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Reactive Sintering of Bimodal WC-Co Hardmetals

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Bimodal WC-Co hardmetals were produced using novel technology - reactive sintering. Milled and activated tungsten and graphite powders were mixed with commercial coarse grained WC-Co powder and then sintered. The microstructure of produced materials was free of defects and consisted of evenly distributed coarse and fine tungsten carbide grains in cobalt binder. The microstructure, hardness and fracture toughness of reactive sintered bimodal WC-Co hardmetals is exhibited. Developed bimodal hardmetal has perspective for demanding wear applications for its increased combined hardness and toughness. Compared to coarse material there is only slight decrease in fracture toughness (K_{1c} is 14.7 for coarse grained and 14.4 for bimodal), hardness is increased from 1290 to 1350 HV units.

Keywords: hardmetals, reactive sintering, bimodal, mechanical properties, microstructure.

1. INTRODUCTION

WC-Co hardmetals are still predominant of hardmetals since the composition of the hard and brittle tungsten carbide phase that is cemented by the Co rich binder phase, provides an efficient complex of mechanical and tribological properties [1, 2]. Mechanical properties are dependent on the Co content and WC grain size [3]. Lower Co content increases hardness and decreases transverse rupture strength (TRS); decreasing WC grain size improves both of these characteristics [4, 5].

When it comes to wear resistance the relations with Co content and WC grain size are not so straightforward. Often only hardness is used in order to evaluate wear resistance of hardmetals, but according to Hack et al. this approach is invalid, since wear resistance is functionally related to hardmetal plane strain bulk fracture toughness. Abrasive resistance increases when fracture toughness increases [6, 5]. Fracture toughness, K_{IC} of WC-Co alloys is known to increase as binder phase volume fraction, mean carbide grain size and binder phase mean free path are increased [4]. The hardmetals with coarser carbide grains have higher toughness than finer grained grades yet lower hardness [7, 8]. Generally, improvement of hardness and toughness concurrently has been the main research topic since cemented carbides were invented [9].

It is found that introducing coarse grains in otherwise fine-ultrafine structure can increase fracture toughness without sacrificing the hardness [10]. It results in microstructure where different grain sizes appear simultaneously, so called bimodal structure. Till now bimodal grain size distribution is achieved by mixing together WC-Co sources with different mean carbide particle sizes [11].

The aim of present study is to explore possibility of achieving bimodal structure via utilising reactive sintering approach. Reactive sintering, also known as the integrated mechanical and thermal activation is a novel method for producing fine and ultrafine grained WC-Co hardmetals [12 – 14]. Since reactive sintering solely yields hardmetals with fine/ultrafine structure there is a need to add additionally coarse grained hardmetal source. During present investigation mechanically activated W and C powder mixture was added to the commercial WC-Co powder with coarse grade carbide grain distribution in order to achieve bimodal structure as result. Prepared specimens were investigated in terms of mechanical properties and microstructure.

2. EXERIMENTAL DETAILS

In order to achieve bimodal structure in WC-Co hardmetal the pre-milled and activated W and C was mechanically mixed with coarse grained commercial WC – 15 wt.% Co with mean carbide grain size of 2 µm (Fig. 1).

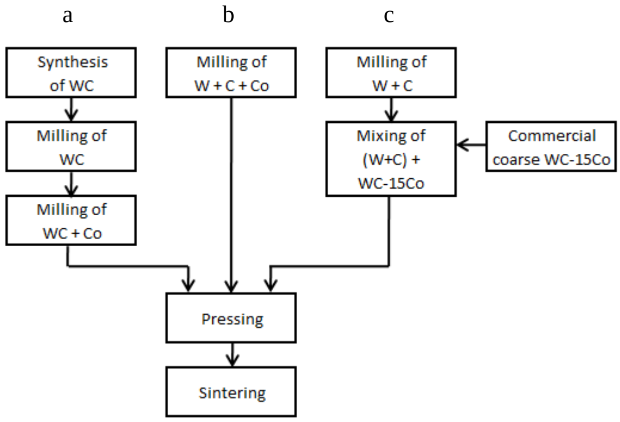

Fig. 1. Production routes for preparing WC-Co hardmetals: a – conventional route; b – reactive sintering; c – reactive sintering combined with conventional method – current research

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Table 1. Prepared materials and their properties (minimum, maximum and mean carbide grain size, hardness and fracture toughness)

Designation	Material	Carbide grain size			Hardness, HV30	K_{IC}, MPa·m$^{1/2}$
		Min., μm	Max., μm	Mean, μm		
Base	commercial coarse WC – 15Co	0.11	7.92	2.00	1030	15.8
R1	conventional coarse WC – 10Co	0.11	4.95	1.60	1290	14.7
R2	conventional fine WC – 10Co	0.14	4.21	0.92	1463	13.2
E1	reactive sintered WC – 10Co	0.12	2.72	0.66	1480	13.5
E2	mixed (bimodal) WC – 10Co	0.12	7.71	0.93	1350	14.4

In WC monocarbide the stoichiometric carbon content is 6.13 wt.% [15]. In current work carbon content in starting W-C mixture was kept at 7.1 wt.% in order to compensate the decarburization in the furnace during sintering [12].

Wet milling of W-C was carried out in conventional ball mill with ball-to-powder ratio of 10 : 1. The vessel of ball mill and balls used are made of hardmetal. Isopropanol was used as milling liquid. WC-15Co and W-C were mixed with ratio of 2 : 1 which yielded 10 wt.% Co in final composition. Dry mixing was performed in mechanical mixing device for 24 h. Paraffin wax was added as plasticiser to aid compacting of powders. Acquired powder mixture of commercial hardmetal and mix of W-C were compacted to the green bodies by uniaxial pressing (90 MPa). The green compacts were directly sintered in sinter/HIP furnace (temperature T = 1390 °C, dwelling time t = 35 minutes, sintering pressure p = 30 bar Ar).

Coarse grained WC-10Co (R1, Table 1) and fine grained WC-10Co (R2, Table 1) were prepared as reference materials using conventional powder metallurgy method for producing WC-Co hardmetals (Fig. 1 a) [2]. In addition WC-10Co (E1, Table 1) produced solely through reactive sintering route was used as comparison (Fig. 1 b) [12].

The microstructures were investigated with SEM (Zeiss EVO MA-15) and grain size analysis was carried out with Image Pro Plus software.

Vickers hardness was measured in accordance to the ASTM Standard E384. The fracture toughness (K_{1C}) was determined by measuring the crack length from the tip of the indentation made by Vickers indentation (Palmqvist method). The toughness is calculated by the following equation [16]

$$K_{1C} = 0.0726 \frac{P}{C^{3/2}}, \tag{1}$$

where P is load of Vickers indenter (N) and C is half of diagonal + crack length (mm).

3. RESULTS AND DISCUSSION

3.1. Microstructures

Fig. 2 depicts the microstructure of commercial WC-15Co that was used in current study as base material. When carbon content is in stoichiometric range the microstructures of WC-Co hardmetals consists of two phases – WC grains embedded in cobalt based binder phase β. Microstructures of coarse and fine grained reference WC-10Co (R1 and R2), reactive sintered WC-10Co (E1) and mixed (bimodal) WC-10Co (E2) are exhibited in Fig. 3.

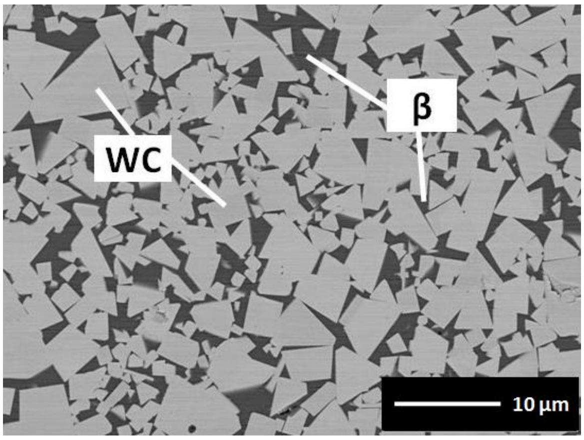

Fig. 2. Microstructure of commercial WC-15Co

Coarse grained R1 (Fig. 3 a) and fine grained R2 (Fig. 3 b) have homogeneous coarse and fine grained structure respectively. Reactive sintering (E1) yields even finer hardmetal structure (Fig. 3 c). The microstructure of mixed experimental material E2 (Fig. 3 d) is more patched – large and fine WC grains appear concurrently. Still the distribution of fine and coarse grains is not uniform. As seen on Fig. 3 d the microstructure consists of coarse grained areas embedded in ultrafine grained matrix (areas surrounded by dashed line). If uniform distribution of coarse grains in microstructure is needed, then additional mixing techniques to mechanical mixing should be used.

3.2. Grain size

Grain size distribution of prepared materials is exhibited in Fig 4. Despite the microstructure of bimodal material E2 (Fig. 3 d) differs from others (Fig. 3 a – c) its grain size distribution resembles the ones of fine grained (Fig. 3 b) and reactive sintered (Fig. 3 c). The large grains that appear in bimodal microstructure change the outlook of its microstructure but when compared their quantity to fine WC grains its evident that they do not impact grain size distribution curvature. Therefore the bimodal state of microstructure is not revealed in graphs.

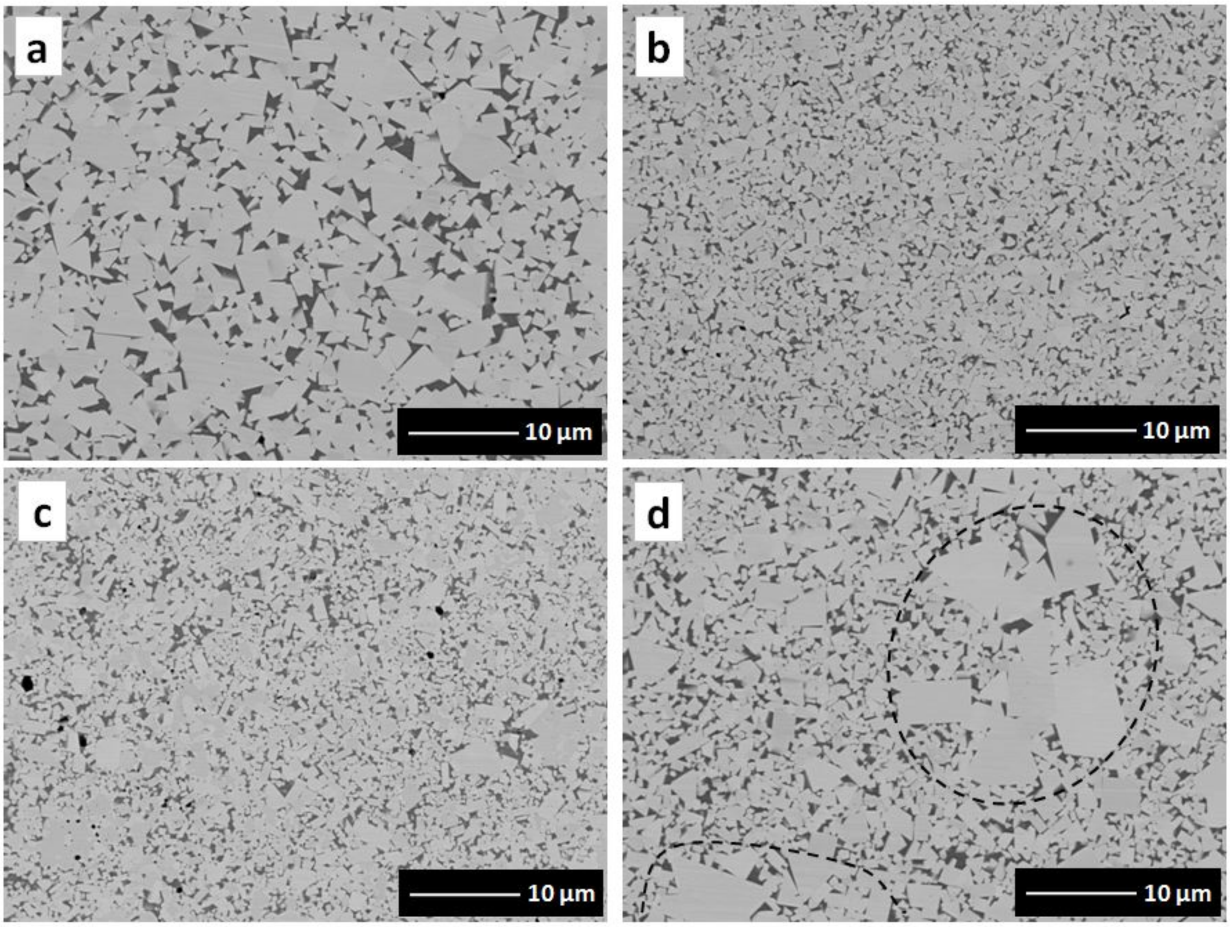

Fig. 3. Microstructures of conventional coarse grained material R1 (a), conventional fine grained material R2 (b), reactive sintered material E1 and experimental bimodal material E2 (d)

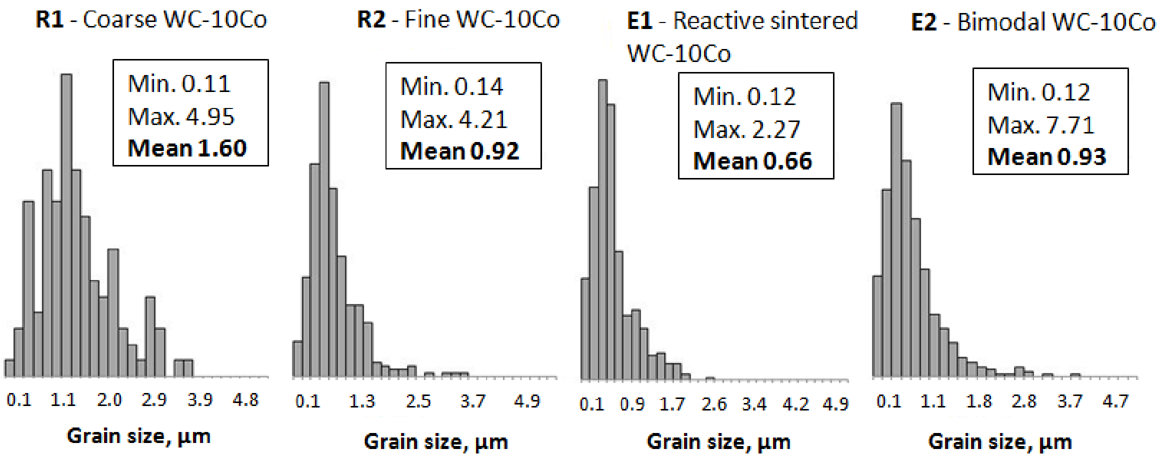

Fig. 4. Grain size distribution of prepared WC-10Co hardmetals

Reactive sintered material E1 yielded smallest average grain size (0.66 µm) – by one third finer than the mean grain size of conventional fine grained R2 (0.92 µm) and mixed hardmetal E2 (0.93 µm). Difference of mean WC grain sizes between E1 and E2 derives from large WC grains that are present in base material WC-15Co as well as mixed E2 (Fig. 3).

3.3. Mechanical Properties

Vickers hardness and fracture toughness values of commercial WC-15Co and prepared materials are exhibited in Fig. 5. Fine grained materials R2 and E1 have highest hardness values. This is well in accordance with other researches have been done in hardmetal field. While materials R1 and E2 have lower hardness values they excel in fracture toughness. At the same binder content (10 wt.%) the increase in fracture toughness can be explained with the presence of large WC grains in structure (Fig. 2 a and Fig. 3), which tends to retard the crack propagation. Studies have shown that appearance of coarser WC grains have the deflection influence to the crack spread and therefore inhibit crack propagation [10]. When comparing experimental mixed material E2 with coarse and fine grained counterpart the results are following:

- Higher hardness than coarse grained and lower hardness than fine grained WC-10Co hardmetal;
- Higher fracture toughness than fine grained and lower fracture toughness than coarse grained hardmetal.

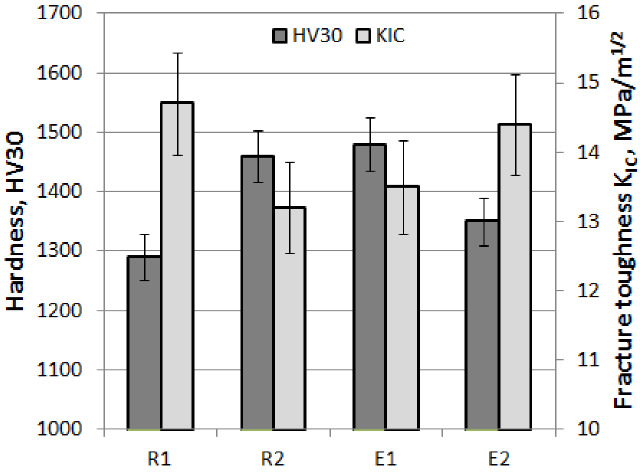

Fig. 5. Hardness and fracture toughness of prepared WC-Co hardmetals

However the uncertainty of fracture toughness values acquired with indentation method diminishes the reliability of these results. Ultimately in terms of hardness and fracture toughness the mixed material E2 yielded similar results to conventional coarse grained WC-10Co R1.

4. CONCLUSIONS

- A novel approach to produce WC-Co hardmetals was developed – pre milled and activated W and C were mixed with with commercial coarse grained WC-15Co. Bimodal microstructure was achieved as a result.
- Acquired microstructure exhibits large and fine WC grains concurrently (bimodal structure). Though the structure is not uniform – areas with larger carbide grains interchange with areas with finer distribution.
- Experimental bimodal material has higher mean carbide grain size value than material that was prepared solely through reactive sintering (0.93 μm and 0.66 μm respectively).
- Novel bimodal material has similar fracture toughness as coarse grained WC-Co (14.4 and 14.7 respectively) and higher hardness values (1350 and 1290 respectively).
- The grain size distribution of experimental bimodal material resembles the one of fine grained material's while the mechanical properties are more comparable to the results that yielded coarse grained material.

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