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$AlZrC_2$ synthesis

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Abstract

$AlZrC_2$ was synthesized using a direct solid-state method. Various types of carbon were used as starting materials together with aluminum zirconium carbide powders. The effect of different carbon on the formation of Al–Zr–C compounds formation were investigated. The atomic arrangement of carbon affects the Al–Zr–C compounds formation, i.e., crystalline carbon facilitates $Zr_2Al_3C_5$ formation while glassy carbon facilitates $AlZrC_2$ formation. High purity $AlZrC_2$ was prepared from the appropriate mol ratio of Al:ZrC:glassy carbon by heating in vacuum at 1600 °C for 1 h. However, a little amount of $Zr_2Al_3C_5$ still formed due to graphitization of glassy carbon at high temperature. Glassy carbon from sugar showed a lower degree of crystallization (graphitization) than glassy carbon from phenolic resin. Finally, the obtained two phase specimen was ground and heat treated again using pulse electric current sintering to produce single $AlZrC_2$.

Keywords: D. Carbide; D. Carbon; $AlZrC_2$; Graphitization

1. Introduction

Carbides are extensively used in various fields due to their excellent properties. For instance, SiC [1] is widely used as an engineering material because of its high-temperature fracture strength and creep resistance. The remarkable thermal stability and chemical inertness of B_4C make it well suited for applications requiring high stiffness or good wear resistance [2]. ZrC is an important structural material owing to its high strength and good corrosion resistance [3].

Several complex carbides have recently been synthesized and studied. For example, $Al_8B_4C_7$ [4] has remarkable antioxidant properties in carbon-containing refractory materials. Michalenko et al. found the $AlZrC_2$ phase in 1978 [5], but little has been reported about this material. Hashimoto et al. [6] produced a composite material of $AlZrC_2$ and Al, and characterized its mechanical properties. They prepared the $AlZrC_2$ by heating a mixture of Al and ZrC, followed by leaching with HCl. After synthesizing, however, ZrC still remained in the sample.

We synthesized high purity $AlZrC_2$ using a direct solid-state method.

2. Experimental procedure

2.1. Starting materials

The starting materials we used were

1. Al, 99.9% pure; 10-μm mean particle size (High Purity Chemicals Co., Ltd.).
2. ZrC, 95% pure (High Purity Chemicals Co., Ltd.).
3. Graphite, 99.7% pure; 5-μm mean particle size (High Purity Chemicals Co., Ltd.).

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Table 1
Al–ZrC–C mixtures with graphite as source of carbon

Composition	Mol ratio of starting materials (Al:ZrC:C)	Mol ratio of elements (Al:Zr:C)
A	1:1:1	1:1:2
B	3.5:3.5:3	3.5:3.5:6.5
C	4:4:2	4:4:6
D	4.5:4.5:1	4.5:4.5:5.5
E	3.5:3:3.5	3.5:3:6.5
F	4:2:4	4:2:6
G	4.5:1:4.5	4.5:1:5.5

(4) Amorphous carbon. In this work, we used three kinds of amorphous carbon, i.e.,
   (a) Prepared by heating phenolic resin in a muffle furnace at 400 °C for 30 min and grinding it into small pieces, reheating it at 400 °C for 5 min, then grinding it into a fine powder.
   (b) Prepared by heating sugar in a porcelain crucible with Bunsen burner for 6 h and grinding it into small pieces, reheating it for 6 h, then grinding it into a fine powder.
   (c) Carbon black, as received from industry (specific surface area, 125 m^2/g).

2.2. Sample preparation and heating

The starting materials were mixed in acetone at various mol ratios as shown in Tables 1 and 2 and Fig. 1. The mixtures were pressed into pellets of ~1.8 g, CIPed at 100 MPa, and heated under two different conditions:

- Ar atmosphere: The samples were placed in a refractory block lined with carbon paper and covered with powder having the same composition to prevent surface oxidation [6]. They were heated from room temperature to 1600 °C for 1 h at a heating rate 10 °C/min.
- Vacuum: The samples were prefired in Ar atmosphere as described above at 900 °C for 1 h to prevent Al vapor from attacking the carbon lining of the vacuum chamber. After prefiring, the covered powder was removed. The samples were wrapped in carbon paper and placed in a carbon crucible before heating in vacuum at a heating rate 10 °C/min from room temperature to the maximum temperature for 1 h.

Table 2
Al–ZrC–C with amorphous carbon as source of carbon

Composition	Mol ratio of starting materials (Al:ZrC:C)
H (resin)	3:3:4
I (resin)	4:3:3
J (resin)	5.5:3:1.5
K (resin)	6:3:1
L (resin)	3:2.5:4.5
M (resin)	3.5:2.5:4
N (resin)	3:2:3
O (resin)	5:2.5:2.5
P (resin and carbon black)	35:28:37
Q (resin and sugar)	21:14:15

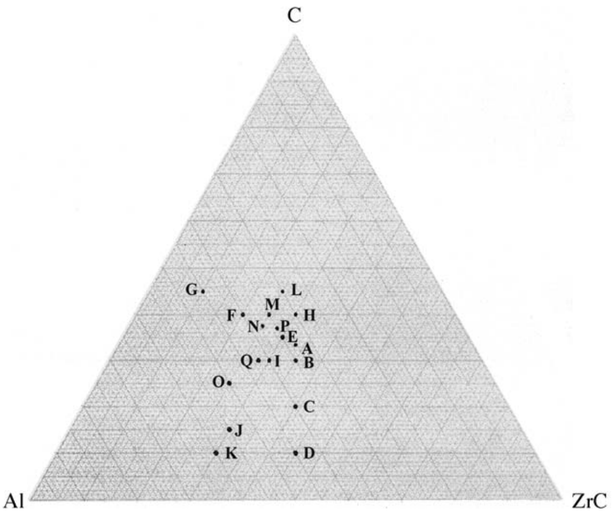

Fig. 1. Composition diagram of Al–ZrC–C mixtures.

2.3. Characterization

Samples were crushed and ground into fine powder. Phase change was characterized by XRD (Shimadzu XD-X1). Thermal analysis was carried out by DTA/TG (Rikaku Thermoplus TG8120) from room temperature to 1200 °C in air to check the exothermic reaction of the residual ZrC around 500–600 °C [7]. After synthesis, fresh crack samples were investigated by SEM (JEOL JSM-6360LV).

3. Results and discussion

3.1. Effect of composition on phase formation

Al–ZrC–graphite mixtures with various mol ratios were heated in Ar atmosphere. Phases formed within the Al–ZrC–graphite pellets after firing at 1600 °C for 1 h are shown in Fig. 2. Phase formation depends on the ratio of the starting materials. Fig. 2a shows the phase formation for an Al:ZrC mol ratio of 1 at varying amounts of graphite. Fig. 2b shows phase formation for an Al:graphite mol ratio of 1 at varying amounts of ZrC. In the middle zone of the composition diagram (Fig. 1), $Zr_2Al_3C_5$ formed after firing. This formation did not depend on the Al:ZrC:graphite ratio, as shown by the XRD patterns of the compositions A, B and E in Fig. 2a and b. The phase formation after firing was completely different away from this middle zone, i.e., closer to the edges of the composition diagram. At a constant mol ratio of Al to ZrC with lower graphite content (compositions C and D in Fig. 2a), no $Zr_2Al_3C_5$ was found. At a constant mol ratio of Al to graphite with lower ZrC content (compositions F and G in Fig. 2b), no $AlZrC_2$ was found

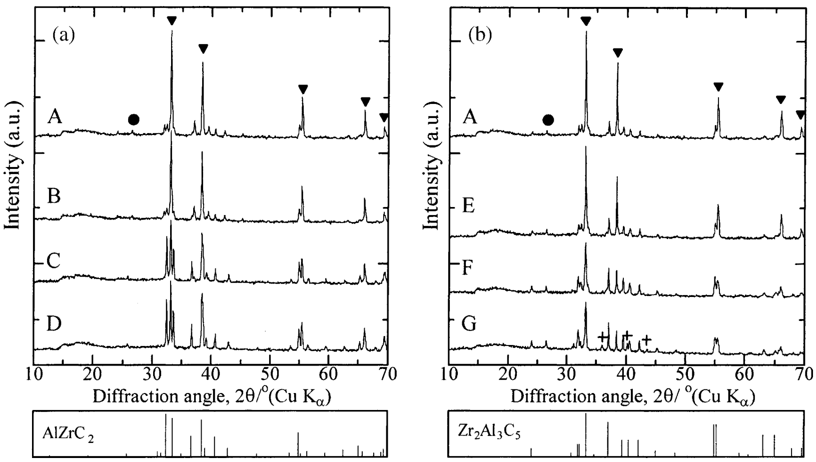

Fig. 2. Phase formation of Al, ZrC and graphite mixtures at various mol ratio after firing at 1600 °C in Ar for 1 h: (a) Al:ZrC = 1; (b) A1:C = 1. (▼) ZrC; (●) graphite; (+) Al_4C_3.

after firing. From Fig. 2, we concluded that the $AlZrC_2$ should be prepared from Al–ZrC–graphite mixture with very low graphite content, however, a very high residual ZrC still remained.

Although the diagram in Fig. 1 is similar to a phase diagram, and the composition axes have to be represented as elements (see Table 1), the carbon from graphite and from ZrC affects Al–Zr–C compound formation differently. Graphite is a carbon compound with hcp structure [8], while carbon in ZrC is in octahedral interstices of Zr close-packed layer [9,10]. Hence, the reaction mechanism of carbon in graphite and the reaction mechanism of carbon in ZrC differ due to differences in the number and type of neighboring atoms or co-ordination number (C.N.). Schuster and Nowotny [5] presented the atomic arrangement of $AlZrC_2$ and $Zr_2Al_3C_5$. The interstitial carbon in both complex carbides shows some relation to the interstitial carbon in ZrC structure. Thus, we describe the mol ratio of the mixtures in terms of the starting compounds, rather than elemental components.

3.2. Effects of carbon phase

We prepared Al–ZrC–C mixtures with compositions A (molar composition equivalent to $AlZrC_2$) and N (molar composition equivalent to $Zr_2Al_3C_5$) with two types of carbon, i.e., graphite and amorphous carbon from phenolic resin, and heated in vacuum at various temperatures for 1 h.

The phase evolutions of the compositions A and N after heating are shown in Fig. 3, where A1, N1 and A2, N2 denote compositions with graphite and amorphous carbon, respectively. The results of thermal analysis of samples, which represent the residual ZrC in samples after firing as exothermic peak [7], are shown in Fig. 4. Based on the discussion in Section 3.1, composition N was expected to yield $Zr_2Al_3C_5$ after heating regardless of the carbon type

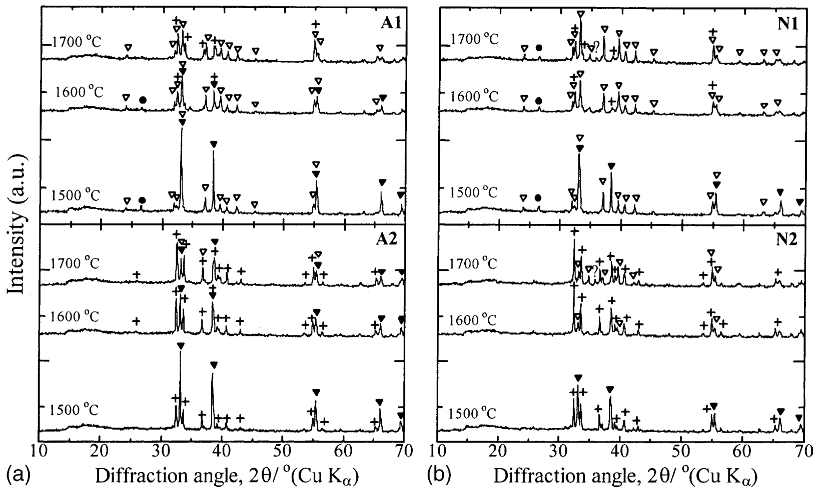

Fig. 3. Phase evolution of Al–ZrC–C mixtures containing different types of carbon upon firing at 1500–1700 °C in vacuum for 1 h; Al, composition A with graphite; A2, composition A with amorphous carbon; N1, composition N with graphite; N2, composition N with amorphous carbon. (▼) ZrC; (●) graphite; (▽) $Zr_2Al_3C_5$; (+) $AlZrC_2$; (?) unknown.

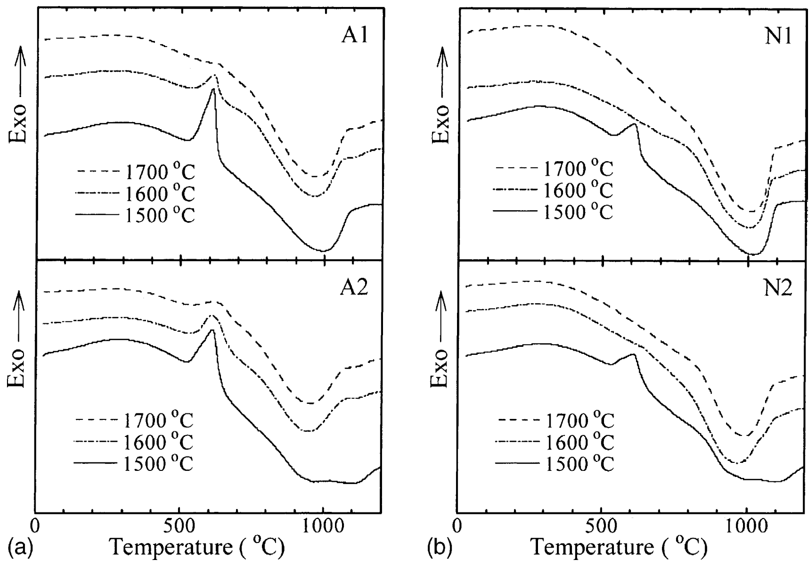

Fig. 4. DTA of Al–ZrC–C mixtures containing different types of carbon after firing at 1500–1700 °C in vacuum for 1 h; Al, composition A with graphite; A2, composition A with amorphous carbon; N1, composition N with graphite; N2, composition N with amorphous carbon.

because this composition lies on the composition line of A–E–F–G (Fig. 1). Fig. 3a and b indicate that $Zr_2Al_3C_5$ formed in the graphite-containing compositions A1 and N1, and $AlZrC_2$ formed in the amorphous carbon-containing compositions A2 and N2. The amounts of $Zr_2Al_3C_5$ and $AlZrC_2$ were higher (Fig. 3) while the amount of ZrC decreased as firing temperature increased (Fig. 4). From Fig. 3, it is obvious that the formation of $Zr_2Al_3C_5$ and $AlZrC_2$ depends on the type of carbon in the composition, not the mol ratio of the starting materials. In other words, the atomic arrangement of carbon in graphite crystal facilitates $Zr_2Al_3C_5$ formation, while the atomic arrangement of amorphous carbon from phenolic resin facilitates $AlZrC_2$ formation.

$AlZrC_2$ in the graphite-containing mixture and $Zr_2Al_3C_5$ in the amorphous carbon-containing mixture heated at 1700 °C presumably came from evaporation during heating because there was weight loss in the samples after heating, and the losses increased as the heating temperature was increased.

Fig. 4b shows that there was no exothermic peak from the ZrC in composition N with both types of carbon after firing at 1600 °C. This means the phase of carbon does not affect the overall reaction between ZrC and other starting materials.

Although the firing atmosphere described in Section 3.1 and here differed, our previous study [7] and the results from studies of other compositions (not shown here) confirm that firing in Ar or in vacuum yields $Zr_2Al_3C_5$ in case of graphite-containing mixtures, and $AlZrC_2$ in case of (phenolic resin-derived) amorphous carbon-containing mixtures. The effects of the firing atmosphere (Ar versus vacuum) were discussed elsewhere [7].

Fig. 3 reveals an interesting fact about Al–Zr–C compound formation. Hashimoto et al. discussed the formation of $AlZrC_2$ in an Al–ZrC–C mixture with a high Al content [6]. After heating, the excess Al–Zr alloy was leached out by HCl. However, as shown in Fig. 3, no Al–Zr alloy was found in samples heated at 1500 °C or above. At 1600 °C, the amount of Al–Zr–C compound still increased. This indicates that there was an Al-containing intermediate phase reacted with ZrC and free carbon to form Al–Zr–C compound, however, this intermediate phase could not be detected. Though we fired the samples at 1600 °C for various short intervals, no Al-containing phase could be detected by XRD. It may be that this Al-containing phase exists only at high temperature. Due to the condition of the vacuum graphite arc furnace, it is impossible to remove the samples from the chamber during the hot stage to characterize this intermediate phase. Our previous study [7] on $Zr_2Al_3C_5$ formation from Al–ZrC–C mixture with a high Al content also confirmed that Al–Zr alloy formed upon firing up to 1400 °C. Thus, the reaction path of Al–Zr–C formation in this present study differs from that in Hashimoto's Al-rich system.

3.3. *Amorphism of amorphous carbon*

The phenolic resin we used as an amorphous carbon source is widely used as binder in refractory industries [11]. However, carbon obtained from heating phenolic resin is too stiff for grinding. Thus, we used another kind of amorphous carbon, namely carbon black, because it is commercially available as powder. XRD patterns of carbon black, graphite and amorphous carbon from phenolic resin are compared in Fig. 5. Al–ZrC–C mixtures of composition P (see Table 2) with amorphous carbon from phenolic resin and carbon black were fired in vacuum at 1600 °C for 1 h.

The resultant phases are shown in Fig. 6. The mixture with carbon from phenolic resin gave $AlZrC_2$ as a main

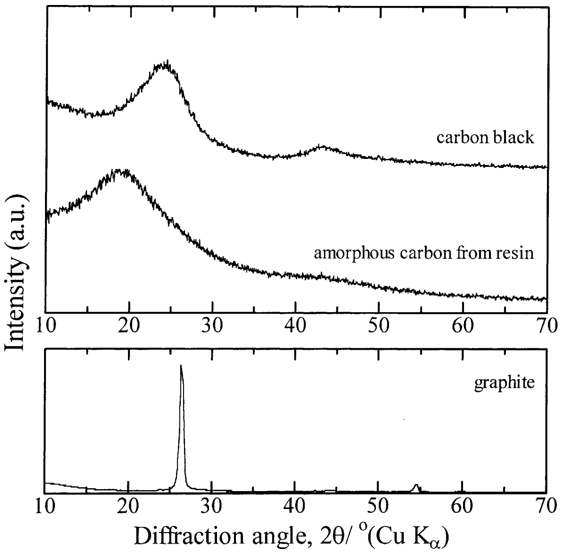

Fig. 5. XRD patterns of carbon black compared with amorphous carbon from resin and graphite.

product with a small amount of $Zr_2Al_3C_5$, while the mixture containing carbon black gave a mixture of $AlZrC_2$ and $Zr_2Al_3C_5$. Although the XRD pattern of carbon black showed the amorphous pattern, the resultant phases in the Al–ZrC–C mixtures after firing differed. This indicated that the amorphisms of the two types differ.

Amorphous carbon obtained by burning phenolic resin is glassy phase [12,13] with a short-range order structure like other inorganic glasses. The glassy material is isotropic and thermodynamically metastable. Therefore, glassy carbon from phenolic resin can be considered as "inherently" amorphous. By contrast, under high TEM resolution [14], carbon black showed very small primary particles surrounded by concentrically deposited carbon layers. The layers were nearly parallel to each other. But the relative position of these layers was random, so that there was no order as in the *c* direction of graphite. Therefore, the carbon atoms arrangement in a carbon black primary particle is non-well crystalline at the surface with an increasing order at the core of the primary particle. For most carbon blacks, these "crystalline" regions are 1.5–2.0 nm in length and 1.2–1.5 nm in height, corresponding to four to five layers. With such small size of "crystalline" regions, carbon black showed "amorphous" XRD pattern since the wavelength of X-ray (Cu Kα, 1.54056 nm) is similar to the "crystalline size" of carbon black.

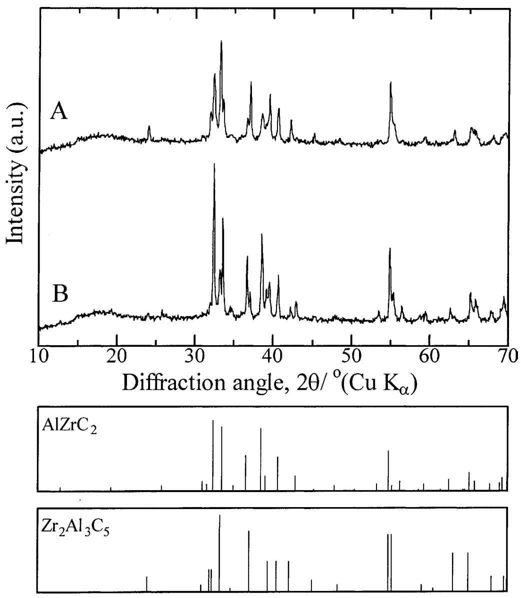

Fig. 6. Effect of type of amorphous carbon as starting material in the same ratio as Al:ZrC:C (mixture P, Al:ZrC:C = 35:28:37) after heating at 1600 °C for 1 h in vacuum. (A) Carbon black and (B) amorphous carbon from phenolic resin.

Based on the results presented in Section 3.2, carbon black in the Al–ZrC–C mixture gave a mixed product of $AlZrC_2$ and $Zr_2Al_3C_5$ because of its mixed characteristic of high reactivity from the non-well crystalline surface and "crystalline" regions within carbon black primary particles.

As mentioned above, the diagram in Fig. 1 is related to phase diagram. However, the results presented in Section 3.2 differ from those presented in Section 3.1. The Al–ZrC–graphite mixture gave the $AlZrC_2$ phase when the main carbon source was ZrC. This means the parent structure of carbon affect the formation of the Al–Zr–C compound. Nowotny et al. compared the crystal structure of Al–Zr–C complex carbides with those of other complex carbides [15]. They found that the degree of filling of the voids by carbon atoms is higher in Al–Zr–C complex carbides than in other complex carbides. Though the mechanism of void filling by carbon atoms in $Zr_2Al_3C_5$ and $AlZrC_2$ was not mentioned, the difference in atomic size between Zr and Al affects this mechanism. Carbon atoms in graphite and glassy carbon are different in many ways, e.g., C.N., bond type between the atom, and thermodynamic state. These factors affect the mechanism of reaction between the Al-containing intermediate phase, ZrC and carbon. The above results suggest that the mechanism of void filling by glassy carbon atoms may be similar to that of the interstitial carbon in ZrC. Thus, at the same Al–ZrC–C composition, the glassy carbon-containing mixture yielded a different Al–Zr–C phase from the graphite-containing composition.

3.4. Composition line

We fired various compositions of Al–ZrC–amorphous carbon in vacuum at 1600 °C for 1 h to find the zone in the composition diagram yielding the lowest amount of $Zr_2Al_3C_5$ and ZrC. Phase analyses of a number of compositions after firing are represented as composition line in Figs. 7 and 8; the two figures show the XRD patterns of composition line H–E–I–J–K and L–M–N–O, respectively. Because the ZrC and $Zr_2Al_3C_5$ peaks in the XRD patterns overlap (at $2\theta \approx 33°$), we conducted thermal analysis of all samples in Figs. 7 and 8 to detect the

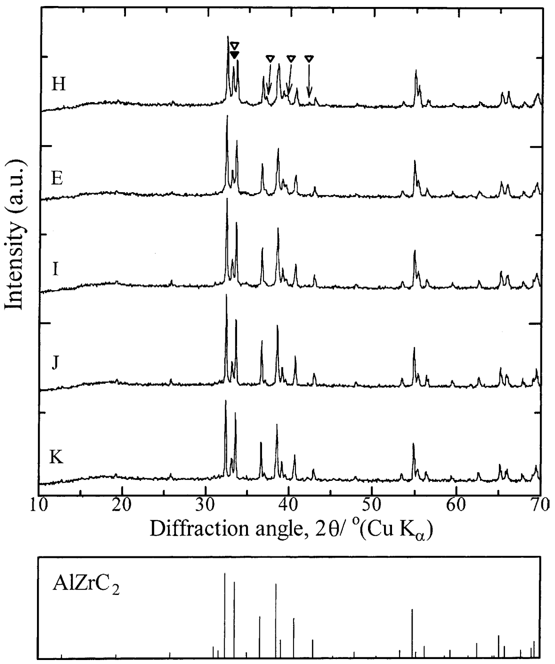

Fig. 7. XRD patterns of Al–ZrC–C composition line “H–E–I–J–K” after firing at 1600 °C in vacuum for 1 h. (▼) ZrC; (▽) $Zr_2Al_3C_5$ (C, amorphous carbon front phenolic resin).

residual ZrC after firing (DTA diagrams of compositions not presented here). The compositions in Fig. 7 gave $AlZrC_2$ as the main product upon firing, with a small amount of $Zr_2Al_3C_5$ and trace amounts of ZrC. The compositions in Fig. 8, slightly richer in A1 than those in Fig. 7, gave $AlZrC_2$ as the main product with a small amount of $Zr_2Al_3C_5$. These results indicate that during the $AlZrC_2$ formation, another phase of Al–Zr–C phase ($Zr_2Al_3C_5$) started to form although there was some ZrC left in the system.

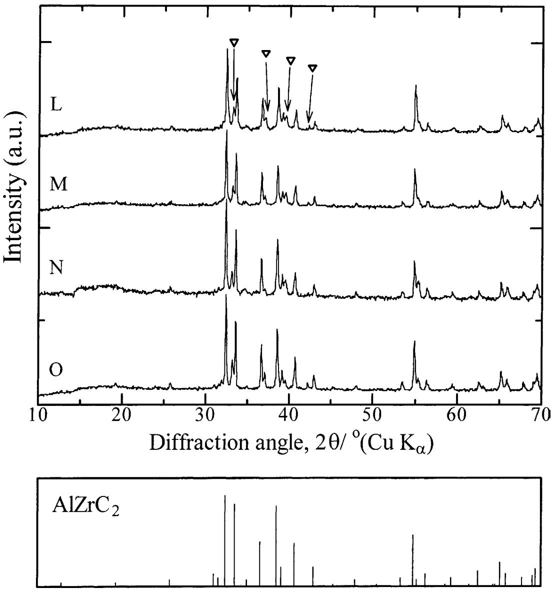

Fig. 8. XRD patterns of Al–ZrC–C composition line “L–M–N–O” after firing at 1600 °C in vacuum for 1 h. (▽) $Zr_2Al_3C_5$ (C, amorphous carbon from phenolic resin).

3.5. Effect of excess aluminum

Schuster and Nowotny [5] studied Al–Zr–C phase diagram at 700 °C and 1000 °C and found that ZrC is very stable and still existed after very long annealing time (longer than 100 h). Gesing and Jeitschko [16] prepared $Zr_3Al_3C_5$ by melting the mixture of ZrC and Al at very high weight ratio of Al (1:5) under Ar for 2 days at 1500 °C to make sure that ZrC was completely reacted with Al and no ZrC was found. The phases of product after melting were $ZrAl_3$ and $Zr_3Al_3C_5$. It is believed that ZrC is very stable and need excessive amount of Al as flux. It is known that ZrC starts to oxidize even at low temperature (300 °C) under low oxygen partial pressure [3]. But no research had studied about the effect of oxygen amount on Al–Zr–C compound formation.

From our previous work, we proved that the significant amount of oxygen in Ar dissolved in ZrC and formed Zr–C–O solid solution which is stable and do not react with other starting materials. The Al–ZrC–graphite mixture of same composition after heating at 1600 °C for 1 h in vacuum and in Ar showed different XRD pattern and no ZrC phase was found in sample heated in vacuum. Therefore, the very excessive amount of Al is needed when the Al–ZrC–C mixture is heated in Ar to form Al melt and cover ZrC grains to protect them from oxidation. However, Al evaporation occurred during heating in vacuum. The excess Al is necessary for Al–Zr–C compound formation, but at much less amount than heating in Ar.

From Section 3.2, the temperature which is suitable for Al–Zr–C compounds formation is 1600 °C. Aluminum has the lowest melting point (660 °C) in the Al–Zr–C system. Excess Al in the mixture may reduce the reaction

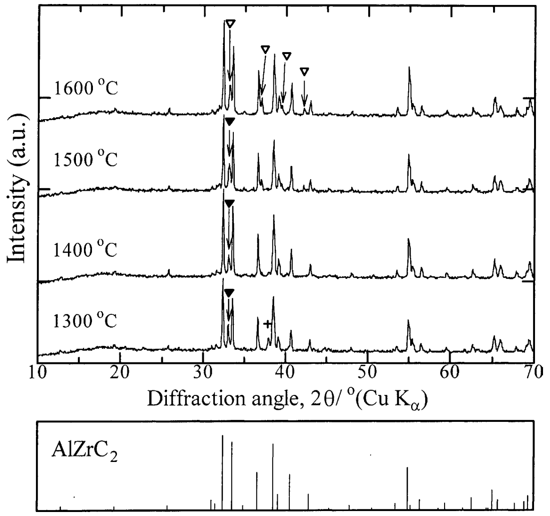

Fig. 9. Phase evolution of Al–ZrC–C at excess-A1-composition (O) after firing in vacuum at various temperatures for 1 h. (▼) ZrC; (▽) $Zr_2Al_3C_5$; (+) Al_3Zr (C, amorphous carbon from phenolic resin).

temperature so that ZrC might be completely consumed in the reaction. The excess-A1 composition (composition O) with amorphous carbon from phenolic resin was fired in vacuum at 1300–1600 °C to determine the effect of excess Al on reaction temperature.

As shown in Fig. 9, although the main phase after firing was $AlZrC_2$, Al_3Zr alloy was found after firing at 1300 °C. Residual ZrC was found after firing up to 1500 °C, and $Zr_2Al_3C_5$ was found from 1500 °C. Moreover, fracture surface of samples fired at 1500 °C revealed an inhomogeneous color pattern inside the sample, suggesting that the reaction between the starting materials was incomplete. Thus, excess Al in the Al–ZrC–C mixture facilitates $Zr_2Al_3C_5$ formation at lower temperatures. These results indicate that the optimal temperature for a complete reaction of the mixture (i.e., one in which ZrC is completely reacted) is 1600 °C.

3.6. Graphitization

Composition Q, which lies between composition lines H–E–I–J–K and L–M–N–O, was selected because it gave only trace amounts of residual ZrC and lowest amount of $Zr_2Al_3C_5$ after firing at 1600 °C for l h in vacuum. Mixtures of composition Q with amorphous carbon from phenolic resin and from sugar were fired in vacuum at 1600 °C for l h. As shown in Fig. 10, the sample with amorphous carbon from sugar gave $AlZrC_2$ with a least amount of $Zr_2Al_3C_5$. The fracture surface of Al–ZrC–amorphous carbon from sugar with composition Q heated in vacuum at 1600 °C for 1 h (Fig. 11), exhibited hexagonal platelets of $AlZrC_2$. The true density of powder obtained from this sample using kerosene as medium is 4.91 g/cm^3.

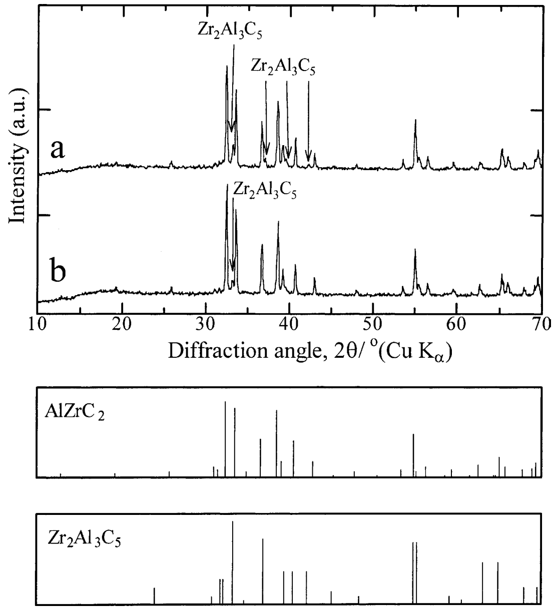

Fig. 10. XRD patterns of composition Q (Al:ZrC:C = 21:14:15) after firing at 1600 °C in vacuum for 1 h compared with ideal XRD pattern of $AlZrC_2$ and $Zr_2Al_3C_5$; with amorphous carbon from (a) phenolic resin and (b) sugar.

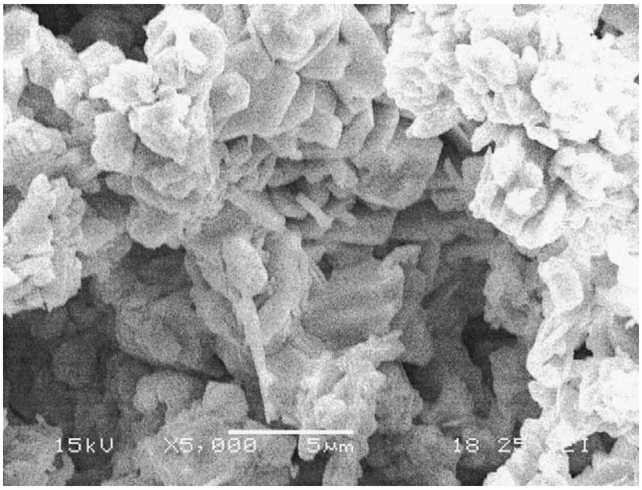

Fig. 11. Fracture surface of pellet of composition Q containing amorphous carbon from sugar after heating in vacuum at 1600 °C for 1 h.

The results presented in Section 3.2 indicate that the phase formation of $AlZrC_2$ and $Zr_2Al_3C_5$ formed in the sample after firing depends on the carbon phase in the starting material. Glassy carbon can transform to a crystalline phase (graphite) at high temperature, so-called graphitization [17]. Graphitization of glassy carbon has been performed at high temperatures and high pressure [18], but the graphitization of glassy carbon in vacuum remains unproven. Thus, we performed a small test to confirm the graphitization of glassy carbons as starting materials. Glassy carbon powder from phenolic resin and glassy carbon powder from sugar were wrapped with clean carbon paper and fired in vacuum at 1600 °C for 1 h, i.e., under the same firing conditions used for our samples.

As evidenced by the high-intense peak in Fig. 12, graphitization occurred in amorphous carbon from phenolic resin while amorphous carbon from sugar showed a lower degree of graphitization. Thus, a small amount of $Zr_2Al_3C_5$ formed spontaneously, and a sample with amorphous carbon from sugar yielded $AlZrC_2$ with less $Zr_2Al_3C_5$ compared with the sample with amorphous carbon from phenolic resin. In general, graphitization is an important step in the manufacture of carbon/carbon composite [17,19]. At this stage, carbon/carbon composites are heated up and disordered carbon transforms into well-ordered graphite structure. Although we prepared amorphous carbon from phenolic resin and sugar by heating in oxidizing atmosphere, a certain amount of organic functional group presumably remained as significant (ppm-level) impurities. Phenolic resin is viscous, high-molecular-weight hydrocarbon. There might be some functional groups left in amorphous carbon after heating phenolic resin at higher amount than heating sugar, which is lower molecular weight. There is a similar phase transformation in the silica glass, i.e., devitrification [20]. The significant amount of impurities in the glassy phase behaves as a mineralizer and initiate crystallization. Thus,

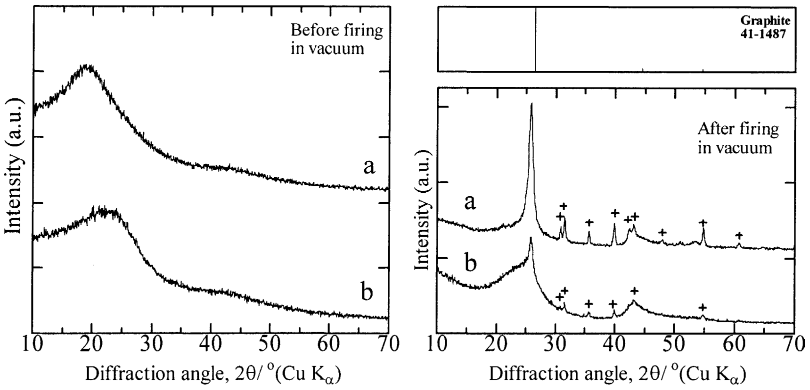

Fig. 12. Phase change of amorphous carbon before and after firing in vacuum at 1600 °C for 1 h; amorphous carbon from (a) phenolic resin and (b) sugar; (+) Al_4C_3.

the graphitization of glassy carbon observed in this study resembles the devitrification in silica glass.

There are some foreign peaks in the XRD patterns of both amorphous carbon powders; they correspond to Al_4C_3. Although the amorphous carbon powders were wrapped with carbon paper, the samples still had to be placed in a small carbon crucible before being loaded into the carbon crucible of the vacuum furnace. Since all of firing tests were done in the same small crucible, Al_4C_3 from the reaction between Al vapor and the crucible may have accumulated on the inner surface of the crucible. Under vacuum, Al_4C_3 evaporated from the crucible surface at high temperature and diffused through the slit in the wrapping. Some of our results (not presented here) indicated that Al_4C_3 has some relation to $AlZrC_2$ and $Zr_2Al_3C_5$ formation. Therefore, Al_4C_3 as impurity during firing the samples does not have negative effect on Al–Zr–C compound formation.

Studies on graphitization of glassy carbon have generally been conducted without presence of other additives. In this work, however, there were other starting materials (Al and ZrC). Therefore, the graphitization of the amorphous carbon in our samples during heating was presumably stronger than graphitization of pure amorphous carbon powder because the other starting materials acted as mineralizer, reducing the graphitization temperature of the amorphous carbon, and hence, accelerating the graphitization process.

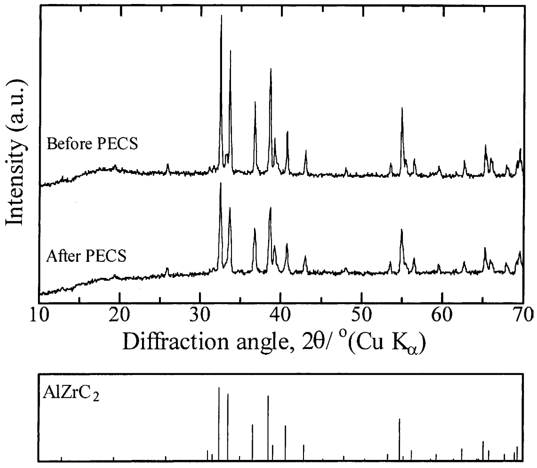

Fig. 13. XRD pattern of compact (composition Q) after sintering by PECS at 1700 °C and 40 MPa in vacuum without soaking.

3.7. *Effect of pressure*

We incidentally found that high purity $AlZrC_2$ from composition Q (with amorphous carbon from sugar as source of carbon) shows only $AlZrC_2$ phase after a 5-min reheat under pressure with electric current by PECS [21]. Therefore, we prepared the mixture of composition Q from Al, ZrC and amorphous carbon from sugar, and heated it at 1600 °C in vacuum for 1 h. Subsequently, we ground it into a fine powder, heated it in PECS under high pressure (40 MPa) in vacuum from room temperature to 1700 °C, and then suddenly stopped. No $Zr_2Al_3C_5$ phase was found, as shown in Fig. 13. The pressure during sintering under PECS may suppress the formation of the $Zr_2Al_3C_5$ phase and rearrange the atomic packing. The effect of pressure on $Zr_2Al_3C_5$ after sintering by PECS [22] also showed the same phenomena.

4. Conclusions

1. The atomic arrangement of carbon in the starting materials affects the Al–Zr–C compound formation.
2. Excess Al does not accelerate the reaction between ZrC and other starting materials.
3. Graphitization of glassy carbon occurs spontaneously as it reacts with the other starting materials at high temperature and affects the Al–Zr–C compound formation.
4. $AlZrC_2$ can be prepared from a mixture of Al, ZrC, and amorphous carbon from sugar at a mol ratio of 21:14:15 by firing the mixture in vacuum at 1600 °C for 1 h and grinding the product into a fine powder, then reheating this powder up to 1700 °C under high pressure and applied electric current.

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