 2Cr - 1Nb- 0.8Ta - 0.2W - 0.15B - 0.3Si	0.52	12
$\gamma/\alpha_2$ Ledge : Crept at 1088 K	Ti - 47Al - 2Cr - 1Nb- 0.8Ta - 0.2W - 0.15B - 0.3Si	0.69	12
$\gamma/\alpha_2$ Interface : Annealed at 1173K	Ti - 47Al - 2Cr - 1Nb- 0.8Ta - 0.2W - 0.15B - 0.3Si	0.35	12
$\gamma/\alpha_2$ Ledge : Annealed at 1173K	Ti - 47Al - 2Cr - 1Nb- 0.8Ta - 0.2W - 0.15B - 0.3Si	0.30	12
$\gamma/\alpha_2$ Interface : Annealed at 1173K	Ti-47Al - 2Cr - 1.8Nb - 0.15B - 0.2W	0.68+/-0.45 0.42 +/-0.25*	10
$\gamma/\gamma$ Interface : Annealed at 1173K	Ti-47Al - 2Cr - 1.8Nb - 0.15B - 0.2W	0.38 +/- 0.13 0.33 +/- 0.15 0.33 +/- 0.15*	10

\* Values obtained for different measurements in the same material

## **Technical Highlights**

### ***Models***

In order to determine if segregation to dislocations is a plausible mechanism to explain the tungsten enrichment at interfaces in lamellar TiAl, two questions must be addressed. The first is whether or not there are any kinetic limitations to this segregation. The second is whether or not this type of segregation is consistent with the numbers reported in Table I.

To determine if diffusion kinetics limited the amount of segregation that could during a test, we used the standard McLean model for interfacial segregation [15]. Although this model is usually applied to segregation to high angle grain boundaries, there is nothing in this model that limits its use to that type of interface. Rather the model simply gives the time required to reach a certain fraction of the equilibrium segregation at any interface.

The equation for this segregation is given by

$$\frac{C - C_0}{C_f - C_0} = 1 - ((\exp(4Dt / (\alpha\delta)^2) * \operatorname{erfc}(2\sqrt{Dt} / \alpha\delta)) \quad (1)$$

where  $C_0$  is the initial concentration,  $C_f$  is the final concentration,  $\alpha$  is the ratio of the initial to the final concentration,  $D$  is the diffusion coefficient,  $t$  is time and  $\delta$  is the grain boundary width. Values used for these calculations are given in Table II.

The second type of calculation that is required is the segregation to the dislocation core. For this calculation we followed the model of Cottrell and Bilby [16] in which one first calculates the interaction energy  $E_I$  between a solute and an edge dislocation using the expression

$$E_I = 4(1+\nu)Gbr_a^3\Delta / (3(1-\nu) \sin\theta/r) \quad (2)$$

and then determines the concentration as a function of distance [17] through the expression

$$C(r) = C_0 \exp [-E_I(r)/kT] \quad (3)$$

In these expressions,  $r$  is the radial distance from the dislocation core,  $G$  is the shear modulus,  $r_a$  is the radius of the lattice site,  $\nu$  is Poisson's ratio,  $\Delta$  is the misfit parameter chosen so that the radius of the solute is  $r_a (1 + \delta)$ ,  $b$  is the magnitude of the Burgers vector and  $\sin\theta$  was taken to be 0.707 for these calculations, where  $\theta$  is a polar coordinate. Table II lists the values used in these calculations.

It should be pointed out here that most considerations of interfacial segregation have dealt with segregation to high angle grain boundaries. It is generally assumed that the variety of sites afforded to the segregant, both in terms of size and coordination, provide a trap for the segregant and that as a result the local concentration of the segregant at the boundary increases [18,19]. It has also been shown that twin boundaries and other low angle boundaries, generally do not provide these types of sites and that segregation to these interfaces is much lower [19]. Thus the driving force for the observed segregation to these lamellar interfaces, which are either twin-related ( $\gamma/\gamma$ ) or semi-coherent ( $\gamma/\alpha_2$ ), must primarily be a result of the presence of the dislocations on these grain boundaries which could provide local sites for segregation. It is for this reason that we have used the Cottrell-Bilby approach to model the segregation in these lamellar materials.

### ***Kinetics of segregation***

We first use McLean's equation to determine if segregation is kinetically limited. Figure 1 shows the results obtained for a temperature of 900°C.

Table II Values of Parameters Used in Calculations	
Parameter	Value
D	$1.45 \times 10^{-5} \exp(-65380/RT)$
$\alpha$	3
$\delta$	10 Å
G	45 GPa
b	3Å
$\Delta$	0.05839
$\nu$	0.33
$r_a$	1.45 Å

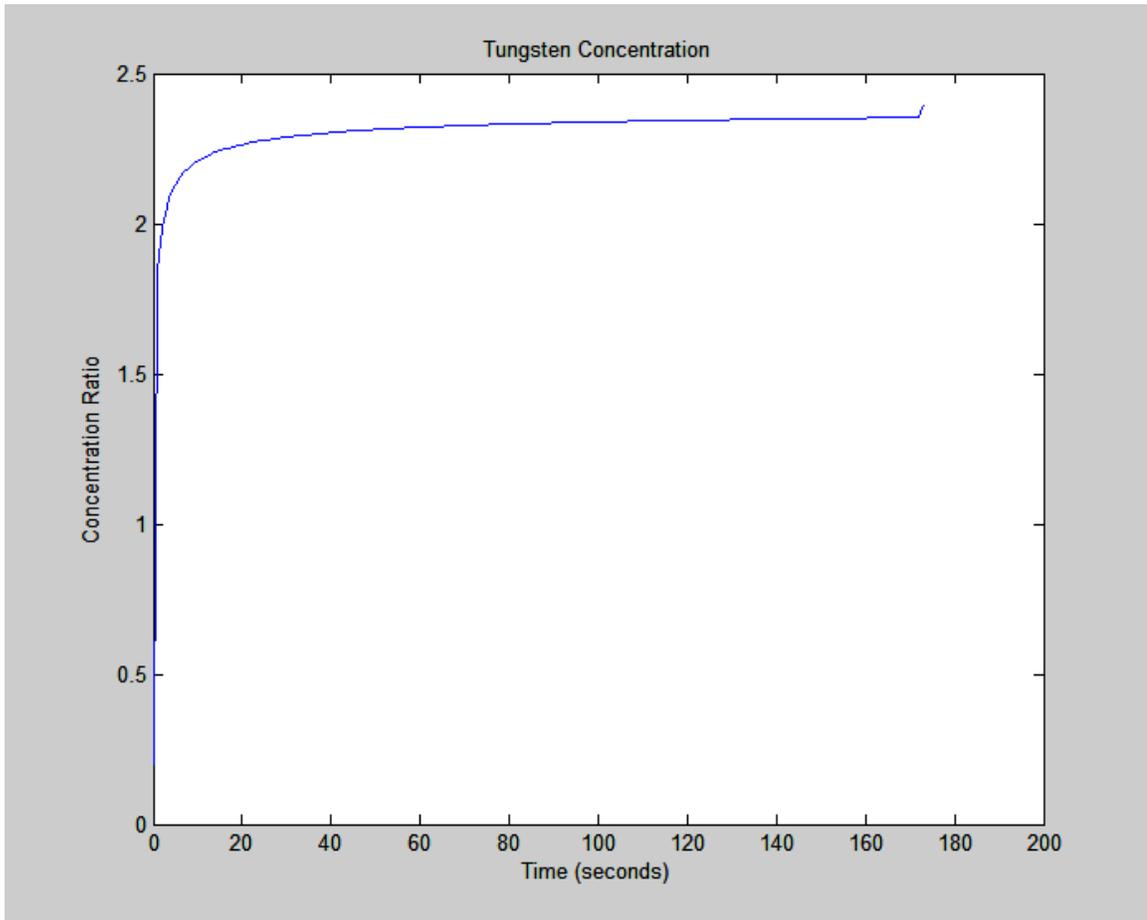


Figure 1 - The kinetics of segregation of W in lamellar TiAl at 900°C. Calculations made using equation 1.

Clearly the tungsten segregation approaches its equilibrium value in a matter of a few minutes. Even at 700°C we found that the segregation was complete in approximately 30 minutes. Thus it would appear that even during the creep tests, segregation to the interfaces could occur in times that were much shorter than the length of the test. Thus we conclude that kinetics limitations are not of great importance in determining the measured values of the tungsten segregation reported in Table I.

### *Segregation to dislocations*

We now use the Cottrell-Bilby approach to calculate segregation to dislocations. Figure 2 shows the segregation at 700°C plotted as a function of distance from the dislocation core. We see that at this temperature the maximum segregation is on the order of 0.6. Figure 3 shows the maximum segregation values calculated for temperatures ranging from 700 to 1400°C. This range was chosen because it is similar to the range used for annealing (between 900 and 1400°C) and creep testing (700-900°C). We see that there is a significant increase in the segregation as a result of decreasing temperature.

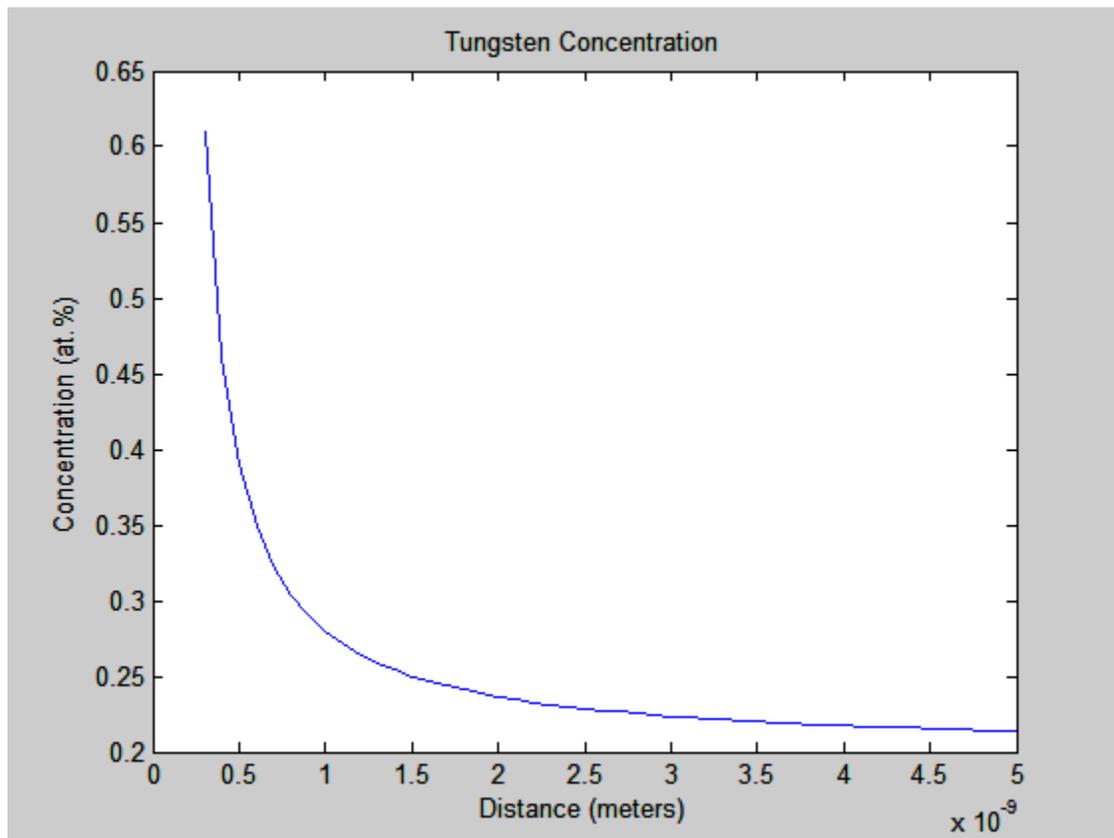


Figure 2 – Segregation of tungsten to a dislocation in lamellar TiAl. The amount of tungsten is plotted as a function of distance from the dislocation. Calculations made using equations 2 and 3. Values are for a temperature of 700°C.

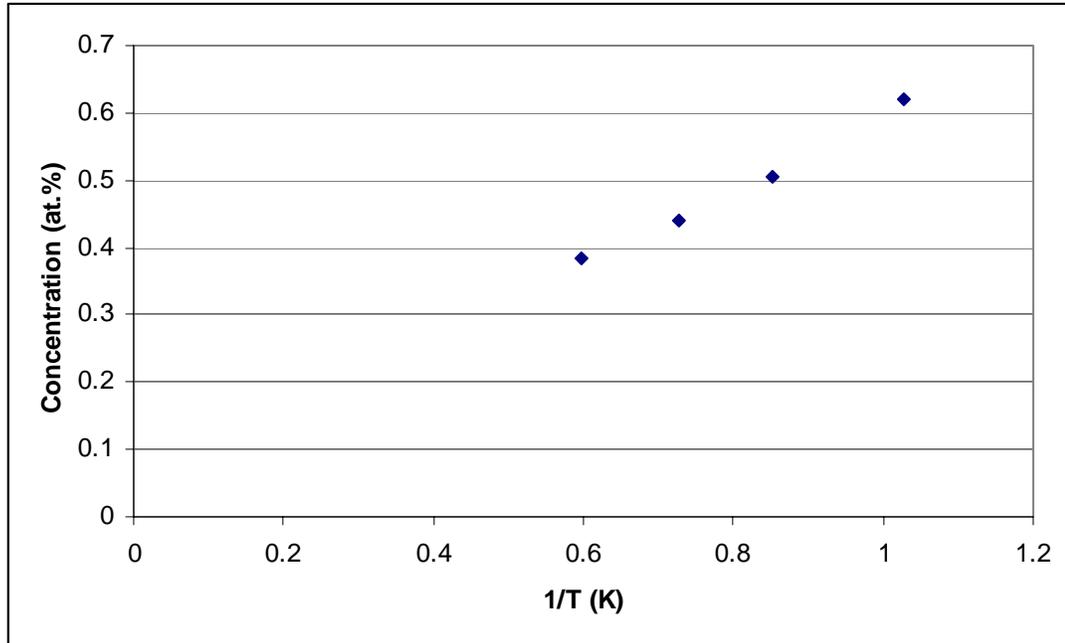


Figure 3 - The maximum concentration plotted of tungsten segregated to a dislocation in TiAl plotted as a function of the inverse of the temperature. Temperature values ranged between 700 and 1400°C. Calculations made using equations 2 and 3.

The values presented above are in good agreement with the measurements reported in the literature (Table I). The data reported were obtained by either atom probe field ion microscopy [10] or energy dispersive spectroscopy in a high resolution TEM [11,12]. To make an exact comparison one would have to include the number of dislocations that are present in the volume of material that is analyzed. However, the simple calculation performed here gives a first order estimate of the amount of segregation one should observe. Several additional points should be noted in making these comparisons. The first is that Larson *et al.* [10] reported that there was less segregation at the  $\gamma/\gamma$  interface than at the  $\gamma/\alpha_2$  interface. Our calculations would not distinguish between these two types of interfaces but if the dislocation density were higher along the  $\gamma/\alpha_2$  interface, then one would expect this difference. These authors also report that they measured different levels of segregation at different interfaces. This difference could be explained by the fact that there are different dislocation densities at different points along the interface. Another important point is that ledges were found to have more segregation than the interface, and this can be explained by the fact that dislocation can pile up at the ledges as the move along the interface [12]. Finally, it should be noted that none of the studies reported the type of cooling used after the heat treatments or creep tests. Since additional segregation could occur during a slow cool down, this part of the heat treatment could be important for creep performance.

### Conclusions

We report calculations in which we have used the Cottrell-Bilby model to estimate tungsten segregation at the lamellar interfaces present in lamellar TiAl. The results show good agreement with measured segregation and also show that this segregation should not be

kinetically limited at the temperatures of annealing or creep testing. Thus it would seem reasonable that tungsten enhances creep resistance by segregating to the dislocation cores and limiting their mobility, both in their glide along the interface and their climb at ledges. If this segregation does have this positive effect, creep resistance might be further enhanced by a low temperature aging, which would increase segregation to existing dislocations and make their motion even more difficult.

### **Status of FY 2004 Milestones**

Milestone: Collaboration with Brown University (Professor Clyde Briant) on theoretical modeling of tungsten segregation in lamellar interfaces was completed.

Milestone: Continue creep tests to investigate the creep resistance and microstructural stability of the nanolaminate composites at elevated temperatures up to 850°C, which will be reported in next quarterly report.

Milestone: "Continue to collaborate with ORNL (Dr. C.T. Liu) to fabricate and characterize the oxidation-resistant class of in-situ TiAl/Ti<sub>3</sub>Al nanolaminate composites with high Nb content (>10 at.%) using hot-extrusion processing techniques."

### **Publications**

L.M. Hsiung and T.G. Nieh, "Microstructures and Properties of Powder Metallurgy TiAl Alloys," *Mater. Sci. Eng.*, **A364**, 1 (2004).

L.M. Hsiung, A. J. Schwartz, and T.G. Nieh, "In Situ TEM Observations of Interface Sliding and Migration in a Refined Lamellar TiAl Alloy," *Intermetallics*, 2004, in press.

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AUSPICE

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