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Fabrication and properties of novel composites in the system Al–Zr–C

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Composite bodies in the system Al–Zr–C, with about 95% relative density, were obtained by heating the compact body of powder mixture consisting of Al and ZrC (5 : 1 mol %) in Ar at 1100–1500 °C for various lengths of time. Components of the material heated at more than 1200 °C were Al, Al_3Zr, ZrC and $AlZrC_2$. The Al_3Zr exhibited plate-like aggregation, and its size increased with increasing temperature. In the material heated at 1500 °C for 1 h, the largest plate-like Al_3Zr aggregation was 2000 μm long and 133 μm thick. Then the $AlZrC_2$ was present as well-proportioned hexagonal platelet particles with a 8–9 μm diameter and a 1–2 μm thickness in the interior of the plate-like Al_3Zr aggregation and Al matrix phase. The average three-point bending strength of the bodies was 140–190 MPa, and the maximum strength was 203 MPa in the body heated at 1300 °C for 1 h. The body heated at 1500 °C for 1 h showed high oxidation resistivity to air up to 1000 °C.

1. Introduction

Recently composite materials composed of ceramics and metals (alloys) are extensively studied because they have excellent properties of both. It is known that fracture toughness of the composites is remarkably improved over that of monolithic ceramic materials. In selecting a metal for fabricating the composites, Al can be noticed due to its light weight, low melting point (660 °C) [1] and high processability. Up to now, for example, Al–Al_2O_3 [2–9], Al–AlN [10, 11], Al–carbon fiber [12, 13], Al (alloys)–SiC [14–16], and Al–(TiC and/or TiB_2) [17, 18] composites were studied on fabrication methods and/or their mechanical properties. However Al matrix ceramic composites have not been used as much as another cermet materials [19, 20] due to the deterioration of mechanical properties at higher temperatures.

Despite the fact that ZrC has superior properties such as a high melting point (3532 °C [21]) and great hardness [22], it has been hardly used due to the difficulty of its sintering [23]. In this study, as one of the fundamental researches on Al matrix composites with high resistivity to temperature, we investigated fabricating and characterizing novel composites in the system Al–Zr–C. Here the composite bodies were obtained by heating the compact body of powder mixture consisting of Al and ZrC. Effects of temperature and duration time on density, microstructure and reaction products were examined. We also discuss a change of the formed microstructure during heating and evaluated its mechanical properties and oxidation resistivity to air.

2. Experimental procedure

2.1. Sintering

A powder mixture consisting of ZrC (1–2 μm) and Al (av. size 10 μm) (5 : 1 mol ratio), which were reagent grade, was uniaxially pressed with 80 MPa into a green body of $5 \times 6 \times 45$ mm^3. The green body was placed in an alumina boat and then was covered with the same powder mixture to prevent a slight oxidation at the surface of the compact. The boat was inserted into an alumina tube with a diameter of 42 mm and a length of 600 mm. The tube was placed in an electric furnace ($400 \times 350 \times 400$ mm^3). Ar was flowed into the tube at a rate of 0.2l/min, and the furance was heated at various temperatures for various lengths of time. Both the heating and cooling rate were then 600 °C/h.

2.2. Analysis

After heating, a dense composite body was obtained. Relative density of the material was calculated by the values of the apparent density, using the Archimedian method, and the true density, using a pycnometer. Reaction products of the body were identified using a powder X-ray diffractometer (XRD). Microstructures were observed using an optical-reflecting microscope and a scanning-electron microscope (SEM). To clarify the components inside the body, the surfaces of the polished body, heated at 1500 °C for 1 h, was analyzed by an electron probe microanalyzer (EPMA). If necessary for the analysis, the body was soaked in 17.5% hydrochloric acid.

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2.3. Properties

For a three-point bending strength test, the bodies were cut into pieces of $3 \times 4 \times 45$ mm^3 and the surfaces were polished using fine Al_2O_3 lapping sheet. The span distance and the crosshead speed of the bending strength machine were 30 mm and 0.5 mm/min, respectively. In each heating condition, six test specimens were prepared.

In order to evaluate the oxidation resistivity of the body to air, a polished piece, which was cut into $4 \times 4.5 \times 5$ mm^3 from the body heated at 1500 °C for 1 h, was reheated at a rate of 10 °C/min up to 1000 °C and held for various times in an electric furnace. After the reheating treatment, the thickness of the oxidation layer was observed.

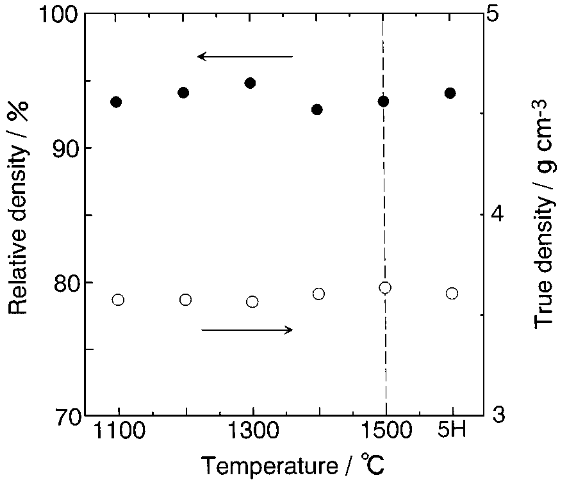

Figure 1 Changes in the relative density and the true density of the materials heated in Ar with temperature and duration time at 1500 °C.

3. Results and discussion

3.1. Analysis

After the body was heated in Ar at 1500 °C, it shrank to 77 vol % of the initial green body, but the shape did not change in spite of the presence of Al liquid. Fig. 1 shows changes of the true and the relative density of the bodies with temperature and duration time at 1500 °C. Regardless of changes in heating temperature, the true and the relative density of the bodies were almost the same—about 3.6 g/cm^3 and 93–95% respectively. Fig. 2 is optical–reflecting microphotographs of the polished bodies heated at 1100–1500 °C for 1 h. In the body heated at more than 1200 °C, needle-like aggregations were observed. The average length/diameter of 10 aggregations in the body heated at 1200, 1300 and 1500 °C for 1 h were 820/85, 1038/101 and 1550/122 (μm) respectively. With increasing temperature, the size of the aggregations increased, while the number of the aggregations decreased. The maximum size of the aggregation in the body heated at 1500 °C for 1 h was 2000 μm length and 133 μm thickness. Fig. 3 is a photograph of a polished piece of the body that was heated at 1500 °C for 1 h and then soaked in hydrochloric acid. The shape of the aggregation was observed like a pillar and/or plate, henceforth we describes it as a plate-like aggregation. Fig. 4 shows changes of the reaction products of the bodies with temperature and duration time at 1500 °C. At 800 °C, in addition to the starting materials, Al_3Zr alloy was detected. At 900 °C, $Al_3Zr_2C_5$ was newly

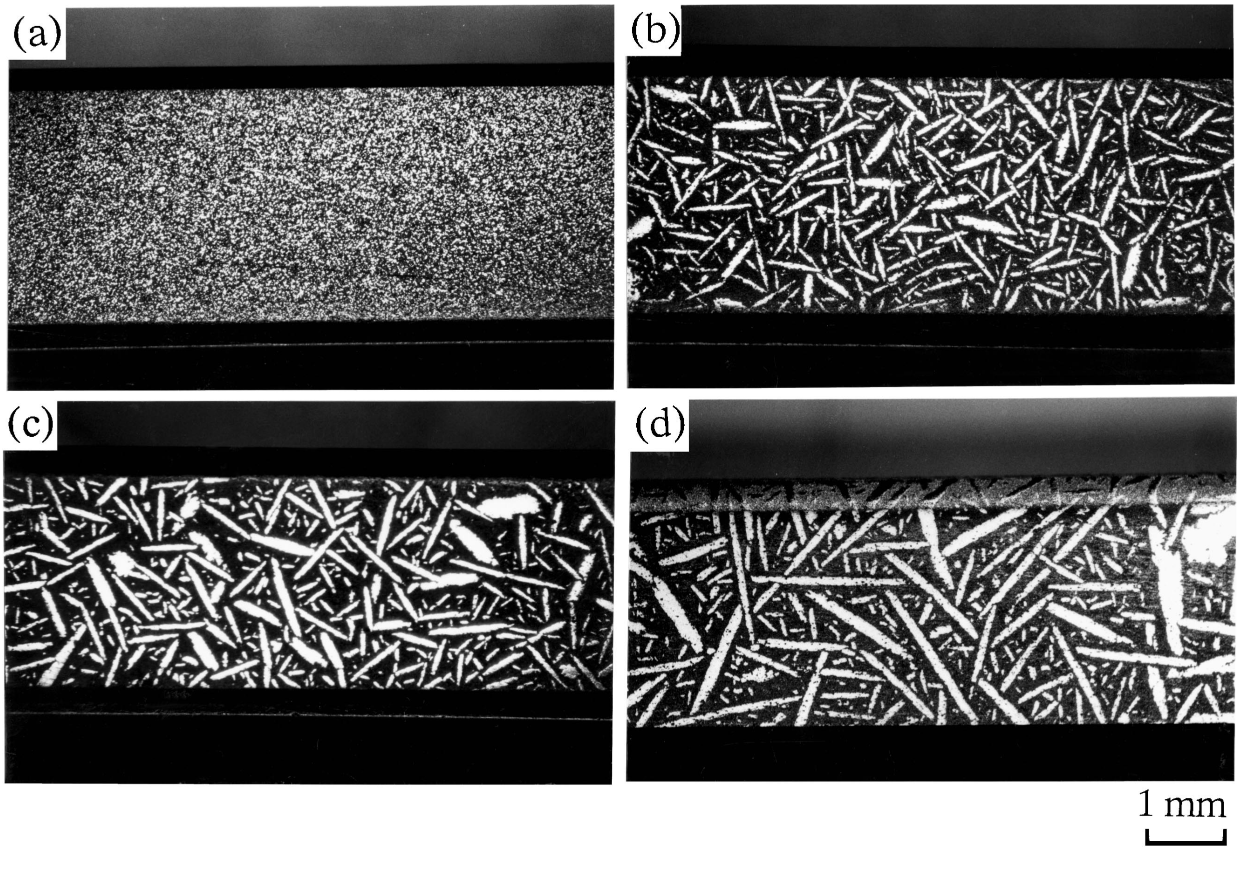

Figure 2 Optical-reflecting microphotographs of the polished materials heated in Ar at (a) 1100, (b) 1200, (c) 1300 and (d) 1500 °C for 1 h.

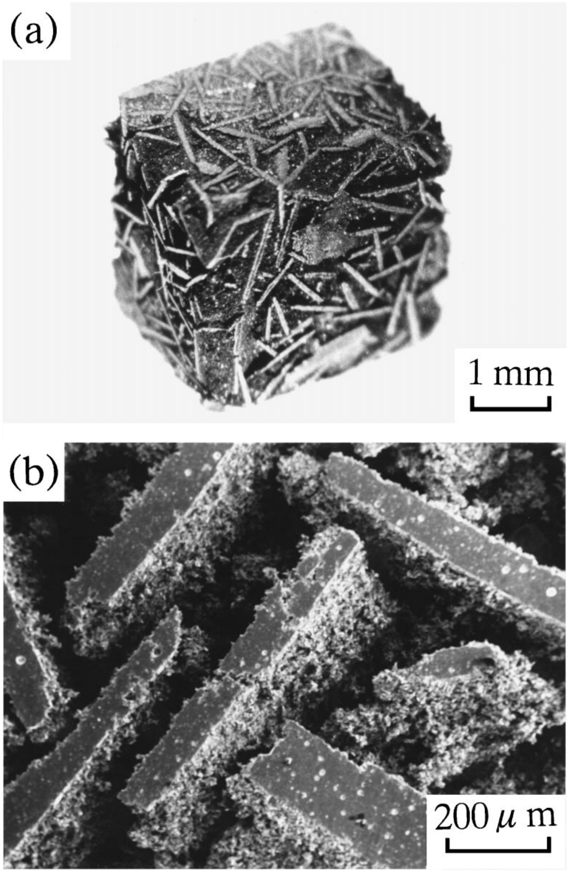

Figure 3 Photographs of a polished piece of the material, which was heated in Ar at 1500 °C for 1 h and then soaked in 17.5% hydrochloric acid for 5 min.

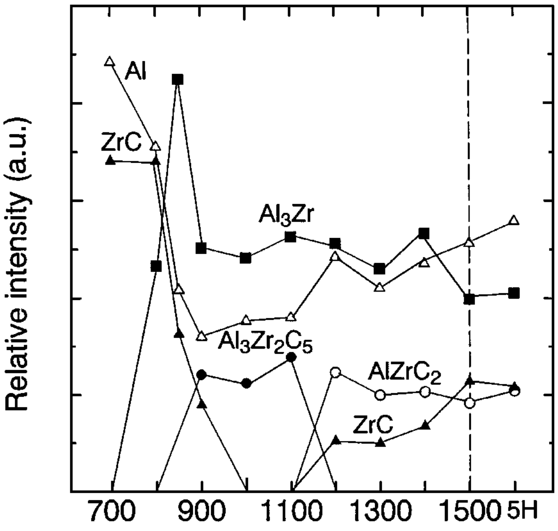

Figure 4 Changes in the reaction products of the materials heated in Ar with temperature and duration time at 1500 °C.

detected, while the intensity of XRD peaks of ZrC decreased. Components of the body heated at 1000 and 1100 °C were identified as Al_3Zr, Al and $Al_3Zr_2C_5$, and the peaks of XRD of ZrC were not detected. In the body heated at more than 1200 °C, Al_3Zr, Al, $AlZrC_2$ and ZrC were detected. The reason why the shape of the green body did not change during heating in Ar at higher temperature in spite of the presence of Al liquid is believed by us to be that Al_3Zr and ZrC, whose melting points are 1580 °C [24] and 3532 °C, respectively, were present in the body. The melting points of $Al_3Zr_2C_5$ and $AlZrC_2$ have not been accurately measured yet. Fig. 5 is (A) a SEM and Al image made by EPMA photographs of the polished body, heated at 1500 °C for 1 h and (B) a SEM photograph of the same body after soaking in hydrochloric acid. Al was strongly detected in the matrix phase around the plate-like aggregation, as shown in Fig. 5A. By the chemical-leaching treatment,

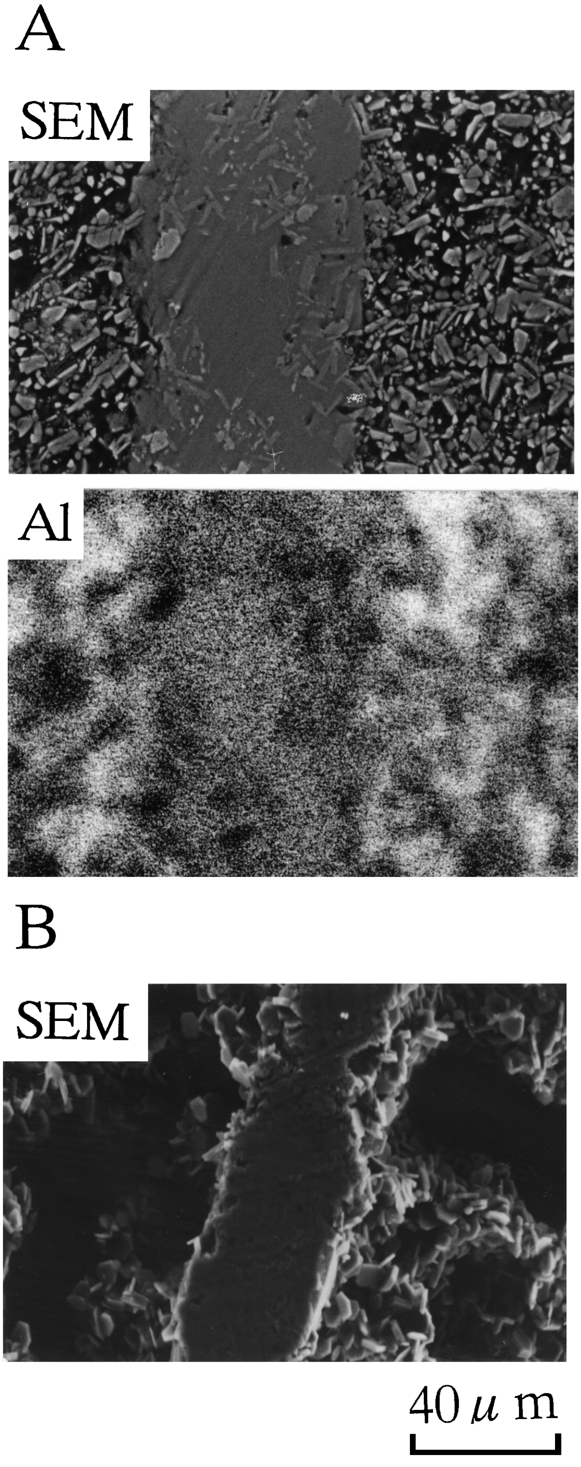

Figure 5 (A) SEM and Al image by EPMA photographs of the polished material heated at 1500 °C for 1 h and (B) SEM photograph of the same material after soaking in hydrochloric acid.

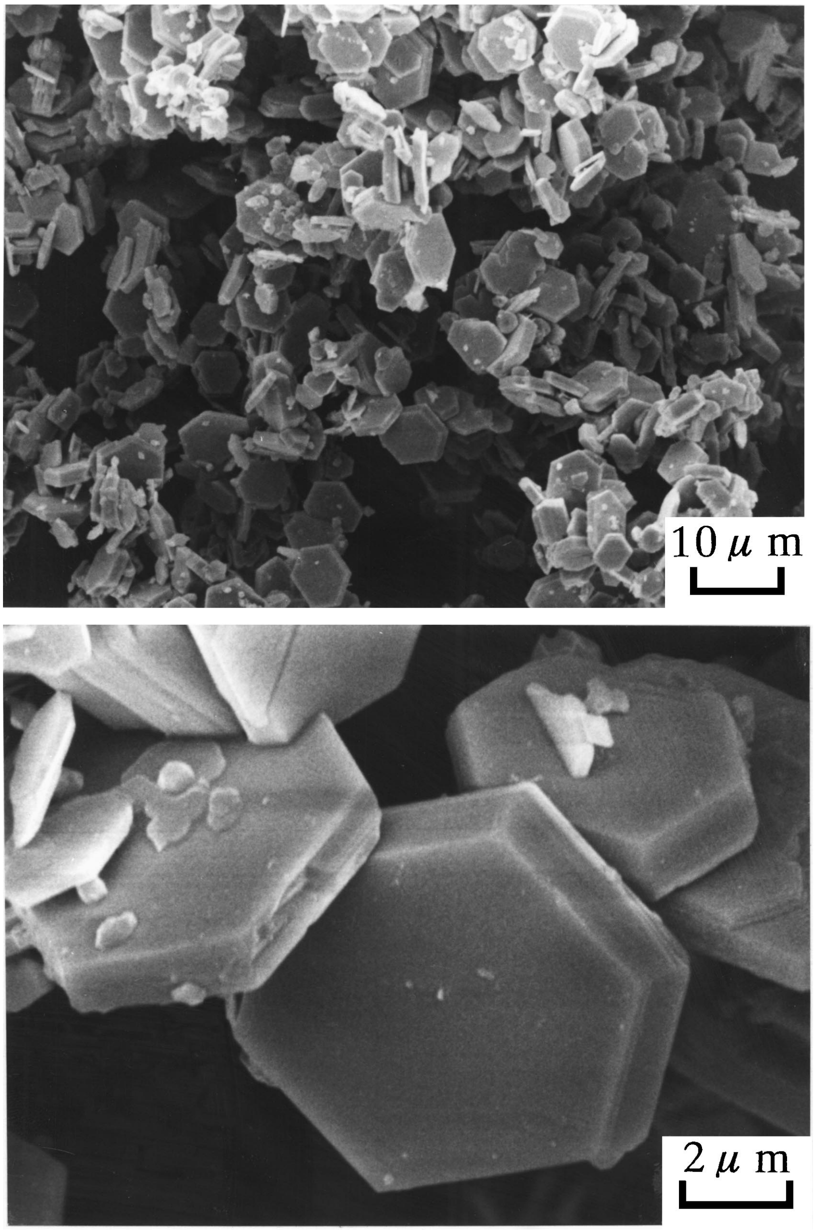

Figure 6 SEM photograph of the remaining dark brown powder after the material, heated at 1500 °C for 1 h, was soaked in 17.5% hydrochloric acid for a day.

the plate-like aggregation at the surface seemed to be slightly floated, since the matrix phase was dissolved, as shown in Fig. 5B. Therefore, Al is considered to be present in the matrix phase. According to the SEM photographs in Fig. 5, smaller platelet particles were observed in the interior of the plate-like aggregation and the Al matrix phase. After the body was soaked in hydrochloric acid for a day, the plate-like aggregation was also dissolved, but a dark brown powder remained. Fig. 6 shows SEM photographs of the powder. It was clear that the powder was mostly composed of the platelet particles observed in the entire body, and their shape was a well-proportioned hexagonal with 8–9 μm diameter and 1–2 μm thickness. Fig. 7 shows a XRD pattern of the powder. Since main peaks belong to $AlZrC_2$, most of the hexagonal platelet particles were identified as $AlZrC_2$. As a result, the plate-like aggregation corresponded to the characteristics of an Al_3Zr alloy. Consequently, the body was roughly classified into two parts; that is, one is hexagonal platelet $AlZrC_2$ particles, containing an Al part (matrix phase in appearance) and the other is hexagonal platelet $AlZrC_2$ particles, containing an Al_3Zr part (plate-like aggregation in appearance). A small amount of ZrC, which was redetected in the body heated at more than 1200 °C, seems to be also present in the entire body.

3.2. Formation process of the microstructure

We discuss a formation process of the microstructure of the body heated at more than 1200 °C as shown in Fig. 2 as follows. During heating, Al being a low melting point metal melts first in the starting body compact. Since ZrC becomes an unstable phase in the Al liquid, Zr and C can dissolve in the liquid. In heating at more than 800 °C, Zr was saturated with the liquid, and then the surplus Zr reacted with Al to form the Al_3Zr alloy. On the other hand, it is believed that C takes an important role of nucleation and nuclear growth of $Al_3Zr_2C_5$ and $AlZrC_2$

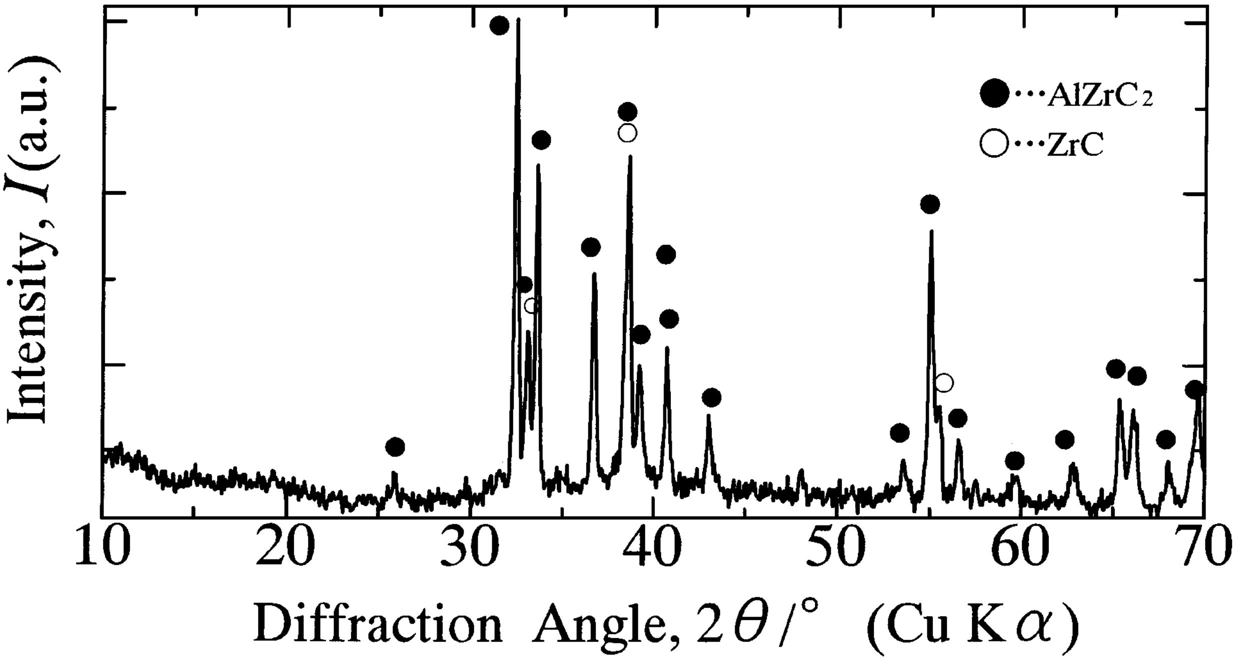

Figure 7 XRD pattern of the remaining dark brown powder after the material, heated at 1500 °C for 1 h, was soaked in 17.5% hydrochloric acid for a day.

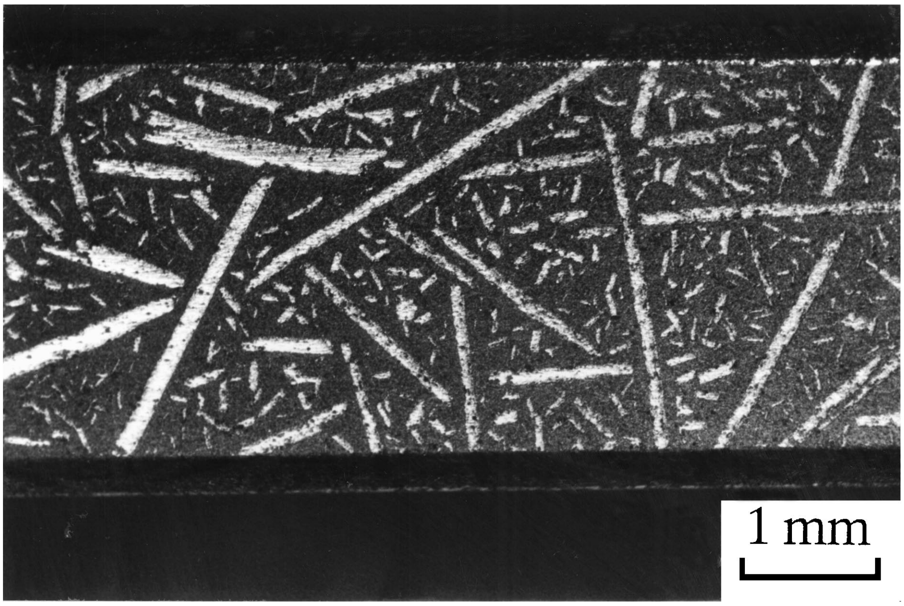

Figure 8 Optical reflecting microphotograph of the polished material heated at 1500 °C in Ar for 5 h.

particles at higher temperature. Since the precipitated $AlZrC_2$ particle exhibits a well-proportioned hexagonal platelet shape, the particle is believed to grow in the liquid. Fig. 8 is an optical-reflecting microphotograph of the polished body heated at 1500 °C for 5 h. As compared with the body heated at 1500 °C for 1 h, as shown in Fig. 2 (d), the larger plate-like Al_3Zr aggregations became larger (the maximum length was 2950 μm), while the number of the smaller aggregations decreased. As a result, the plate-like Al_3Zr aggregation is considered to grow by resolution-precipitation reaction. At 1200 °C, the rate of the resolution-precipitation reaction of the Al_3Zr alloy remarkably becomes fast to form a large plate-like Al_3Zr aggregation during heating and cooling. Therefore, in heating at more than 1200 °C, the plate-like Al_3Zr aggregation grows, including the hexagonal platelet $AlZrC_2$ particles in appearance. Fig. 9 shows a schematic drawing for the change of the microstructure during heating and cooling at temperatures above 1200 °C.

3.3. Mechanical properties

Fig. 10 shows the three-point bending strength of the material heated to 1200–1500 °C for 1 h and 1500 °C for 5 h. The average strength of the material was 140–190 MPa. The material heated to 1300 °C for 1 h had the greatest strength. Its value was 203 MPa. The strength of the bodies heated at more than 1300 °C was decreased with increasing temperature. Bending strength is considered to be related to the grain size. Fig. 11(a) is an optical-reflecting microphotograph of the bottom

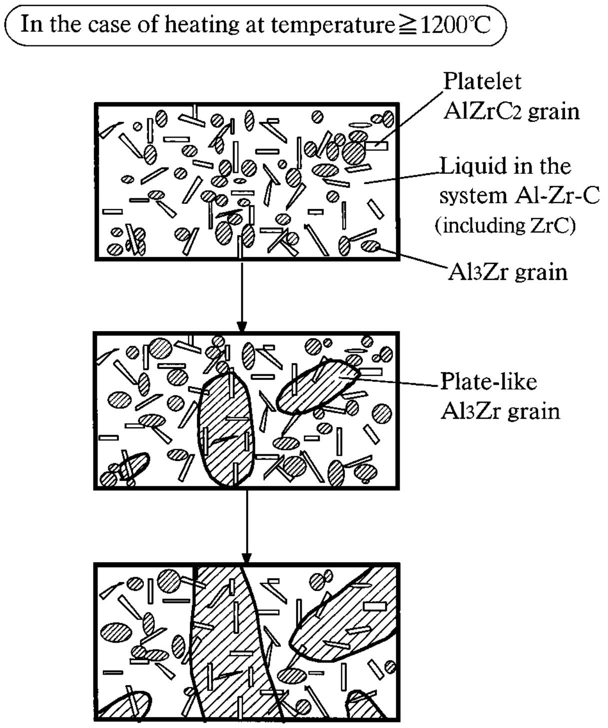

Figure 9 Schematic drawing for the change of the microstructure during heating and cooling as heated at more than 1200 °C.

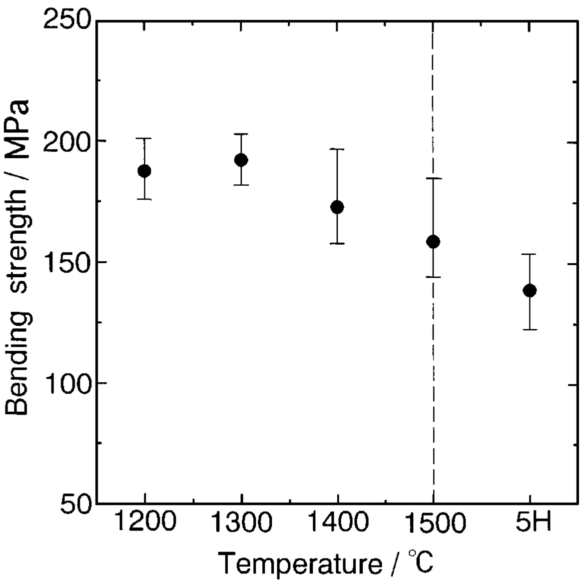

Figure 10 Three-point bending strength of the materials heated in Ar at 1200–1500 °C for 1 h and 1500 °C for 5 h.

plane, where a crack was initiated, (b) and (c) are photographs of both fractured surfaces of the sample after a bending-strength test. Since the test sample was the body heated at 1500 °C for 1 h, the size of the plate-like Al_3Zr aggregation was larger than that in the body heated to a lower temperature. It was observed that the crack began at the plate-like Al_3Zr aggregation and propagated inside of it. The strength of the plate-like Al_3Zr aggregation, namely hexagonal platelet $AlZrC_2$ particles containing the Al_3Zr part, seems to be lower than that of the matrix phase, namely hexagonal platelet $AlZrC_2$ particles containing an Al part. Therefore, growth of the plate-like Al_3Zr aggregation with increasing temperatures is considered to weaken the strength of the body.

3.4. Oxidation resistivity

Fig. 12 is a microphotograph of the cut surface of the material heated in Ar at 1500 °C for 1 h after being exposed to air for 10 h at 1000 °C. The thickness of the formed oxidation layer near the surface of the body was almost the same—100 μm after 1 and 10 h. The material is considered to have a high-oxidation resistivity to air up to 1000 °C. According to the XRD analysis, crystal phases in the oxidation layer were identified as Al_2O_3 and ZrO_2.

4. Conclusions

By heating a compact body of powder mixture consisting of Al and ZrC (5 : 1 mol %) in Ar at 1000–1500 °C, novel composite materials were created. Relative density, reaction products, microstructure, three-point bending strength and oxidation resistivity to air were examined. Following are the results:

1. The composite body did not change its shape in Ar up to 1500 °C. The true and the relative density of the bodies heated at more than 1100 °C were about 3.6 g/cm^3 and 93–95% respectively. In heating at 1200–1500 °C for 1 h, the materials were identified as Al, Al_3Zr, ZrC and $AlZrC_2$. The Al_3Zr alloy exhibited plate-like aggregation, and its size increased with increasing temperature. In the material heated at 1500 °C for 1 h, the maximum plate-like Al_3Zr aggregation was 2000 μm length and 133 μm thickness. Then the $AlZrC_2$ exhibited well-proportioned hexagonal platelet particles with a 8–9 μm diameter and a 1–2 μm thickness and in its interior was the plate-like Al_3Zr aggregation and Al matrix phase. ZrC seemed to be also present in the entire material.
2. The average three-point bending strength of the materials was 140–190 MPa, and the maximum strength was 203 MPa in the material heated to 1300 °C for 1 h. The material heated at 1500 °C for 1 h showed high oxidation resistivity to air up to 1000 °C.

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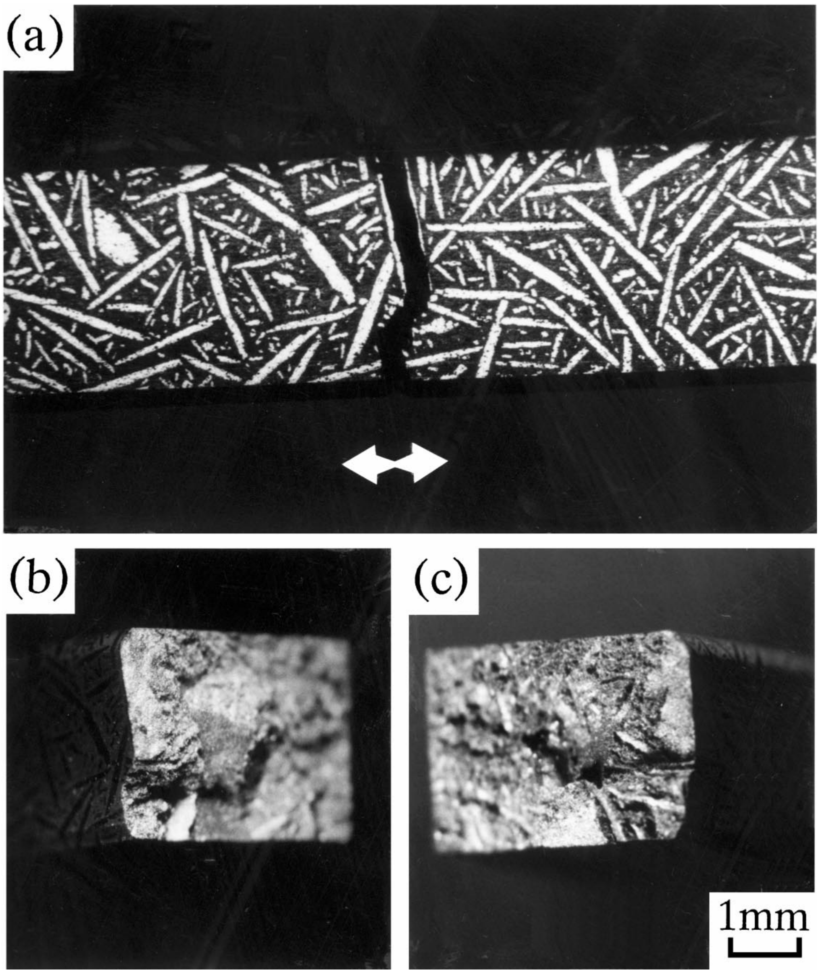

Figure 11 (a) optical reflecting microphotograph of the bottom plane, where cracking began; (b) and (c) are photographs of both fractured surfaces of the sample, which was obtained by heating at 1500 °C for 1 h, after a bending-strength test.

Figure 12 Microphotograph of the cut surface of the material, heated in Ar at 1500 °C for 1 h after exposing to air at 1000 °C for 10 h.

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