Carbon-Dispersed WC–FeAl Hard Material Fabricated by Mechanical Milling and Subsequent Pulsed Current Sintering

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A new metal mold material for pulsed current sintering (PCS) methods at high temperatures with higher electrical resistivity than cemented carbide molds, was fabricated using mechanical milling and PCS. The constituent (100−x)(WC−10 or 30FeAl) + xC (x = 0–8; mass%) hard material with dispersed spherical carbon particles were synthesized via mechanical milling of the source powders and PCS. The three-point flexural strength and electrical resistivity of the hard material decreased and increased with an increase in the carbon content, respectively. The 98(WC−10FeAl) + 2C alloy showed a flexural strength of 1 GPa and resistivity of 0.59 × 10−4Ωcm. The material did not exhibit plastic deformation at 1073 K at 100 MPa under compression. The metal mold made from the 97(WC−10FeAl) + 3C was used for PCS at 1073 K at 200 MPa, suggesting that the carbon-dispersed WC–FeAl hard material was capable of being employed as a new mold material for the PCS method. [doi:10.2320/matertrans.M2014081]

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1. Introduction

The pulsed current sintering (PCS) method involves Joule heating of the sample, mold, and punches for sintering under uniaxial pressure.1 This method can be employed in a wide range of fields, e.g., for consolidation of a poorly sinterable and metastable-phase material, making a porous material, and joining of materials.2–14 In this process, carbon is usually used in the mold and punches, as it can be employed at high temperatures above 2000 K and it possesses high electrical resistivity, which means that electrical energy is efficiently converted to heat. However, the strength of carbon is low (~100 MPa under compression); thus, for high-pressure sintering, a cemented carbide mold, composed of tungsten carbide and cobalt (WC–Co), is used.15 Cemented carbide displays high strength, but oxidation and deterioration of the strength occur at high temperatures (above 870 K); thus, cemented carbide is used for sintering at high pressures and low temperatures. In addition, cemented carbide is a good electrical conductor. Hence, the electrical energy conversion to heat is inefficient as compared to carbon. Therefore, a metallic mold material with high electrical resistivity that can be used at higher temperatures than molds made from cemented carbide is desired.

An iron–aluminum intermetallic compound (FeAl) exhibits mechanical properties without degradation at temperatures ranging from ambient temperature to approximately 800 K.16,17 Also, a hard material composed of WC and FeAl (WC–FeAl) possesses mechanical properties comparable to WC–Co18 and better oxidation resistance than WC–Co.19–21 Hence, the WC–FeAl is a candidate for the type of mold material desired in the PCS process as mentioned above. Although WC–FeAl exhibits suitable high temperature properties, its electrical resistivity is low, so an increase in the resistivity is necessary for use as a mold material in the PCS process. In this study, we examine an increase in electrical resistivity of the WC–FeAl alloy by dispersion of carbon particles.

2. Experimental Procedure

For sample preparation, WC, Fe, Al, and C powders were mechanically milled. The WC and Fe powders were milled for 10.8 ks. Subsequently, Al and C powders were added to the WC and Fe mixture, and further milling was carried out for 1.8 ks. The milling processes were carried out in an Ar atmosphere. The nominal compositions of the mixture were (100−x)(WC−10 or 30Fe3Al2) + xC (x = 0–8; mass%). Planetary ball milling (Fritsch P-4) was employed, and the rotation speed was set to 170 rpm. The speed of the counter-rotating revolution was set to 2.17 times that of the rotation. A chromium steel vial (500 ml) and cemented carbide balls (ϕ5 mm) were used as the milling vessel and media. The ball-to-powder weight ratio was 0.07.

The milled powders were consolidated by the PCS method in a vacuum of 10−2 Pa. For sintering, carbon mold with an outer diameter of 50 mm and inner diameter of 30 mm was used. The milled powder was poured into the mold, followed by sintering at 1423 K for x = 0 mass% and 1473 K for x = 2, 4 and 8 mass% samples at 40 MPa. The sintered compact was cut to a rectangular shape with 2 mm height and 3.5 mm width, and then, the three-point flexural strength was measured with a span of 10 mm. The electrical resistivity of the sample was investigated by the 4-probe method using the same sample as for the three-point flexural test. The microstructure of the sintered samples was observed using a scanning electron microscope (SEM) and the phase was detected by the X-ray diffractions (XRD) technique using Cu Kα1 radiation. The temperature raise by Joule heating of the samples was investigated. The sample was cut to form a 4 mm × 3 mm × 20 mm rectangular shape. The cut sample was sandwiched between carbon electrodes, and then, a direct
A current of 50 A was passed through the sample for 60 s. The temperature rise of the sample was monitored using a K-type thermocouple attached to the center of the sample. Strength at high temperatures was measured as follows by a simple procedure. The cylindrical sample with diameter of 10 and 15 mm height was sintered using carbon mold with an outer diameter of 30 mm and inner diameter of 10 mm. The same sintering conditions as mentioned above were used. The sintered cylindrical sample was heated up to 1073 K in vacuum, and then, the desired compression stress was applied. Afterwards, the sample was cooled down to the ambient temperature, and the sample height was measured. The deformation strain was calculated by comparing the sample heights before and after applying stress.

3. Results and Discussion

Figure 1 shows the elemental powders of WC, Fe, Al, C, and the milled powder. The carbon powder used in this study is composed of spherical shape with an average diameter of 5 µm, required for the elimination of strength anisotropy after dispersion in WC–FeAl. After milling, significant reduction in powder particle size and agglomeration are observed in the WC, Fe, and Al powers. In contrast the carbon powder particles retain their original shape and size and do not agglomerate.

The XRD patterns of the sintered samples, \((100 - x)(WC-10\text{ FeAl}) + xC\) with \(x = 0–8\text{ mass}\%\), are shown in Fig. 2. The sintered compact with \(x = 0\text{ mass}\%\) is composed of WC and FeAl compound. The Al–Fe binary alloy system shows a FeAl (B2) and Fe3Al (D03) phases. In this system, the FeAl phase is stable at the sintering temperature and at the nominal composition of binder phase used in this study. Hence, the obtained phase is expected to be the FeAl phase. The milled powders were comprised of the elemental powders, since the FeAl phase was formed during the sintering process, during which the molten Al reacted with solid Fe.22 Even after the carbon content is increased up to \(x = 8\text{ mass}\%\), significant carbon peaks are not detected, because the used carbon particles in this study having an amorphous-like structure. However, when carbon content is increased to \(x = 8\text{ mass}\%\), formation of the carbide, AlFe3C, is clearly detected. In the \((100 - x)(WC-30\text{ FeAl}) + xC\) sintered sample, the phases were the same as shown in Fig. 2, with the WC and FeAl phases being detected in all the samples. The AlFe3C phases were detected in the sample with \(x = 8\text{ mass}\%\).

The SEM images of the sintered \((100 - x)(WC-10\text{ FeAl}) + xC\) sample with various carbon content is shown in Fig. 3. The sample without carbon dispersion, \(x = 0\text{ mass}\%\), has a fine microstructure and is composed of WC and FeAl compounds. The inset shows an enlarged image, where the bright and dark regions correspond to WC and FeAl,
respectively. In the carbon-dispersed sample, the carbon particles are seen as black spots and are homogeneously distributed. The original spherical shape is almost unchanged, but a slight distortion in the lateral direction due to compression during sintering is observed. The carbon particles are isolated in the samples with $x = 2$ and 4 mass%.

When the carbon content is increased up to $x = 8$ mass%, the carbon particles create spontaneous carbon–carbon networks, as the volume fraction of carbon is about 37% in the sample with $x = 8$ mass%.

Figure 4 shows changes in the three-point flexural strength and electrical resistivity as a function of carbon content. In both samples with different binder fractions, WC–10FeAl and WC–30FeAl, the same trends are exhibited, i.e., the electrical resistivity and flexural strength increase and decrease with increase in the carbon content, respectively. The strength and electrical resistivity of the WC–30FeAl sample are higher than for the WC–10FeAl sample with the same carbon content. The FeAl compound demonstrates higher electrical resistivity ($1.3 - 1.8 \times 10^{-4} \Omega \text{cm}$) than WC ($0.19 \times 10^{-4} \Omega \text{cm}$), and the small fraction of binder phase leads to an increase in the WC/FeAl contiguity fraction. As a result, the WC–10FeAl samples have lower strength and resistivity than those WC–30FeAl samples with the same carbon content.

The strength of both samples exhibits a significant decrease with addition of 2 mass% carbon. Carbon strength is much lower than that of WC and FeAl, thus the dispersed carbon acts as a fracture initiation site. Significant decrease in strength is also noticeable when carbon content is increased from $x = 4$ to 8 mass% due to the spontaneous carbon–carbon network formation at $x = 8$ mass% as shown in Fig. 3.

Investigation of the heating characteristics of the samples was carried out using direct current. The temperature change in the sample due to Joule heating is shown in Fig. 5. The temperature reaches 590 K in the sample without carbon dispersion. With increase in carbon content, the maximum temperature increases, due to increase in electrical resistivity.

Figure 6 shows the deformation behavior in the 98(WC–10 FeAl) + 2C and 98(WC–30 FeAl) + 2C samples at 1073 K. The 98(WC–30 FeAl) + 2C alloy is more deformable than the 98(WC–10 FeAl) + 2C alloy as the metal binder phase becomes soft at 1073 K. The permanent deformation under 100 MPa compression is not detected in the 98(WC–10 FeAl) + 2C alloy.

The metal mold and punches for actual use are fabricated from the 97(WC–10 FeAl) + 3C alloys as shown in Fig. 7. To build the mold and punches, the same processing methods as for cemented carbide were employed, and the mold and punches show processing accuracy comparable to the cemented carbide molds. The sintering of Co alloy powders was examined using the mold and punches at 1073 K for 60 s under 200 MPa. The appearance of the sintered Co alloy is shown in the inset of Fig. 7, and its relative density attained to 99.7% even though the sintering temperature was 1073 K, suggesting that the carbon dispersed WC–FeAl alloys are potentially capable of being used as a new mold material with...
higher electrical resistance. They can also be used at a higher temperature than those formed from cemented carbide.

4. Conclusion

A metallic mold material for PCS methods at higher temperatures with higher electrical resistivity than cemented carbide molds, was fabricated using mechanical milling and pulsed current sintering. Spherical-particle carbon powder was dispersed in the (100 − x)(WC−10 or 30FeAl) + xC hard materials. In the sample with x = 8 mass%, the formation of aluminum iron carbide phase was confirmed by XRD. In contrast, the sintered sample with x < 4 mass% was composed of WC, FeAl, and carbon phase. The three-point flexural strength and electrical resistivity decreased and increased with an increase in the carbon content, respectively. The strength and resistivity in the WC−10FeAl sample with x = 4 mass% was 1 GPa and 0.59 × 10^−4 Ω cm, respectively. The resistivity was about 2–3 times higher than that of cemented carbide. The metallic mold was processed using the WC−10FeAl with x = 3 mass% hard material. This mold enabled sintering at 1073 K under 200 MPa, suggesting that the carbon-dispersed WC−FeAl hard materials can be used as metal mold materials for the PCS method.
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REFERENCES