Microstructure and some properties of TiAl-Ti$_2$AlC composites produced by reactive processing

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Abstract

The TiAl–Ti$_2$AlC composites with and without impurities, Ni, Cl and P, were prepared by combustion reaction from the elemental powders and cast after arc melting. The resulting composites had about 18 vol% Ti$_2$AlC in the lamellar matrix consisting of γ-TiAl and Ti$_3$Al (α$_2$). In the homogenized specimens, the α$_2$ phase decomposed to γ-TiAl and Ti$_2$AlC. The composite material had a high strength both at ambient and elevated (1173 K) temperatures; about 800 and 400 MPa, respectively, with an ambient temperature ductility of 0.7% at bending test. The fracture toughness test also proved that the homogenized composite has higher toughness than the as cast one. The toughness value reached to 17.8 MPa m$^{1/2}$. The zigzag cracks propagated in the homogenized composite and the reinforcement Ti$_2$AlC particles and the finely precipitated Ti$_2$AlC particles were main obstacles to the crack propagation. The composite with impurities showed a marginal improvement in the oxidation resistance over the composites without impurities. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The intermetallic compounds have become a subject of intensive research with the aim of developing new materials which can be used in wide range of high temperature applications. Particular attention has been paid to the aluminides especially γ-TiAl which is one of the most promising candidate due to its low density, high melting point, excellent corrosion and oxidation resistance when compared to Ti$_3$Al (α$_2$) and orthorhombic (Ti$_2$AlNb) classes of aluminides. However, the major problems limiting the practical use of this compound are its low ductility and fracture toughness at ambient temperature and poor high-temperature strength with low oxidation resistance above 1073 K [1,2]. To improve these properties, recently many composites have been studied with ductile particle reinforcements like β-TiNb [3,4] and with brittle particle reinforcements TiB$_2$ [5,6], Ti$_2$AlC [7–11], Ti$_2$AlN [12], TiB$_2$+Ti$_2$AlN [13] and TiB$_2$+Ti$_2$AlC [14]. The ductile reinforcements improve the toughness of the composites and the brittle ones improve the strength, both at ambient and elevated temperatures. Thus, intermetallic composites could provide the right combinations of high-temperature strength, creep resistance, environmental stability with adequate ambient temperature ductility and low density. Such a composite with good oxidation resistance would extend its potential for engine component applications such as high pressure compressor, turbine and to some combustor applications.

Recently, combustion reaction synthesis or self-propagating high-temperature synthesis (SHS) using powder compacts has been developed to produce intermetallics or ceramics [15]. In this process, the exothermic heat of formation energy releases within the order of seconds or minutes and intermetallic or ceramic compounds are formed. It is also possible to form intermetallic–intermetallic, ceramic–ceramic, or intermetallic–ceramic
composites from combustion reactions between corresponding elemental constituents. In addition, it has the advantage of an in situ forming technique compared with conventional artificial composite production approaches. The products formed by the combustion synthesis, in general, have extensive porosity. Therefore, this porosity must be substantially reduced by various techniques. The recent techniques used to produce a fully dense synthesis product include the ‘XD’ process [16,17], reactive sintering [18], reactive hot pressing [19], and reactive HIPing [20]. In these processes, large pressure is applied during or after the synthesis reaction. In the present study, densification was achieved by an arc-melt casting technique without pressure after the synthesis reaction. By these processes, it should be possible to form the intermetallic TiAl and ceramic Ti$_2$AlC, and to produce the composite material with full density.

For elevated temperature applications, however, the oxidation resistance of this composite should be enhanced. The oxidation resistance of the $\gamma$-class of titanium aluminides and its composites can be improved marginally by the addition of alloying elements such as Nb, Mo, and W and impurities like Cl and P [21]. The addition of Cl and P to the elemental powders is possible only by the electroless process [22]. So we have selected the electroless deposition process to deposit the impurity elements, Cl and P with Ni, on titanium powders. In this work, composites of $\gamma$-TiAl reinforced with Ti$_2$AlC and containing small amounts of above mentioned impurities were studied for the microstructure and some properties, e.g. ductility, strength, fracture toughness, and oxidation resistance.

2. Experimental

High purity elemental powders of Ti (99.5%, −350 mesh; containing 3500 ppm level of oxygen), Al (99.9%, −150 mesh), and C (graphite type, 99.99%, −400 mesh) were taken to prepare the intermetallic alloys of TiAl−Ti$_2$AlC. Initially the elemental titanium powders were given a coating of nickel by the electroless process discussed elsewhere [22]. The electroless nickel coating given to the titanium powder deposits P and Cl with Ni, which are used to increase the oxidation resistance of the composite. Hereafter, the above said elements Ni, P and Cl are referred to as impurities. The Ni addition to the matrix was maintained all below 1 at% to avoid the Laves phase formation, which ultimately weakens the composites by reducing its ductility. The coated Ti powders and Al, C powders were mixed thoroughly for further processing with an initial composition of Ti(Ni)$_{50}$Al$_{50}$C$_5$ (in at%). The elemental powder compositions for the $\gamma$-matrix with and without impurities are shown in Table 1. The volume fraction of the reinforcement cement was calculated as about 18 vol% from the microstructure analysis and the density measurement [7]. In this process the mixtures of powders were compacted and subjected to exothermic synthesis for a duration of 10 min in a silica tube at a temperature (1273 K) under a vacuum of $\sim 10^{-4}$ Pa. Subsequently, the reactive processed materials with high porosity were arc-melted repeatedly (two or three times), under Ti gettering high purity argon, in order to obtain high density composites. In Table 2 the measured composition of the ingots after processing is shown. For the matrix in the ingots with and without impurities, EPMA-analyzed composition had slightly more titanium and less aluminum than the equiatomic TiAl. In addition, a small amount of Ni, Cl, and P was measured in the matrix with impurities. However, the carbon composition in the matrix with and without impurities was not presented in the Table 2 because it could not be determined quantitatively by the EPMA-measurement.

Fig. 1 shows the binary phase diagram [23] of TiAl at the two phase region of $\alpha_2 + \gamma$. The as cast composites were annealed at 1273 K for 144 h to homogenize them. The microstructure of as cast and homogenized composites were characterized using X-ray diffraction, optical microscope, and transmission electron microscope (TEM). The as cast and homogenized specimens were cut to dimensions of $3 \times 3 \times 5$, $20 \times 3 \times 2$, $20 \times 3 \times 3$, and $10 \times 3 \times 2$ mm$^3$ for compression, bending, fracture toughness and oxidation resistance tests, respectively. The compression tests at ambient and elevated temperatures ($\sim 1400$ K) were carried out on an Instron testing machine driven at a crosshead speed of 0.1 mm min$^{-1}$. Three-point bend tests were performed at ambient temperature in air using an Instron testing machine at a constant crosshead deflection rate of 0.1 mm min$^{-1}$. Strain was precisely measured with a

<table>
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<tr>
<th>Alloy (powder, at%)</th>
<th>Matrix (at%)</th>
<th>Reinforcement (vol%)</th>
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<tr>
<td>Ti$_5$Al$_3$</td>
<td>Ti$_5$Al$_3$</td>
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<tr>
<td>Ti$_5$Al$_3$C$_5$</td>
<td>Ti$_5$Al$_3$</td>
<td>~18</td>
</tr>
<tr>
<td>Ti(Ni)$<em>{50}$Al$</em>{50}$C$_5$</td>
<td>Ti$_5$Al$_3$</td>
<td>~18</td>
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Table 1 Nominal compositions of the alloys used, and the estimated matrix composition and the calculated volume fraction of reinforcement, Ti$_2$AlC.
3. Results and discussion

3.1. Microstructures

The composite formed by the combustion synthesis had a matrix of two phase $\alpha_2 + \gamma$, the reinforcement particles Ti2AlC, and some porosity [7]. Subsequent arc melting retained the matrix and reinforcement as before with significant reduction in porosity. Also, because of
the dispersed particulate reinforcements, these composites are much more resistant to recrystallization and grain growth than single phase alloys. Fig. 2(a)–(d) show the optical microstructures of the as cast and homogenized composites with and without impurities. In Fig. 2(a) and (c), the microstructure of the as cast composites consists of grains of nearly lamellar $\alpha_2 + \gamma$ structure with a dispersion of randomly oriented particles of Ti$_2$AlC. For the formation of this lamellar structure, as well as that in the conventionally cast titanium-rich TiAl alloy, it seems that the carbon content in the present composites may play a more important role than the Ti/Al composition, although the specimens with and without impurities have slightly more titanium and less aluminum than the equiatomic TiAl as shown in Table 2. While, in Fig. 2(b) and (d), such lamellar structure is not observed in the homogenized specimen. Instead, smaller particles are visible in the matrix grain and appear to form in place of solutionizing lamellar structure. This microstructure was also confirmed by examination of the TEM. The micrographs taken before homogenizing show the lamellar structure as shown in Fig. 4(a) and reveal the precipitates after homogenizing as shown in Fig. 4(b). These particles have been identified as a Ti$_2$AlC phase. This suggests that during the homogenizing process the $\alpha_2$ phase containing carbon is decomposed to $\gamma$-TiAl and Ti$_2$AlC particles. The $\alpha_2$ phase can dissolve carbon up to about 2 at% whereas the $\gamma$ phase can dissolve less than about 0.5 at% as known from the Ti–Al–C phase diagram [24] shown in Fig. 3.

There is no change in the microstructure of the composites with and without impurities. As shown in the optical micrographs, reinforcement Ti$_2$AlC particles are uniformly distributed in the matrix. The particles are rod-like in shape with sizes of 10–20 $\mu$m in length, and the aspect ratio is estimated to be about 5–10 for these reinforcement particles. Whereas the precipitated particles are about 0.1–0.3 $\mu$m in diameter.

3.2. Strength and ductility

The result of compression tests of homogenized composites with and without impurities is presented in Fig. 5 as a plot of the 0.2% proof strength versus a testing temperature. Included for purpose of comparison is the 0.2% proof strength of the un-reinforced Ti$_{50}$Al$_{50}$ alloy homogenized at 1273 K for 144 h. The composite with impurities shows a slight improvement over the composite without impurities. The strength of the composites, as in the case of the un-reinforced matrix Ti$_{50}$Al$_{50}$, decreases very gradually at low temperatures and rapidly at high temperatures, while the stress level is more than two times as high as that of the un-reinforced Ti$_{50}$Al$_{50}$ alloy for the temperature region tested. Thus the strength of the composite both at ambient and elevated temperatures clearly increased by the dispersion

Fig. 4. TEM micrographs of the composite with impurities (Ti(Ni)$_{50}$Al$_{45}$C$_5$), showing smaller precipitates in place of lamellar disappeared: (a) as cast; (b) homogenized at 1273 K.

Fig. 5. Compressive 0.2% proof strength as a function of the testing temperature. Included for purpose of comparison is the proof strength of binary TiAl alloy.
of reinforcement Ti<sub>2</sub>AlC to about 800 MPa at ambient temperature and about 400 MPa at 1173 K.

Fig. 6 shows the stress–strain curves of the composites and the un-reinforced Ti<sub>50</sub>Al<sub>50</sub> alloy (homogenized at 1273 K for 144 h) obtained by the bending test. The difference in the ductility of the composite with and without impurities is negligible. The composites with impurities show 0.7% ductility which is more than that for the matrix Ti<sub>50</sub>Al<sub>50</sub>. The strength of as cast composite is higher but the ductility low because the carbon dissolved α<sub>2</sub> lamellar will make the composite brittle.

3.3. Fracture toughness

Fracture toughness tests have been carried out at ambient temperature on the as cast and homogenized TiAl–Ti<sub>2</sub>AlC composites. Fig. 7(a) and (b) shows the crack propagation in the as cast and homogenized composites with impurities, respectively, during the fracture toughness test. The zigzag cracks propagate in the homogenized composites unlike in the as cast composites in which is the crack propagation linear. The zigzag crack propagation in the homogenized composites is caused because of the presence of dispersed particulate reinforcements and finely precipitated particles, as shown in Fig. 8. Fracture toughness values are presented in Table 3 and it can be seen that the higher value, 17.8 MPa m<sup>1/2</sup>, is obtained for homogenized composite with impurities, which is more than that for the as cast one. In general, the lamellar microstructure exhibits significantly increased values of fracture toughness [25]. However, in the case of the present composites, because the α<sub>2</sub> phase in the lamellar structure dissolves carbon, more detailed examinations in the effect of carbon on the fracture toughness will be required.

3.4. Oxidation resistance

High temperature applications demand a high level of oxidation resistance. The oxidation rate (mass gain) of the matrix and the composites at 1173 K in air under cyclic oxidation is shown in Fig. 9. Composites with impurities show marginal improvement in oxidation resistance over the composites without impurities. This is because of the presence of Cl and P that enhances the formation of Al<sub>2</sub>O<sub>3</sub> on the surface of the composite. The presence of Cl forms AlCl<sub>3</sub> which assists in bringing Al to the surface of the composite [26]. The P addition effectively reduces the oxygen vacancies in the TiO<sub>2</sub>, resulting in the suppression of the inward diffusion of oxygen via vacancies [27]. The combined effect of the Cl and P is to improve the oxidation resistance of the composites at 1173 K in air by enhancing the external

Fig. 6. The stress–strain curves of bend tests at ambient temperature.

Fig. 7. Optical micrographs of the fracture toughness tested composites with impurities (Ti(Ni)Al<sub>2</sub>C<sub>5</sub>): (a) as cast; (b) homogenized at 1273 K.
Al₂O₃ formation in preference to the mixed oxide layer of TiO₂ and Al₂O₃.

There is hardly any mass gain of the composites with impurities after 20 h of exposure at this temperature. This suggests the formation of a highly adherent layer which prevents further oxidation and spalling. Further work is being carried out to study the effect of impurity on oxidation resistance.

4. Conclusion

During homogenizing the carbon dissolved in the matrix forms the precipitated particles. The reinforcement carbide particles formed during combustion reaction and the precipitated carbide particles are the main obstacles to the crack propagation, thereby enhancing fracture toughness. Composites containing impurities, both as cast and homogenized, show very good oxidation resistance.

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