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Technical Report

Effect of nano-yttria addition on the properties of WC/Co composites

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ABSTRACT

Nano-grained yttria additions to WC/Co based composites have the potential to replace standard materials for tools, dies and wear parts because of their increased hardness and toughness. By means of particle size reduction, the fracture toughness of WC/Co can be increased significantly. This work aims at processing and sintering of composites from WC/Co and 5–20 wt.% nano-grained yttria. The composite mixtures were mixed, formed and sintered at 1450 °C under vacuum. The properties of these composites in terms of densification parameters, fracture toughness, and hardness were measured. The results explored a significant improvement in the properties of WC/Co with addition of 5 wt.%Y_2O_3. However, the addition of less or more quantity of nano-grained yttria than 5 wt.% has been shown a negative effect on the properties. Fracture toughness (K_{1C}) of the WC/Co–5 wt.%Y_2O_3 showed remarkable enhancement (~13.611 MPa $m^{0.5}$) compared by the reported data of WC–6.5%Co composite (~9–11 MPa $m^{0.5}$). The microstructure was correlated with changes of these properties.

1. Introduction

Tungsten carbide [WC]-based composites have been extensively used in various engineering applications such as cutting tools, rock drill tips, tools, dies as well as general wear parts [1–9] due to their unique combination of mechanical, physical, and chemical properties. Co-bonded aggregated WC particles via liquid phase sintering are commercially one of the oldest cemented carbides and most successful powder metallurgy products [10,11]. The exceptional mechanical properties of these composites in terms of elastic modulus, hardness and fracture toughness are derived from a combination of the hard refractory WC and soft ductile Co [12].

The mechanical properties of WC–Co composite materials can be further improved by decreasing the WC grain size to the submicrometer or nanometer scales [13]. Therefore, designation of ultrafine-grained and nanocrystalline WC–Co cemented carbides has become one of the hot issues in the field of high-performance hard materials during the last decade. However, WC grain growth occurs during sintering of the nanometer sized WC–Co raw powder mixtures through conventional pressureless sintering, especially in liquid state [14,15]. Therefore, much efforts have been made and ongoing research focusing on the development of full densification at lower sintering temperature and/or within a shorter thermal cycle time, such as hot pressing [16], microwave sintering [17] or spark plasma sintering (SPS) [18,19].

However, the high cost is hardly avoided with such processes in industrialization. Till now, the most successful method of controlling the WC grain growth is the addition of small amounts of grain growth inhibitors, typically metallic carbides and oxides such as VC, Cr_3C_2, Y_2O_3, NbC or Mo_2C to the raw powder mixtures with content less than 1 wt.% [20–24]. Also, The dispersion of nanograined second phase particles within the matrix or along the grain boundary of the micron and/or submicron-sized matrix material leads to significant improvement in strength and fracture toughness by the order of two to four times compared to a conventional composite material [25].

Despite the promising properties of conventional as well as nanostructured WC-based composites, the presence of a metallic phase severely limits the performance and hinders the use of such materials, particularly in applications demanding high hot hardness and high-temperature properties. This is due to the partial softening of the less refractory metallic phase at high temperatures. Such a metallic phase with inferior corrosion/oxidation resistance is more likely to be the preferential site for the initiation of unwanted corrosion/oxidation-induced failures, [26–29] thus limiting the life and performance of the composites in corrosive environments. To overcome such drawbacks, some researchers explored the feasibility of developing binderless monolithic WC using SPS [6,27–29]. However, in the absence of the metallic binder phase, extremely high sintering temperatures (1700–1900 °C) are required to obtain near fully dense (~97–98%) bulk WC even with the use of SPS. Furthermore, such monolithic WC ceramics possess significantly inferior fracture toughness properties in comparison to the Co-containing cemented carbides.

This work aims at processing and sintering of composites from WC/Co and 5–20 wt.% nano-grained yttria. The physical and mechanical properties of the obtained composites will be explored.

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2. Materials and experimental procedures

WC (93.35%), Co (6.5%), TaC + NbC 0.5% (San Diego, California, 92121-259) was used. The grain size of tungsten carbide powder was less than 125 mesh as starting material. High purity Y_2O_3 (99.995%) of crystallite size of 81 nm (Tung. Heavy powder Inc.) was used as additives.

5–20 wt.% Nano-grained Y_2O_3 in increments of 5 wt.% were added to WC/Co powders. These powder mixtures were well-mixed in a planetary mill for 2 h in presence of wax binder (1 wt.%). The produced composite powders Y_2O_3–WC/Co were cold compacted in die diameter of 0.7 cm under pressure of 600 MPa using an uni-axial press. The compacted specimens were dried, and sintered in a vacuum furnace at 1450 °C for 3 h. The applied heating rate was 2 °C/min up to 450 °C with dwell times of 15 min at 250 °C and 15 min at 450 °C, and then the heating rate was raised to be 5 °C/min from 450 to 1450 °C with dwell times of 30 min at 1000 °C and 3 h at 1450 °C.

Densification parameters of the sintered samples in terms of apparent porosity and bulk density were measured in aqueous media by Archimedes' method according to JIS R2205-1992 [30].

Polished surfaces of the specimens were investigated using Scanning Electron Microscope (SEM, Model JSM-5410, JEOL, Tokyo, Japan) with electron dispersive spectroscopy (EDS). Such investigations were performed to identify the sample textures, phases and their distribution. From these data, it is possible to understand the behavior of the samples after sintering and their correlation with changes of the sintering parameters.

Macrohardness and fracture toughness values have been determined, at room temperature, on the polished surface considering an average of five indentation using Vickers indentation method [31,32] with 20 kg load for 15 s. The crack paths, introduced by Vickers indentation with 20 kg load, were investigated in order to evaluate toughening mechanisms.

Calculation of the fracture toughness "K_{IC}" was carried out based on the nature of cracks observed. In case of palmqvist cracks, K_{IC} was calculated based on the palmqvist shaped-crack model using the following equation:

$$K_{IC} = 0.0515P/C^{3/2} \quad (1)$$

However, in the case of halfpenny cracks, K_{IC} was calculated based on the half-penny shaped-crack model using the following equation:

$$K_{IC} = 0.0726P/C^{3/2} \quad (2)$$

where C is the crack length measured from the middle of the Vickers indentation (m), P is the indentation load (N), K_{IC} is the fracture toughness (MPa $m^{1/2}$).

3. Results and discussion

3.1. Densification

The properties related to densification in terms of bulk density and apparent porosity of the sintered samples are presented in Fig. 1. In general the apparent porosity of the sintered specimens is inversely proportional to their bulk densities, i.e. the apparent porosity increases following the decrease of the bulk density and vice versa. The densification parameters of the presented results are in agreement with this behavior. On the other hand, the apparent porosity of the WC/Co–5 wt.%Y_2O_3 specimen is close to 1% and bulk density close to 13 g/cm^3. This means that the composite specimen containing 5 wt.% Y_2O_3 is near fully dense. This is due to the outstanding coupling between WC and Co represented by low dihedral angle of WC–Co system, which is reported to be zero,

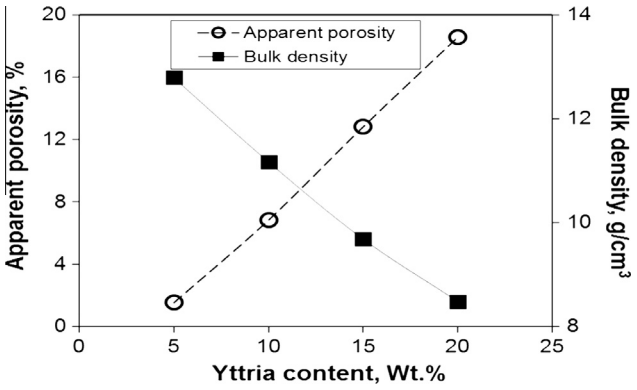

Fig. 1. Density and apparent porosity of WC/Co–Y_2O_3 composite specimens sintered at 1450 °C for 3 h.

dissolution of significant amount of WC by Co and formation of a ternary eutectic reaction at 1275 °C. With the increase of the Y_2O_3 content in the studied mixtures above 5 wt.%, the apparent porosity increased from ~6% to ~18% and bulk density decreased from ~6 to ~8 g/cm^3. The significant increase of the apparent porosity and in turn the decrease of bulk density can be understood in terms of the addition of nano-grained yttria on micron/submicron WC/Co. The nano-grains have a high surface area and the volume of nano-grained yttria weight to the volume of the same weight of micron/submicron grain system of WC/Co is twice. This means that nano-grained yttria occupies a large area and is easy to agglomerate and hinder densification. Therefore the addition of small amounts of nano-grained yttria will be effective and overcome agglomeration and facilitate the densification. Based on these results, addition of 5 wt.% from nano-grained yttria is equivalent for 90 wt.% WC/Co grains from the volume term and this amount is sufficient to cover the distances or spaces between WC/Co grains without agglomeration. Thus, the addition of large amounts from these grains on micron/submicron grains hinders the densification.

3.2. Microstructure of the sintered composites

Fig. 2 shows the SEM micrographs of WC/Co–Y_2O_3 composites sintered at 1450 °C for 3 h. The microstructure of WC/Co composite without yttria as seen in Fig. 2a revealed that WC/Co exists in rounded to sub-rounded coarse and fine grains (grey colour) cemented by liquid phase (black colour). The tailoring of the texture can be understood according to the published work [33], whereas, solid state sintering proceeds in three stages: (1) Co matrix spreads over the WC particles covering their surfaces and separating them from each other; (2) the spreading Co agglomerates neighboring WC particles, acting like a cement and; (3) the resulting agglomerates form a network and sinter together as large particles. The details of this mechanism are schematically shown in Fig. 3. During the sintering process, the pores are closed, the WC particles change their shape and the binder phase spreads throughout the structure.

In case of yttria free WC–Co composite, Co particles would preferentially occupy the pores between the WC particles, forming Co agglomerates. As a consequence of this, the number of contacts between WC and Co particles decreases as the WC means size increases. On the other hand, several small WC particles surfaces are wetted and covered by Co. These particles move along relatively (rotationally or sliding) short distances by capillary forces to be closer to each other. Thus the WC–Co agglomerates with fine WC particles were more easily formed than the case of coarse WC particles. This in turn exhibited uniform distribution of the