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K. Fox. Modelling of high temperature interfacial reactions in continuously reinforced Ti/SiC metal matrix composites (MMCs). Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-1699-C7-1704. 10.1051/jp4:19937266 . jpa-00251906

HAL Id: jpa-00251906

<https://hal.science/jpa-00251906>

Submitted on 1 Jan 1993

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Modelling of high temperature interfacial reactions in continuously reinforced Ti/SiC metal matrix composites (MMCs)

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Abstract

Previous experimental work by Gundel and Wawner showed that the matrix alloy has a strong effect on reaction layer growth in Ti alloy/SCS-6 composite systems. A finite difference technique was used to model the reaction layer growth, which predicts the same trends as those exhibited by the experimental data. Matrix alloying elements such as Mo and Cr in metastable β alloys will affect the equilibrium compositions and diffusivities in the matrix, but matrix diffusion is not found to be rate controlling. Regular solution thermodynamic models indicate that the main affect of matrix composition is in controlling carbon-flux through the reaction layer by altering equilibrium C-TiC-Ti interfacial compositions.

Introduction

Titanium based alloys reinforced uniaxially with silicon carbide fibres are currently being considered for use in gas turbine engines, where they offer advantages in terms of higher specific strength and stiffness over monolithic alloys. One method of producing these composite plates involves diffusion bonding Ti alloy foils around an array of fibres at temperatures in the range 900-910°C. During fabrication, reaction between the fibres and the titanium matrix can occur. The nature of any reaction product formed is important in controlling the degree of load transfer between fibres and matrix. This may be via any chemical bonds formed or mechanical bonding introduced through volume changes during the formation of the fibre/matrix reaction product and matrix solid state transformations. Exposure of the processed composite to service temperatures (300-400°C) can lead to further microstructural changes, which will affect matrix-fibre load transfer. Hence, it is necessary to be able to predict the development of reaction layer and matrix microstructure during processing and service.

The nature and development of reaction layers formed in these fibre/matrix systems has already been extensively studied^[1-7]. The two main types of reaction product that have been identified are a carbon-rich phase, $\text{TiC}_{(1-y)}$, and a silicon-rich phase, Ti_xSi_y . The exact morphology and composition of these phases appear to be dependent on:

- (i) the matrix alloy being considered,
- (ii) any heat treatment given to the composite, and
- (iii) the presence or absence of a fibre coating.

Previous work, by Martineau et al ^[1] investigated the growth of the reaction layer in a Ti-6Al-4V/SiC composite. The composite was aged at 950°C for up to 300 hours in vacuum and the thickness of the reaction layers was measured. Figure 1 shows the growth in reaction layer in a system where the SiC fibres were coated in a 3 μm layer of pyrolytic carbon. Three different stages of growth were identified; stage I appeared to exhibit parabolic growth of the form, $x = kt^{1/2}$, where x = thickness, k = rate constant and t = time. This stage was not seen in similar exposures of Ti-6Al-4V reinforced with uncoated SiC fibres, which suggests reactions between the pyrolytic carbon coating and the Ti alloy. The change in growth rate at the onset of stage II corresponds to the exhaustion of the carbon layer, and silicon diffusion becomes

significant. A further decrease in reaction layer growth occurs in stage III, when the diffusion fields of adjacent fibres overlap and the matrix no longer acts as a semi-infinite couple. Most composites for engineering use will be processed to retain some of the carbon coating and so reaction layer growth will be represented by stage I.

Modelling

There have been few attempts to model the diffusion processes taking place in Ti/SiC composites during fabrication and subsequent heat treatment. This is mainly due to the scarcity of diffusional data for the phases involved, and the complex nature of the reaction product formation. In this paper, reaction layer growth in stage I is predicted using a finite difference technique for the case of various titanium alloys reinforced with SCS-6 fibres. SCS-6 denotes a SiC fibre of 140µm diameter, which has a multilayer C/Si coating of about 3µm thickness. Initial nucleation of the reaction product is not considered in this model, but it is unlikely to be significant compared with the processing time, as the incubation time will be very short at fabrication temperatures (around 900°C). Hence the starting condition assumes a thin layer of reaction product, $\text{TiC}_{(1-y)}$, which forms between the carbon coating and the matrix. The diffusion of silicon and the formation of silicides is not considered at this stage, as carbon diffusion will be dominant during the first stages of reaction layer growth. Equilibrium is assumed at both the carbon coating/reaction layer and the reaction layer/matrix interfaces, with interfacial carbon concentration controlling the flux of carbon through the reaction layer and into the matrix.

Previous work by Van Loo and Bastin^[8] found the diffusion coefficient for carbon in $\text{TiC}_{(1-y)}$ to be strongly concentration dependent. For a composition of $\text{TiC}_{(1-y)}$, the interdiffusion coefficient is given by equation (1.0)

$$\tilde{D}_{TC} = \left[0.48 \exp(9.2y) \right] \left[\exp - \left(\frac{39,500}{T} \right) \right] \quad (1.0)$$

where T = absolute temperature

The diffusion of Ti through the reaction product, $\text{TiC}_{(1-y)}$ is negligible under these conditions and can be ignored ^[9]. Therefore the diffusion coefficient of carbon in $\text{TiC}_{(1-y)}$ is of the order of 10^{-16} - $10^{-18} \text{m}^2 \text{s}^{-1}$ at 1000°C.

In the matrix, the competing factors are the diffusion of carbon through the matrix, and the partition and redistribution of any alloying elements ahead of the reaction layer/matrix interface. The diffusivity of carbon in β -Ti, D is given by

$$D = D_0 \exp -Q/RT \quad (1.1)$$

where Q and D_0 are alloy dependent, and lie within the ranges 79 to 172 kJmol⁻¹ and 7×10^{-9} to $2 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ respectively, which gives a diffusivity of around $D \sim 10^{-12} \text{m}^2 \text{s}^{-1}$ at 1000°C ^[10,11]. The flux of carbon into the matrix is limited by mass balance at the interface, where

$$D_C^{\text{TiC}} \frac{\partial C_C^{\text{TiC}}}{\partial x} = D_C^{\text{Ti}} \frac{\partial C_C^{\text{Ti}}}{\partial x} \quad (1.2)$$

However, the diffusivity of alloying elements in titanium (see Table 1) is also an important factor if partition occurs. Mass balance equations at the interface similar to (1.2) must be obeyed for all alloying elements. The use of a finite difference method allows the concentration dependence of $\tilde{D}_{\text{TiC}}$ and interfacial constraints to be incorporated. Soft impingement of diffusion fields can also be readily accounted for by use of this method.

Experimental Procedure

Gundel and Wawner^[2] measured reaction layer growth in various Ti alloy/SiC systems. The alloy/fibre systems considered, with compositions given in wt %, were:

(a) UA Ti/SCS-6 (99.7% pure titanium)

- (b) Ti-6Al-4V/SCS-6 (an $\alpha+\beta$ matrix)
- (c) Ti β 21s/SCS-6 (a metastable β matrix of composition Ti-15Mo-3Al-2.7Nb-0.2Si wt)
- (d) Ti-15V-3Al-3Cr-3Sn/SCS-6 (a metastable β matrix referred to as Ti-15-3 later)
- (e) Ti-14Al-21Nb/SCS-6 (an $\alpha_2+\beta$ matrix)
- (f) Ti-1100 (Ti-6Al-2.8Sn-0.4Mo-0.07O₂-0.02Fe)

These were exposed at 1000°C for up to 100 hours and the reaction layer thicknesses were measured. This experimental data was used to validate the model.

Specimens from a Ti β 21s/SCS-6 composite were given solution treatments at 910°C in vacuum for up to 32 hours. Transverse sections were taken from the specimens, which were then polished and the reaction layers were measured using scanning electron microscopy. The resulting measurements were then compared to predictions from the model.

Results and Discussion

The first system to be modelled was the UATi/SCS-6 system as this was the simplest situation. The diffusivity of carbon in pure titanium and the self diffusion rate in titanium is so rapid that the growth of the reaction layer is limited only by the rate of carbon diffusion through the TiC layer. Initially the model predicted a rather higher growth rate than the observed growth rate, but this is consistent with an activation barrier between the carbon and the titanium in the initial stages of diffusion and between the carbon layer and the reaction layer, both of which are neglected in the model. The model is also only considering diffusional processes, whereas in reality, the process is a "reactive diffusion" situation. In further modelling, a factor of 2.0 was used to compensate for this effect (see Figure 2(a)).

In the systems where alloying elements are present in the titanium matrix, a number of factors may affect the growth rate of the reaction layer:

- (i) The effect of alloying elements on the diffusivity of the matrix (see Table 1). If the diffusivity is reduced by the presence of alloying elements, then the reaction layer growth may be controlled by the rate of diffusion of the alloying elements in the matrix.
- (ii) The partitioning effects of various alloying elements between the matrix and reaction layer.
- (iii) The effect of alloying elements on the interfacial carbon levels. The Ti-C phase diagram^[12] predicts these to be at about 48.8 and 37.0 atomic % carbon respectively, and these may be significantly affected by alloying elements.

Effect (i) was accounted for by modelling multicomponent diffusion, whilst regular thermodynamic models based on substitutional and interstitial sub-lattice approaches^[13] for a variety of data ^[14-17] were used to assess(ii) and (iii).

In the Ti-6Al-4V/SCS-6 composite, the presence of the alloying elements V and Al will reduce matrix diffusion rates (see Table 1), but not sufficiently to limit reaction layer growth. The partitioning behaviour of Ti and V is very similar, and interfacial carbon levels will not be affected (see Table 2). The model therefore predicts the same reaction layer growth rates as in the unalloyed Ti case, which is close to that of the observed growth rate (see Figure 2(b)).

The Ti β 21s alloy contains 15wt% Mo, which being a strong carbide former, strongly affects the interfacial carbon concentrations (see Table 2) as well as the diffusivity of the matrix. When this change is incorporated into the model, the reaction layer growth rates are significantly reduced from those of the UATi/SCS-6 composite. The predictions from the model can be seen to be in close agreement to the experimental data both at 910°C and 1000°C (see Figure 2(c) and (d)).

Ti-15-3 alloy contains 15% V, which has little effect on reaction growth rates (as can be seen in the Ti-6Al-4V system). However, the presence of 3% Cr, which is a strong carbide former, causes partitioning in the matrix, and changes the interfacial carbon compositions (see Table 2). When this is incorporated in to the model, the reaction layer growth rates are closely predicted (see Figure 2(e)).

Ti-1100 and Ti-14Al-21Nb are currently being modelled, but diffusional and thermodynamic data is less well established. However, the trends are consistent with the higher thermodynamic stabilities of these matrices.

Thermodynamic modelling of equilibria in the Ti β 21-s matrix at 910°C and the Ti-15-3 matrix at 1000°C is less accurate than for the other systems, which is the cause of the larger deviations in Figure 2(d) and 2(e).

Conclusions

Reaction layer growth rates in various Ti alloy/SCS-6 systems have been predicted using a model based on finite difference techniques. A factor was used to fit the model to the experimental data, which takes into accounts for activation barriers in the process, and the model then closely predicted the trends in reaction layer growth seen in the experimental data. Growth for a variety of matrices can be predicted as it is controlled by the effects of alloying elements the interfacial composition terms, which determines the rate of carbon transport through the reaction layer.

Acknowledgements

The authors are grateful to Professors M. H. Loretto and J. F. Knott for the provision of laboratory facilities in the IRC in Materials for High Performance Applications and the School of Metallurgy and Materials, respectively. One of the authors (KMF) is supported by an SERC CASE award with Rolls-Royce plc, Derby and thanks are also due to M. V. Hartley at Rolls Royce plc, Derby for his support during this programme.

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Tables and Figures

Table 1. Diffusivities of alloying elements in titanium [18]

Element in Titanium	Activation energy, Q/kJmol^{-1}	Diffusion constant, $D_0/\text{m}^2\text{s}^{-1}$	Diffusivity at 1000°C $D/\text{m}^2\text{s}^{-1}$
Ti (self diffusion)	131	3.6×10^{-8}	1.56×10^{-13}
V	135	3.1×10^{-8}	8.95×10^{-14}
Cr	148	5.0×10^{-7}	4.23×10^{-13}
Mo	180	8.0×10^{-7}	3.29×10^{-14}

Table 2. Interfacial compositions at 1000°C predicted by thermodynamic modelling.

System	Main alloying elements/wt%	Predicted interfacial C-TiC composition	Predicted interfacial TiC-Ti composition
UATi	none	48.8	37.0
Ti-6-4	6%Al, 4%V	48.8	37.0
Ti β 21s	15%Mo	48.8	41.0
Ti-15-3	15%V, 3%Cr	48.8	39.0

Figure 1. Stages in reaction layer growth in a Ti-6Al-4V/SiC composite exposed at 910°C [after Martineau et al [1]]

(a) UATi/SCS-6 at 1000°C

(b) Ti-6Al-4V/SCS-6 at 1000°C

(c) TiB21-s/SCS-6 at 1000°C

(d) Ti B21-s/SCS-6 at 910°C

(e) Ti-15-3/SCS-6 at 1000°C

Figure 2 (a-e). Comparison between predicted reaction layer thicknesses and experimental measurements for various Ti alloy/SiC composites. Dashed lines indicate 95% confidence limits.