Microstructure and Mechanical Properties of $L1_2-(Al, Cr)_3Ti/Ti_2AlC$ Composites Prepared by Combustion Synthesis *

Atsushi Kakitsuji¹, Hiroki Miyamoto¹, Hiroshi Mabuchi², Hiroshi Tsuda² and Kenji Morii²

¹Technology Research Institute of Osaka Prefecture, Izumi 594-1157, Japan

²Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan

$L1_2-(Al, Cr)_3Ti/Ti_2AlC$ composites have been prepared by the reactive arc-melting technique using elemental powders of Ti, Al, Cr, and C. Resulting composites have been reinforced using 4.5, 9, and 18 vol% Ti_2AlC in a matrix of $L1_2$ trialuminide Ti-61 mol% Al-13 mol% Cr alloy. The Ti_2AlC particles having a rod-like morphology of 1.5 μm width and 5–20 μm in length were homogeneously dispersed in the matrix. The matrix grain size was reduced through addition of Ti_2AlC particles. These composite materials have revealed higher mechanical properties (bending strength and fracture toughness) than that of the monolithic alloy. This improvement is attributed to the Ti_2AlC particles dispersion and to the fine grain of the matrix.

(Received October 24, 2001; Accepted December 26, 2001)

Keywords: intermetallic compound, $L1_2$ -trialuminide, composite material, Ti_2AlC , arc-melting, in-situ process, combustion synthesis, mechanical property, fracture toughness

1. Introduction

The $D0_{22}$ structure of Al_3Ti can be changed to the related cubic $L1_2$ structure with the addition of a third element, such as Zn, Ni, Cu, and Fe.^{1–4} Also, many studies on the Ti–Al–X (X=Ni, Fe, Cu, Mn, Cr, Ag, Pt, etc.) systems have focused on the mechanical properties of the ternary $L1_2$ trialuminide compounds.^{5–11} These potential (Al, X)₃Ti compounds have good oxidation resistance and some ductility because the $L1_2$ structure has the five independent slip systems condition required for homogeneous deformation. However, the ternary $L1_2$ compounds are still brittle in tension and/or bending, although they exhibit appreciable compressive ductility at ambient temperature. Recently, much work has been made on the microstructure, especially on the role of second phases and porosities generally induced by the homogenization treatment, and also on the microstructure-mechanical property relationships of the ternary $L1_2$ trialuminide compounds.^{12–16} Ti–67Al–8Cr alloy with $L1_2$ structure especially possesses intrinsic bend ductility at ambient temperature to some extent, and Ti–61Al–14Cr and Ti–61Al–13Cr alloys are more ductile in bending with a plastic strain of 0.9%. More interestingly, no porosities were observed after homogenization in these higher Cr content alloys.^{17,18} The major problems, however, which limit practical use of these compounds, are the low ductility and fracture toughness at ambient temperature and the poor strength at ambient and elevated temperatures. Fabrication of composite materials is a convenient route to make up those deficiencies. In practice, TiB_2 particle reinforced composites have been studied with the $L1_2$ trialuminides, Ti–67Al–9Fe, Ti–67Al–8Cr, and Ti–66Al–9Mn, as matrices.^{19,20}

Recently, self-propagating high temperature synthesis or combustion reaction synthesis using powder mixture compacts has been developed to produce intermetallics or ceramics. In this process, elemental powders are mixed and

compacted, and the temperature of the compacts is rapidly increased to initiate the synthesis reaction, and intermetallic or ceramic compounds are formed. It is also possible to perform *in-situ* synthesis of the composites by the addition of the third elements or extra compounds into the raw material, as shown in Fig. 1. $TiAl/Ti_2AlC$,^{21,22} $TiAl/Ti_2AlN + TiB_2$,^{23,24} and $TiAl/Ti_2AlC + TiB_2$ ²⁵ composites were developed by this technique. $L1_2-(Al, Cr)_3Ti/Ti_2AlN$ ²⁶ and $L1_2-(Al, Cr)_3Ti/TiB_2 + Ti_2AlC$ ²⁷ composites were also prepared by this route. One major defect of this process, however, is the highly porous nature of the products. The porosity has to be substantially reduced by efficient techniques if structural applications are required. Recent processes used to fabricate fully dense synthesis products include the ‘XD’ process,^{28,29} reactive hot pressing,³⁰ and reactive HIP’ing.³¹ In these processes, large pressure is required during or after the synthesis reaction. In the present investigation, densification was achieved by a newly developed reactive arc-melting technique.^{26,27,32} Using this process, it becomes possible to form the intermetallic matrix and ceramic dispersoids, and to produce a composite material fully dense without applying external pressure. In this work, the $L1_2$ trialuminide Ti–61Al–

Fig. 1 Schematic representation of the reactive synthesis for producing composite materials.

*This Paper was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Fukuoka, on September 23, 2001.

Table 1 Powder compositions of studied alloys, the estimated matrix composition and the calculated volume fraction for reinforcement, Ti_2AlC .

Alloy (powder, mol%)	Matrix (mol%)	Ti_2AlC (vol%)
Ti-61Al-13Cr	Ti-61Al-13Cr	0
Ti-59.2Al-12.3Cr-1.3C	Ti-61Al-13Cr	4.5
Ti-57.4Al-11.7Cr-2.5C	Ti-61Al-13Cr	9
Ti-53.9Al-10.4Cr-5.0C	Ti-61Al-13Cr	18

13Cr alloy base composites reinforced with Ti_2AlC particles were produced by this new technique and microstructure and mechanical properties of these composites are examined.

2. Experimental Procedure

High purity elemental powders of titanium (99.5 mass% purity, -350 mesh; containing 3500 ppm of 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. These powders were mixed in a mortar for 10 minutes to prepare compositions for L1_2 matrix, with and without reinforcement, as shown in Table 1. It is assumed that the composite consists of the two phases, *i.e.*, L1_2 -(Al, Cr) $_3$ Ti and Ti_2AlC . The estimated matrix composition and calculated volume fraction of the reinforcement are also given in Table 1. The powder mixture, about 5 g, was pressed at about 260 MPa into a cylindrical compact of 10 mm diameter. Several compacts, approximately 30 g in total, were fabricated into an ingot by non-consumable electrode arc melting under an argon atmosphere. The combustion reaction occurred immediately after inducing the electric discharge between the electrode and the compacts. The reaction product was effectively arc-melted. The arc-melted buttons were re-melted three times to promote homogeneity and densification. The as arc-melted composites were annealed at 1423 K for 48 h for better homogenization. The microstructures of the homogenized composites were characterized using X-ray diffraction (XRD), optical microscope, and electron probe microanalysis (EPMA).

The homogenized specimens were cut to rods with $20 \times 3 \times 1.5$ or $20 \times 3 \times 5 \text{ mm}^3$ in size for bending and fracture toughness tests, respectively. These specimens were mechanically polished, electropolished, and etched with Kroll's reagent ($\text{HF} + \text{HNO}_3$) for optical microstructure observation. Three-point bend tests were carried out at room temperature using an Instron testing machine driven at 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, the 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 set at 0.1 mm and length at approximately 0.3–0.4 mm. Fracture toughness measurements were accomplished by the Single-Edge-Notched Beam (SENB) method.³³⁾ These mechanical tests were performed more than three samples.

Fig. 2 The XRD patterns of 18 vol% Ti_2AlC composite: (a) as-cast, (b) after homogenized.

3. Results and Discussion

3.1 Microstructure analysis

To analyze the reactive arc-melted products, XRD analysis was performed on the as-cast and homogenized samples. Figure 2 shows the corresponding XRD patterns using Cu-K α radiation for the composition of Ti-53.9Al-10.4Cr-5.0C. In the as-cast sample, the peaks of raw materials are not detected, whereas those of the L1_2 trialuminide (Al, Cr) $_3$ Ti as matrix and Ti_2AlC as reinforcements are detected together with a slight amount of the additional phase such as Cr_2Al . In the higher Cr content L1_2 trialuminide, Ti-61Al-13Cr alloy, the Cr_2Al phase is slightly formed as reported elsewhere.^{17,18)} As the composite was annealed at 1423 K, the detected phases were same as in the case of the as-cast sample except for the decomposition of the Cr_2Al phase. No oxide phases are detected in these XRD patterns. The composition of the matrix was revealed by EPMA analysis to be 26.9 mol% Ti, 60.8 mol% Al, and 12.3 mol% Cr. The difference in the matrix composition among the composite specimens was negligible, indicating that all composites obtained by the present investigation have the same matrix of Ti-61Al-13Cr alloy, as expected from Table 1.

Figure 3 shows an optical micrograph of the 18 vol% Ti_2AlC composite after annealing at 1423 K. There were few pores produced by the reaction synthesis, or porosities induced by the homogenizing treatment, as observed in the other annealed L1_2 -trialuminide. It is seen that the reinforcing Ti_2AlC particles are uniformly distributed in the matrix. Ti_2AlC particles are rod-like in shape with sizes of $1.5 \mu\text{m}$ width and $5\text{--}20 \mu\text{m}$ in length. There is no difference in the basic feature of microstructure among the composites with varied volume fractions of reinforcements. However, the grain size of the matrix, calculated by the intercept method, is widely distributed (especially in the alloy without reinforcements), and tends to decrease by the addition of the Ti_2AlC particles, as shown in Fig. 4. It is assumed that the melting point of the Ti_2AlC phase is higher than the temperature set for arc-melting operations. The dispersed Ti_2AlC particles react as the nucleation sites of the L1_2 grains. Thus, because of

Fig. 3 Optical micrograph of the 18 vol% Ti_2AlC composite after homogenizing.

Fig. 4 Change in the matrix grain size with the volume fraction of Ti_2AlC .

the dispersed particulate reinforcements, these composites become much more resistant against recrystallization and grain growth than the single phase alloys.

3.2 Mechanical properties

Three-point bending tests were performed on the homogenized specimens at room temperature. Figure 5 shows stress strain curves from bend tests. In this figure, the data for the $Ti-61Al-13Cr$ alloy with no reinforcement prepared by the reactive arc-melting is also plotted for comparison. The bending strength of composites increases with increasing volume fraction of reinforcements to about 400–510 MPa (0.1% proof strength). Whereas, the plastic bending strain at ambient temperature decreases gradually by increasing content of the Ti_2AlC reinforcement to about 0.6–0.2%. The lattice parameter of $L1_2-(Al, Cr)_3Ti$ phase was changed from 0.3944 to 0.3950 nm after preparing the composites. This result suggests that carbon may dissolve into the $L1_2$ matrix. The ductility of the composite is lowered because the reinforcement makes the composite brittle.

Fracture toughness tests were carried out using the SENB method for both the studied composites and non-reinforced alloy. The results are shown in Fig. 6. Fracture toughness value, K_{Ic} , is plotted versus the volume fraction of the reinforcement. The fracture toughness was slightly improved from 11.0 $MPa \cdot m^{1/2}$ to 11.5–12.8 $MPa \cdot m^{1/2}$. Figure 7 shows propagation of a crack occurred in the 18 vol% Ti_2AlC com-

Fig. 5 Stress-strain curves of bend test at ambient temperature.

Fig. 6 Fracture toughness as a function of volume fraction of reinforcement.

posite during the fracture toughness test. A zigzag crack run, that is, crack deflection is observed. The zigzag crack propagation in the composite is caused by the presence of dispersed particulate reinforcements. Thus, reinforcing Ti_2AlC particles are main obstacles to crack propagation, thereby enhancing fracture toughness of the composite. Therefore, in the composites thus prepared, it is expected that the reinforcing particles hinder recrystallization and grain growth of the matrix, and the decreased grain size should lead to improved fracture toughness.

4. Conclusion

The reactive arc-melting technique is found effective for the improvement of the mechanical properties of titanium trialuminides, $L1_2-(Al, Cr)_3Ti/Ti_2AlC$ composites at ambient temperature. The compacts of titanium, aluminum, chromium, and carbon were reacted and arc-melted. A composite of $L1_2$ trialuminide $Ti-61Al-13Cr$ alloy with finely and homogeneously distributed Ti_2AlC particles was successfully fabricated. Preparation of $L1_2-(Al, Cr)_3Ti$ matrix composites reinforced by the Ti_2AlC particles was conducted to improve the mechanical properties at ambient temperature (bending strength and fracture toughness). Two main parameters explain the mechanical properties improvement of these composites; namely: the presence of Ti_2AlC dispersoids and the fine grain nature of the matrix.

Fig. 7 Optical micrograph of 18 vol% Ti_2AlC composite after fracture toughness testing.

Acknowledgements

The authors acknowledge the Research Institute for Advanced Science and Technology, Osaka Prefecture University. The authors would like to thank Dr. S. D. De la Torre (Advanced Materials Research Center CIMAV) for his valuable discussions and encouragement.

REFERENCES

- 1) A. Raman and K. Schubert: *Z. Metallkde.* **56** (1965) 40–43.
- 2) A. Raman and K. Schubert: *Z. Metallkde.* **56** (1965) 99–104.
- 3) P. Viridis and U. Zwicker: *Z. Metallkde.* **62** (1971) 46–51.
- 4) A. Seibold: *Z. Metallkde.* **72** (1981) 712–719.
- 5) K. S. Kumar and J. R. Pickens: *Scr. Metall.* **22** (1981) 1015–1018.
- 6) S. C. Huang, E. L. Hall and M. F. X. Gigliotti: *J. Mater. Res.* **3**(1) (1988) 1–7.
- 7) J. Tarnacki and Y.-W. Kim: *Scr. Metall.* **22** (1988) 329–334.
- 8) S. Zhang, J. P. Nic and D. E. Mikkola: *Scr. Metall. Mater.* **24** (1990) 57–62.
- 9) H. Mabuchi, K. Hirukawa and Y. Nakayama: *Scr. Metall.* **23** (1989) 1761–1766.
- 10) H. Mabuchi, K. Hirukawa, H. Tsuda and Y. Nakayama: *Scr. Metall. Mater.* **24** (1990) 505–508.
- 11) W. O. Powers and J. A. Wert: *Metall. Trans.* **21A** (1990) 145–151.
- 12) D. D. Mysko, J. B. Lumsden, W. O. Powers and J. A. Wert: *Scr. Metall.* **23** (1989) 1827–1830.
- 13) D. G. Morris and S. Gunter: *Acta Metall. Mater.* **40** (1992) 3065–3073.
- 14) N. Durlu and O. T. Inal: *Mater. Sci. Eng.* **A152** (1992) 67–75.
- 15) M. B. Winnicka and R. A. Varin: *Metall. Trans.* **24A** (1993) 935–946.
- 16) Z. L. Wu, D. P. Pope and V. Vitek: *Mat. Res. Soc. Symp. Proc.* **288** (1993) 367–372.
- 17) Y. Nakayama and H. Mabuchi: *Intermetallics* **1** (1993) 41–48.
- 18) H. Mabuchi, H. Tsuda, T. Matsui and K. Morii: *Mater. Trans., JIM* **38** (1997) 560–565.
- 19) M. S. DiPietro, K. S. Kumar and J. D. Whittenberger: *J. Mater. Res.* **6** (1991) 530–538.
- 20) K. S. Kumar, M. S. DiPietro and J. D. Whittenberger: *Acta Metall. Mater.* **41** (1993) 1379–1389.
- 21) H. Mabuchi, K. Harada, H. Tsuda and Y. Nakayama: *ISIJ Int.* **31** (1991) 1272–1278.
- 22) R. Ramaseshan, A. Kakitsuji, S.K. Seshadri, N. G. Nair, H. Mabuchi, H. Tsuda, T. Matsui and K. Morii: *Intermetallics* **7** (1999) 571–577.
- 23) H. Mabuchi, H. Tsuda and Y. Nakayama: *Scr. Metall. Mater.* **32** (1995) 253–257.
- 24) A. Kakitsuji, H. Miyamoto, H. Mabuchi, H. Tsuda and K. Morii: *Mater. Trans., JIM* **40** (1999) 942–945.
- 25) H. Mabuchi, S. Shiraishi, H. Tsuda and K. Morii: *J. Jpn. Soc. Powder and Powder Metal.* **44** (1997) 535–541.
- 26) H. Nagayama, R. Ramaseshan, H. Mabuchi, H. Tsuda, H. Matsui and K. Morii: *Mater. Trans., JIM* **41** (2000) 1064–1067.
- 27) H. Mabuchi, H. Morimoto, A. Kakitsuji, H. Tsuda, T. Matsui and K. Morii: *Scr. Mater.* **44** (2001) 2503–2508.
- 28) A. R. C. Westwood: *Metal. Trans.* **19A** (1988) 749–758.
- 29) D. Lewis: *Metal Matrix Composites: Processing and Interfaces*, ed. By R. K. Everett and R. J. Arsenault (Academic Press, 1991) pp. 121–149.
- 30) J. C. Rawers and W. R. Wzresinski: *Scr. Metall. Mater.* **24** (1990) 1985–1990.
- 31) A. Kakitsuji, H. Miyamoto, H. Shingu, H. Mabuchi, H. Tsuda and K. Morii: *Rev. High Pressure Sci. Technol.* **7** (1998) 1075–1077.
- 32) A. Kakitsuji, H. Miyamoto, H. Mabuchi, H. Tsuda and K. Morii: *Mater. Trans.* **42** (2001) 1897–1900.
- 33) R. F. Pabst: *Fracture Mechanics of Ceramics, Vol. 2, Microstructure, Materials and Applications*, ed. by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, 1974) pp. 555–565.