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High hardness-high toughness WC-20Co nanocomposites: Effect of VC variation and sintering temperature

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ABSTRACT

WC-Co nanocomposites with variable VC content are synthesized by liquid phase sintering at two different temperatures. The as synthesized samples are characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and optical microscope. The mechanical properties are obtained by Vickers indentation method. The high content of VC, lead to high porosity when sintering temperature is increased from 1350 to 1400 °C. The relative density of all the samples is more than 95%. Microstructure reveals that agglomeration of W-Co-C and V-W-C increases at 1400 °C, which generates layered interfaces in radial direction and hence the material inhomogeneity. XRD pattern shows that the formation of η phase increases at 1400 °C, which is responsible to decrease the fracture toughness of the present samples. The average particle size of 102 nm, highest hardness of 1870.6 kgf/mm^2 with fracture toughness of 14.4 MN/mm$^{3/2}$ is observed in sample having 7.5 wt% VC, sintered at 1350 °C for one minute. This combination shows the highest hardness and reasonably high toughness as compared to conventionally sintered materials reported so far.

1. Introduction

Tungsten carbide (WC) has always been the good choice of the tool making industries throughout the world. Characteristics of high hardness, cost effectiveness and advancements in processing over the years make it highly acceptable as a cutting tool material for various industries. Use of nano materials and advanced processing techniques like spark plasma sintering (SPS), high frequency induction heated sintering (HFIHS), microwave sintering, pulse plasma sintering (PPS) and other fast sintering techniques [1 – 5] could further improve the hardness and toughness of the materials. However these sophisticated advance-processing techniques are not cost effective for the mass production, on the other hand conventional liquid phase sintering (CLPS) method is cost effective technique to synthesize high hardness nano material. Although, it is difficult to control the grain growth of WC-Co nanocomposite during LPS, however optimizing the processing parameters and different material combinations can enhance to achieve desired results [1,6–9]. Maintaining high hardness along with high toughness is of major concern for WC-Co nanocomposites. Many methods have been used to increase the wear resistance of as produced materials by coating diamond, TiC or TiN film on WC-Co composite. The coating on WC-Co composite may create some other problem, like crack development in thin film of high hardness material due to mismatching of thermal expansion coefficient. Small cracks initiated at cutting edge accelerate very rapidly into the WC-Co composite, which leads to majority of tool failures. There is need to develop WC-Co nanocomposite having high toughness with limited fall in hardness. Generally, high hardness materials have poor toughness as reported by many researchers [3–5,8–13]. The addition of VC forms secondary phase, which segregates along the boundaries of tungsten/cobalt to prevent the grain growth and refine the microstructure of WC-Co [10,14–18]. Basically formation of the interface between VC and WC-Co not only decrease the grain growth but also increase the hardness as well as toughness. For instance, a sample sintered through SPS [19] has high hardness of 2480 kgf/mm^2 but possess very low fracture toughness of 6.6 MN/m$^{3/2}$. Similarly a sample having high fracture toughness [9] of 20.8 MN/m$^{3/2}$ was reported with 1264 kgf/mm^2 hardness. All the samples consolidated through modern techniques as well as through CLPS technique were biased either for high hardness or high toughness. The selection of grain growth inhibitor depends on parent materials, solubility of inhibitor in binder phase, particle size of starting material and binder content in the mixture [20]. In case of WC-Co, usually VC, Cr_3C_2, NbC, TaC, CeO_2 etc. are widely used [1,4,10,11,20] grain growth inhibitors (GGI). VC is among the most effective and widely used grain growth inhibitor in WC-Co

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Table 1
Chemical composition of samples.

Sample no.	Composition (wt%)	Sintering temp. (°C)	Pellet dia. (mm)	Pellet thickness (mm)	Relative density (g/cm^3)	Hardness (kgf/mm^2)	Fracture toughness (MN/m$^{3/2}$)
P33	WC-20Co	1350	9.015	1.11	97.87	1582.1	14.3
P34	WC-20Co-2.5VC	1350	8.915	1.18	97.69	1693.8	14.1
P35	WC-20Co-5VC	1350	8.855	1.12	98.33	1709.8	15.1
P36	WC-20Co-7.5VC	1350	8.970	1.23	98.64	1870.6	14.4
P37	WC-20Co	1400	9.091	1.07	97.43	1566.3	15.5
P38	WC-20Co-2.5VC	1400	9.023	1.15	95.95	1701.3	13.8
P39	WC-20Co-5VC	1400	8.875	1.21	96.51	1649.8	14.7
P40	WC-20Co-7.5VC	1400	8.895	1.22	97.96	1687.4	12.4

mixture [1,21]. Using very low quantity of VC, very fast heating rate and isothermal holding of very small interval is the concept of most of the advanced sintering techniques to control the grain growth. Techniques like SPS and HFIHS, even claim to produce sufficiently high strength material without the use of GGI [3,5]. Moreover, selection of sintering temperature must be close to the melting point of ingredients i.e. $0.98T_m$ [20–22] to achieve good sintered specimen for better properties. Effectiveness of GGI and its role in controlling the grain growth over wide range of sintering temperature is also of great importance [14,20,21]. Studies represented that 0.01–2 wt% of VC as GGI in WC-Co composite worked well to control the grains up to submicron or even nanometer scale [8–10,11]. Scope of using high wt% VC as a GGI as well as supporting constituent is rarely reported in literature [23,24]. However, some research work has discussed the role of VC in increasing the hardness of the WC-Co composite [8,15,20,24].

The small amount of grain growth inhibitor is effective for the bulk material where initial particle size is in the range of micrometer. However, in case of nanomaterials the surface area of the matrix material is very large. Also, the intra and interdiffusion of initial material among the ingredients is very fast during sintering, hence more amount of grain growth inhibitor may required to encapsulate more and more WC particles. Moreover, the high content of VC may also form interface layers, which results to prevent the movement of dislocations.

Present study represents the effect of high VC wt% on the phase formation and segregation into gradient layers of VC, formed during conventional LPS. Idea behind the use of high wt% VC is that the Young's modulus of VC is 422 GPa, which is higher than that of cobalt i.e. 207 GPa and lower than that of WC (696 GPa). Their phases improve the strength of the composite. Fast heating rate (10 °C/min), fast cooling rate (25 °C/min), very short holding time of one minute and high value of VC as grain growth inhibitor, aimed to achieve final particle size in nanometer scale. High cobalt content increases the toughness of WC-Co composites but reduces its hardness. In contrast to that VC contributes in increasing the toughness and suppresses the grain growth to high extend for maintaining reasonably high hardness. The present study provides a novel combination of high hardness along with high toughness achieved through conventional liquid phase sintering of WC-20Co nanocomposite.

2. Experimental methods

2.1. Materials and processing

Ultrafine WC nanopowder of particle size 55 nm (free carbon 0.08%) and VC of particle size 600–800 nm with 99.9% purity were supplied by US Research Nanomaterials, USA. Sigma Aldrich, USA, supplied cobalt powder having particle size of 2 μm with 99.8% purity. Samples with different composition were prepared by varying the quantity of VC from 0 to 7.5 wt% in a step of 2.5. The samples were uniformly mixed into acetone media. After drying samples were again ground to break large size agglomerates.

2.2. Sample preparation

Mixed powder was uni-axially compressed using high quality tungsten carbide die-set [19] to make pellets of diameter (ϕ) 10 mm and thickness 1.6 mm in hydraulic press (Polyhedron, India- Model 5010) under compressive load of 206.8 MPa. Specially designed compaction method [23] was used to maintain the high green density and defect free structure of the pellet. Pellets were made without the use of any wax or bonding material to attain maximum density during sintering.

The pellets with different chemical composition as described in Table 1 were sintered in a tubular furnace under controlled argon atmosphere. Uniform heating-rate of 10 °C was maintained and sintering temperature was 1350 °C and 1400 °C in two sets with holding time of 1 min. Fast cooling rate of 20–25 °C/min was followed until 800 °C to control the grain size. The as sintered samples were mirror finished using diamond paste up to grit size of 1 μm for further characterization.

2.3. Characterization and testing

Relative density of the sintered samples was measured using Archimedes principal. Shrinkage along the diameter and thickness was also calculated by measuring the size of the pellet before and after sintering, using Mitutoyo digital vernier caliper. Vickers micro-hardness of polished samples was measured using Mitutoyo (MVK-HO, Japan), hardness testing machine under 1 kgf indentation load and 20 s dwell time. Average micro-hardness of ten different locations over the whole surface was considered. Fracture toughness (K_{IC}) was measured using Anstis Eq. (1), which is based on median crack system and gives indentation fracture toughness (IFT) [3,10,25] under 10 kg indentation load.

$$K_{IC} = 0.016(P).(E/H)^{1/2}.(C)^{-3/2} \quad (1)$$

where K_{IC}=Fracture toughness (MN/m$^{3/2}$), P=Load (kg), E=Young's Modulus (GPa), H=Hardness (kgf/mm^2) and C=Crack length (mm) of the indentation. Average value of ten different locations was considered for every sample. Crack length measurement and surface analysis was done with Nikon 3300 Metallurgical Microscope at different resolutions (100× to 1500×).

After the measurement of micro-hardness and fracture toughness the polished samples were etched with solution of 15 ml HNO_3, 15 ml H_2O, 15 ml Acetic Acid and 60 ml HCl. Etching solution was prepared fresh and aged for one hour prior to etching. Samples were immersed for 60 s to effectively remove cobalt from the polished surface of the samples.

Scanning Electron Microscopy (SEM) and Energy Dispersive