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Rapid synthesis of highly pure Nb_2AlC using the spark plasma sintering technique

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ABSTRACT

In this work, highly pure Nb_2AlC was successfully synthesized using the spark plasma sintering (SPS) technique with Nb, NbC and black carbon as raw materials at 1450 °C and 30 MPa for 8 min. The obtained Nb_2AlC grain shows a characteristic layered structure. More interestingly, the obtained Nb_2AlC exhibits good electrical, thermal and mechanical properties. The coefficient of thermal expansion is $9.0 \times 10^{-6} K^{-1}$ from room temperature to 1200 °C. The electrical conductivity reaches $1.3 \times 10^6 S m^{-1}$ at 500 °C, indicating excellent high-temperature conductivity. The Vickers hardness and flexural strength are 4.0 GPa and 440 ± 10 MPa, respectively. Importantly, fracture toughness of the obtained Nb_2AlC material reaches 7.8 ± 0.2 MPa $m^{1/2}$, which is higher than that of other previously studied MAX materials. Therefore, SPS is a very effective method to fabricate Nb_2AlC materials and can also be used to prepare other MAX materials.

1. Introduction

Nb_2AlC belongs to a class of ternary-layered compounds called $M_{n+1}AX_n$ (where M is an early transition metal, A is mostly IIIA and IVA group elements, X is carbon and/or nitrogen, and n = 1–3), which combine the characteristics of ceramics and metals [1–3]. When n = 1, these layered compounds M_2AX are also called H-phase [2]. Like ceramics, they have high strength, high melting point and thermal stability; like metals, they are good thermal and electrical conductors, easy to machine using conventional tools, and resistant to thermal shock. Because of their unique properties, they are expected to be applied in various fields; for example, they can be used as structural materials for high-temperature applications, as a substitute for machinable ceramics, and in nuclear protection devices, kiln furniture, and heat exchangers [4–6]. Among these $M_{n+1}AX_n$ materials, most studies are focused on relatively lower density materials, such as Ti_3SiC_2 in the Ti-Si-C system [7–10], Ti_2AlC and Ti_3AlC_2 in the Ti-Al-C system [11–18], or Ti_2AlN and Ti_4AlN_3 in the Ti-Al-N system [19–21]. Compared to $M_{n+1}AX_n$ mentioned above, Nb_2AlC in the Nb-Al-C system has been ignored.

In fact, the discovery of Nb_2AlC powders is traced back to the 1980s, and it was first fabricated by Schuster and Nowotny [22] by arc melting and annealing at 1000 °C for 170 h in the Nb-Al-C system. Reactive hot isostatic pressing (HIP) was used to fabricate bulk Nb_2AlC materials obtained from the precursors including Nb, C and Al_4C_3 at 1600 °C for 8 h and 100 MPa. About 3 vol% impurities, including Al_2O_3 and Nbcarbides, were also detected. The thermal and electrical properties of Nb_2AlC were reported by Barsoum et al. [24]. Reactive hot pressing was used to synthesize the dense Nb_2AlC material from NbC, Nb and Al power mixture at 1650 °C and at a pressure of 30 MPa for 90 min [25]. Afterwards, the layered ternary carbide Nb_2AlC was prepared by combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) from Nb_2O_5-Al-Al_4C_3 powder compacts [26]. The optimum evolution of Nb_2AlC was obtained from the powder compacts with a Nb_2O_5:Al:Al_4C_3 ratio of 3:11:1, and 5% of NbC was also detected in the final products. However, the above-mentioned methods are very time-consuming or require high pressure and high temperature. In this sense, it is necessary to develop a new rapid synthesis technique to prepare highly pure Nb_2AlC.

Recently, spark plasma sintering (SPS) has been regarded as an effective method to synthesize many ceramics. Compared to hot pressing (HP) or HIP method, SPS showed an obvious advantage in the heating system, in that the samples can be heated by a pulsed direct current (typically a few thousand amperes and a few volts) in SPS [27–30]. Thus, fully dense materials can be synthesized via the SPS technique at lower temperatures and shorter cycle times compared with conventional hot pressing (HP) or HIP techniques. In previous works, the SPS technique was used to prepare highly pure Ti_2AlC, Ti_3AlC_2, Ti_3SiC_2, Ta_2AlC, Cr_2AlC, Ti_2AlN and Nb_4AlC_3 [31–39]. However, to the best of our knowledge, no related works have focused on the preparation of

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highly pure Nb_2AlC material using the SPS technique. In this work, highly pure Nb_2AlC was prepared rapidly using SPS. Additionally, the obtained Nb_2AlC shows better thermal and electrical as well as mechanical properties than other MAX phases obtained using other methods in previous studies.

2. Experimental procedure

Highly pure powders of Nb (99.9% pure, 4.5 μm), Al (99.8% pure, 12.8 μm) and NbC (99.8%, 8.5 μm) powders were used as raw materials to synthesize Nb_2AlC. The admixture with a molar ratio of Nb:Al:NbC = 2:1.2:1 was first mixed in ethanol for 24 h and then compacted uniaxially under 20 MPa in a graphite mold pre-sprayed with a layer of BN, and finally sintered in vacuum in Spark Plasma Sintering System (Dr. 1050, lzumi Technology). The processing parameters were set as follows: heating temperature was 1450 °C, the SPS chamber was evacuated to about 10^{-2} Pa, heating rate was 100 °C/min, mechanical pressure was 30 MPa. The external pressure was applied from the start of the heating up to the end of the holding time. The holding time is 8 min. The temperature was measured by an optical pyrometer through a hole set in the die. After sintering, the sample was cooled down to room temperature. Before examination, the surfaces of the sintered samples were machined to remove the layer contaminated by the carbon sheet, using a fine grit, high-speed diamond wheel.

The sintered sample was polished, and the density was measured using the Archimedes method. Powders were drilled from the bulk samples for X-ray diffraction (XRD) characterization. The phase identification was characterized by XRD using a rotating anode X-ray diffractometer (Model D/MAX-RB; Rigaku Corporation, Japan). Scans were made with Cu Kα radiation (40 kV and 50 mA) at a rate of 1°/min, using a step of 0.02°. The XRD data was refined for lattice parameters by Rietveld analysis. Pure silicon was added as an internal standard.

The fracture surface microstructures of the samples were investigated via scanning electron micrographs (SEM) (Model JSM-5610LV; JEOL Ltd., Japan). The micro-hardness was measured using a Leitz Microhardness Tester (Leitz Wetzlar, Germany) at 100 N with a loading time of 30 s. The hardness was calculated by averaging at least 10 measurements. Three-point bending tests were performed to measure flexural strength and fracture toughness (K_{IC}). The size of specimens for flexural strength testing is $3 \times 4 \times 36\ mm^3$ and the crosshead speed is 0.5 mm/min. K_{IC} was measured using the single-edge notch beam (SENB) method with specimen dimensions of $4 \times 8 \times 36\ mm^3$. The notch, which was 4 mm in length and ~0.15 mm in width, was made using the electrical discharge method. The notch root radius is about 0.15 mm. The crosshead speed for fracture toughness testing is 0.05 mm/min. Thermal diffusivity α and heat capacity C_p were directly measured by a thermal constant measuring instrument (SINKU-RIKO Model TC-7000) using the laser flash method. The thermal conductivity, λ (W/(m·K)), can be calculated using the following equation:

$$\lambda = d \cdot Cp \cdot \alpha, \quad (1)$$

where d, Cp and α are the density (kg/m^3), the heat capacity (J/kg·K) and the coefficient of temperature conductivity (m^2/s), respectively.

The thermal expansion of the bulk polycrystalline samples was measured in air from room temperature to 1200 °C in a dilatometer. Electrical conductivity was tested using the four-probe method from room temperature to 500 °C in vacuum. The Seebeck coefficient was evaluated to 500 °C in vacuum.

3. Results and discussions

3.1. Synthesis and microstructure of Nb_2AlC

When Al powders are used as raw materials to prepare MAX phases, an appropriate amount of extra Al should be added to compensate for the loss of Al during the sintering process [40]. In our previous work [31], highly pure Ti_2AlC was also obtained from Al-excessive powder mixture of 2Ti/1.2Al/C at 1100 °C and 30 MPa for 8 min using the SPS technique. Therefore, in this work, samples with starting materials having a molar ratio of Nb: Al: C = 2:1.2:1 are investigated. There are five expected merits of SPS: (1) generation of spark plasma; (2) effect of the electric field; (3) effect of electric current on the conductor or skin current on the semiconductor and insulator; (4) impact of spark plasma; (5) rapid heating and cooling. There are no insulators and heating elements of large heat capacity, and the graphite die is heated directly by an electric current. These conditions result in rapid heating and cooling. Al particles are covered with aluminum oxide film, and cannot be sintered by normal and hot press sintering. The oxide film cannot be broken and removed by heat, and persists in the sintered product. The plasma of SPS only makes holes in the film. For the generation of plasma, the powders must be pressed, because the high resistance of the loose contact of die alignment does not allow the passage of electric current. The combined force of weak plasma and stress enables the creation of small holes in the oxide film. The diffusion of Al commences through these holes for further reaction. In this sense, the fabrication time by use of SPS is obviously decreased compared with other methods.

Fig. 1(a) shows the XRD patterns of the resultant products sintered at 1450 °C. It is found that the only phase is Nb_2AlC, and no other phases are detected. The measured lattice parameters of Nb_2AlC are $a = 0.3106 \pm 0.0002$ nm and $c = 1.3884 \pm 0.0002$ nm, which are very close to those reported by other authors [23,41]. Fig. 1(b) and (c) presents the SEM images for the fractured surface of samples sintered at 1450 °C. The grains with the layered features characteristic of Nb_2AlC can be clearly seen in the samples. The average grain size of Nb_2AlC is about 10 μm. The surface of particles is very clean, and there are few nanoparticles on the surface because they can be purified by plasma generated by pulse current.

3.2. Mechanical properties of Nb_2AlC

The physical and mechanical properties of obtained Nb_2AlC were measured and are summarized in Table 1 together with those of typical H-phase including Ti_2AlC, Ti_2AlN, Cr_2AlC and Ti_2SC for comparison. The density of bulk material sintered sample is 6474 kg/m^3, i.e., 99.6% of the theoretical value (6500 kg/m^3). The fracture toughness of Nb_2AlC is 7.8 ± 0.2 MPa m$^{1/2}$, which is higher than that of the other H-phase, and much higher than that of conventional ceramics such as Al_2O_3, SiC, Si_3N_4, and TiB_2. This is probably related to the characteristic layered structure of Nb_2AlC grains. The flexural strength of Nb_2AlC is 440 ± 10 MPa, which is higher than that of Ti_3AlC_2 and Ti_3SiC_2. Vickers indentation hardness is tested on the polished polycrystalline Nb_2AlC surface. The ultimate polished surface of the sample shows metallic luster. The measured Vickers hardness of the Nb_2AlC sample is 4.0 GPa, which is slightly lower than that of other reported results. More importantly, similar to other MAX phases, the material has the same machinability and could be easily machined using ordinary machining tools. For example, holes could readily be drilled using common steel drills without adding lubrication.

3.3. Thermal and electrical properties of Nb_2AlC

As shown in Fig. 2(a), the average expansion coefficient of the Nb_2AlC sample in the range of 25–1200 °C (298.15–1473.15 K) is $9.0 \times 10^{-6}\ K^{-1}$, in good agreement with the value ($8.7 \times 10^{-5}\ K^{-1}$) reported in a previous study [24], and very close to that of Ti_2SC ($9.3 \times 10^{-6}\ K^{-1}$) [42] and Ti_3AlC_2 ($9.0 \times 10^{-6}\ K^{-1}$) measured from 25 °C to 1200 °C [14]. The specific heat capacity and thermal conductivity of the sample are increased from 25 °C (298.15 K) to 500 °C (773.15 K), as shown in Fig. 2(b). The heat capacity at 25 °C is 0.290 J/(g·k), which is very close to that of Nb_2AlC in a previous report [25]. However, this value is still lower than that of Ti_2AlC (0.624 J/(g·K))