Synthesis of TiAl(Cr)/Ti2AlC Composites by Reactive Arc-Melting

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TiAl(Cr)/Ti2AlC composites have been prepared by a reactive arc-melting technique using elemental powders of Ti, Al, Cr and C. Resulting composites have been reinforced using 3.5, 10 and 18 vol% Ti2AlC in a matrix of TiAl with and without addition of Cr. The axial ratio of γ-phase has been lowered through the complete solid solution of chromium. The grain size of the matrix has been found to decrease whereas its distribution converges along the content of Ti2AlC. The lamella grains in the matrix have been changed both into TiAl and very fine Ti2AlC particles by a homogenizing treatment. Compared to TiAl single-phase alloy, studied composite materials have revealed superior mechanical properties, such as bending strength, compressive strength and fracture toughness. This improvement is caused by the formation of Cr solid-solution for hardening, dispersion of the Ti2AlC particles and the fine grain of the TiAl matrix.

Keywords: intermetallic compound, titanium aluminide, composite material, Ti2AlC, arc-melting, in-situ process, combustion synthesis, mechanical property, fracture toughness

1. Introduction

Intermetallic compounds based on γ-TiAl are currently receiving considerable attention due to their potential use at elevated temperatures, because of low density, outstanding specific strength and oxidation resistance. However, some factors such as low ductility and fracture toughness at room temperature, as well as the lack of high temperature strength and creep resistance limit their applications as structural materials. The conventional route to improve these properties is to control the microstructure with the addition of a third element, such as Cr, Nb, V and Mn. Another common route to prepare those is to synthesis composite materials containing a second phase such as boride, carbide, nitride and oxide. In practice, various kinds of techniques have been developed to prepare TiAl base composites.

Self-propagating high temperature synthesis, also termed combustion reaction synthesis using powder mixture compacts has been developed to produce intermetallics or ceramics. In this process, the addition of third elements or extra compounds makes it possible to perform in-situ synthesis of composites. As for the TiAl compound, TiAl/Ti2AlC, TiAI/Ti2AlC+TiB2 and TiAl/Ti2AlC+TiB2 composites were developed by this technique starting from the elemental powder mixture of Ti + Al + C, Ti + Al + AlN, Ti + Al + BN and Ti + Al + B4C, respectively. One major defect of this process, however, is the highly porous nature of the products, which has to be substantially reduced by efficient techniques if structural applications are required. Recent techniques to fabricate fully dense products include the ‘XD’ process, reactive hot pressing and reactive HIP’ing. In the present investigation, densification was achieved by a newly developed reactive arc-melting technique. Using this process, it becomes possible to form an intermetallic matrix having ceramic dispersoids, and to produce the composite material fully dense without applying external pressure. In this work, TiAl(Cr)/Ti2AlC composites were produced using this new technique. Two kinds of the matrix compositions were tested in this investigation; namely with and without the addition of Cr. The microstructure and mechanical properties evaluated for these composites are reported.

2. Experimental Procedure

High purity elemental powders of titanium (99.5 mass% purity, −350 mesh; containing approximately 3500 ppm oxygen), aluminum (99.9 mass% purity, −150 mesh), chromium (99.6 mass% purity, −200 mesh), and carbon powder (99.99 mass% purity, −400 mesh) were used to prepare the composites. Those powders with right compositions for the Ti–50Al and Ti–49Al–2Cr alloys with and without reinforcement shown in Table 1 were mixed in a mortar for 10 minutes. It is assumed that composites consist of the two phases, i.e.,

<table>
<thead>
<tr>
<th>Alloy (powder, mol%)</th>
<th>Matrix (mol%)</th>
<th>Ti2AlC (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–49Al–2Cr</td>
<td>Ti–49Al–2Cr</td>
<td>0</td>
</tr>
<tr>
<td>Ti–48Al–2Cr–1C</td>
<td>Ti–49Al–2Cr</td>
<td>3.5</td>
</tr>
<tr>
<td>Ti–46Al–2Cr–3C</td>
<td>Ti–49Al–2Cr</td>
<td>10</td>
</tr>
<tr>
<td>Ti–44Al–2Cr–5C</td>
<td>Ti–49Al–2Cr</td>
<td>18</td>
</tr>
<tr>
<td>Ti–50Al</td>
<td>Ti–50Al</td>
<td>0</td>
</tr>
<tr>
<td>Ti–49Al–1C</td>
<td>Ti–50Al</td>
<td>3.5</td>
</tr>
<tr>
<td>Ti–47Al–3C</td>
<td>Ti–50Al</td>
<td>10</td>
</tr>
<tr>
<td>Ti–45Al–5C</td>
<td>Ti–50Al</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 1 Powder compositions of studied alloys, the estimated matrix composition and the calculated volume fraction for reinforcement, Ti2AlC.
$\gamma$ phase and Ti$_2$AlC phase and Cr is not dissolved in the Ti$_2$AlC. The estimated matrix composition with and without addition of 2 mol% Cr and calculated volume fraction of the reinforcement are also given in Table 1. Five grams of the powder mixture was pressed at about 260 MPa, into a cylinder of 10 mm diameter. Several compacts, approximately 30 g in total, were fabricated as ingots using non-consumable electrode arc melting under an argon atmosphere. The combustion reaction occurred immediately after inducing the electric discharge between electrode and compacts. The reaction product was subsequently arc-melted. The arc-melted buttons were remelted three times to promote homogeneity and densification. The as arc-melted composites were annealed at 1273 K for 144 h to attain further homogenization. The microstructures of homogenized composites were characterized using X-ray diffraction (XRD) using Cu–K$_\alpha$ radiation, optical microscope, scanning electron microscope (SEM), electron probe micro-analysis (EPMA) and transmission electron microscope (TEM).

The homogenized specimens were cut to $3 \times 3 \times 5$, $20 \times 3 \times 1.5$ and $20 \times 3 \times 5 \text{ mm}^3$ for compression, bending and fracture toughness tests, respectively. The compression tests were carried out at ambient and elevated temperature, (up to 1173 K) using an Instron testing machine, driven at a crosshead speed of 0.1 mm·min$^{-1}$. Three-point bend tests were carried out at room temperature using an Instron testing machine driven at a constant crosshead speed of 0.1 mm·min$^{-1}$. Strain was precisely measured with a strain gauge attached to the tension side of the bend specimen. For the fracture toughness test, samples were prepared with U-notch on the polished and etched sample. U-notch width was set to 0.15 mm. Radius of curvature at the tip was set to 0.1 mm and length to approximately 0.3–0.4 mm. Fracture toughness measurements were accomplished by the Single-Edge-Notched Beam (SENB) method.

3. Results and Discussion

3.1 Reaction

To analyze the reactive arc-melted products, XRD analysis was performed on the as-cast and homogenized samples. Figure 1 shows the corresponding XRD patterns using Cu–K$_\alpha$ radiation for the composition of Ti–46Al–2Cr–3C. Peaks of raw materials are not detected in the as-cast sample, whereas those of the $\gamma$-TiAl matrix and Ti$_2$AlC reinforcements are detected together with a small amount of the additional Ti$_3$Al ($\alpha_2$) phase. As the composite was annealed at 1273 K, the amount of Ti$_3$Al decreased whereas the peak height of Ti$_2$AlC rose. To be noted is that not oxides, carbides, nor other phases especially involving chromium, such as Cr$_2$C$_3$ or Ti$_2$AlCr (β), were detected in all studied samples. EPMA analysis revealed that there was no Cr in the Ti$_2$AlC particles. These results suggest that Cr was almost dissolved into $\gamma$-TiAl matrix. In addition, the lattice parameters of $\gamma$-TiAl matrix were calculated from XRD patterns of the annealed samples with and without Cr addition. The axial ratio (c/a) was changed from 1.021 (Ti–50Al; a: 0.4002 nm; c: 0.4085 nm) to 1.015 (Ti–49Al–2Cr; a: 0.4000 nm; c: 0.4060 nm) by adding Cr into the matrix. These values are independent of carbon contents.

3.2 Microstructure observation

Optical micrograph of as-cast Ti–49Al–2Cr/10 vol% Ti$_2$AlC sample is shown in Fig. 2. The matrix structure consists of nearly lamellar grains, which is composed of alternative plates of $\gamma$ and $\alpha_2$. The reinforcement particles, Ti$_2$AlC, are uniformly dispersed in the matrix, having rod-like forms of 0.5–1 $\mu$m width and 5–10 $\mu$m length. There is no difference in the basic features of microstructure among the matrix compositions and the composites with varied volume fractions of reinforcements. The grain size of the matrix, calculated by the intercept method, is of widely range (especially in the alloy without reinforcements), and tends to decrease by the addition of the Ti$_2$AlC particles, as shown in Fig. 3. Chromium addition is also effective to induce grain refinement of the matrix. However, a wide variation of the matrix grain size is still observed in the non-reinforced alloy. In the Ti–Al system of stoichiometric Ti–50 mol%Al, the $\alpha$-grain crystallizes out of solution, and transforms to lamella ($\alpha_2 + \gamma$) on cooling. It is assumed that the melting point of Ti$_2$AlC is higher than the temperature set for arc-melting operations. These results sug-
gest that dispersed Ti₂AlC particles react as nucleation sites crystallizing the α-grains inhibiting grain growth.

The composites were then annealed at 1273 K for 144 h. As shown in Fig. 4, taken by SEM, the lamella grains in the matrix were transformed to γ-phases and very fine precipitates. TEM analysis revealed that fine Ti₂AlC particles of 300–500 nm precipitated along the γ-TiAl plates. As reported previously,11) the α₂ phase can dissolve carbon up to about 2% whereas the γ phase can dissolve less than about 0.5% in Ti–Al–C system. The precipitation of the fine Ti₂AlC particles is attributed to the decomposition of the Ti₃Al and supersaturated carbon in the Ti₁Al phase.

3.3 Mechanical properties

Three-point bending tests were performed on homogenized specimens at room temperature. Figure 5 shows stress strain curves of bend tests. Bending strength of the composites improved by increasing the volume fraction of Ti₂AlC in both matrix compositions. Stress level of the matrix with the addition of Cr is higher than that of without Cr at the same reinforcement composition. Plastic bending strain of Ti–49Al–2Cr at failure is also enhanced as compare to Ti–50Al because of the higher symmetry of the axial ratio in the γ-phase.23) In addition, twin deformation may be enhanced by the addition of Cr. Tsujimoto et al.24) report that the addition of Mn promotes the generation of deformation twins in Ti-rich TiAl. Room temperature ductility of the composites reached 0.5–0.9% plastic strain, which is nearly equal or higher than that of non-reinforced TiAl alloy.

Compression tests were performed five times on the Cr doped matrix specimens. Figure 6 shows the temperature dependence of the 0.2% compressive proof stress strength (average of five measurements, respectively) as a function of Ti₂AlC content. In this figure, data of non-reinforced TiAl alloy with no Cr addition is also plotted for comparison. The composites show a significant improvement in strength over the unreinforced matrix Ti–49Al–2Cr alloy both at room and elevated temperature, up to 1173 K. The compressive strength is also enhanced by the solid-solution hardening of chromium. The stress level of the Ti–49Al–2Cr compound and its composites is more than two or three times as high as that of the binary Ti–50Al alloy at 1173 K.

Fracture toughness tests have been carried out using the SENB method on the studied composites and non-reinforced alloy. The average results of five measurements, respectively, are summarized in Table 2. Fracture toughness values were improved from 11.7 MPa·m¹/₂ of non-reinforced TiAl
4. Conclusions

To improve the mechanical properties of γ-TiAl alloy, TiAl(Cr)/Ti₂AlC composites have been successfully synthesized by means of reactive arc-melting technique. Microstructure observations and several mechanical tests have been performed on these specimens to characterize their complex nature. The results are summarized as follows.

(1) The axial ratio of the γ-TiAl is lowered and closed to 1 by dissolving Cr into TiAl matrix. Grain refinement also takes place by the addition of Cr into TiAl matrix.

(2) The grain size of the matrix is found to decrease whereas wide variation of the grain size converges along the distribution of rod-like Ti₂AlC particle synthesized through the reaction.

(3) Matrix structure of as-cast specimens shows a fully lamella structure. Ti₃Al decomposes to TiAl and also to fine precipitated Ti₂AlC particles by conducting a homogenizing treatment at 1273 K.

(4) The composite materials have revealed higher strength and better fracture toughness with adequate ductility rather than those TiAl binary alloys. This improvement is attributed to the formation of Cr solid-solution for hardening, to the Ti₂AlC particle dispersion attained, and to the fine grain of the matrix.

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