



of Achievements in Materials and Manufacturing Engineering VOLUME 20 ISSUES 1-2 January-February 2007

Structure and properties of TGM manufactured on the basis of cobalt

G. Matula, L.A. Dobrzański*, B. Dołżańska

Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland * Corresponding author: E-mail address: leszek.dobrzanski@polsl.pl

Received 03.11.2006; accepted in revised form 15.11.2006

Materials

ABSTRACT

Purpose: It has been demonstrated in the paper structure and properties of tool gradient materials manufactured by powder metallurgy on the basis of cobalt.

Design/methodology/approach: Light microscope, SEM, image analysis, microhardness tests, density examination.

Findings: Basing on the investigations of the cemented carbides reinforced with deffrerent ceramics particles fabricated it was found of that density of sintered samples depend on reinforced particles, temperatures and atmosphere of sintering. Increasing of sintering temperature increase the density of sintering samples. Moreover the sintering under vaccum atmosphere produce samples with higher quality than using argon atmosphere and prevent of surface oxidation during sintering.

Practical implications: The Powder Metallurgy gives the possibility to manufacturing tools gradient materials on the basis of cobalt which characterised very high hardness on the surface.

Originality/value: In the paper the manufacturing of tool gradient materials on basis of cobalt reinforced with hard ceramics particles carried out in order to improve the tool cutting properties.

Keywords: Tool materials; Cemented carbides; Tool Gradient Materials; Powder Metallurgy

1. Introduction

Sintered carbides introduced in twenties of XX century by Krupp concern have the longest history as the sintered tool materials. Continued investigations and search for new, better tool materials, carried out by research centres dealing with tool materials have caused that structure and properties of sintered carbides have changed diametrically during these more than 80 years. Their high abrasion wear resistance and relatively low price compared to other tool materials have made sintered carbides most popular in this material group. The idea proposed by K. Schröter to use cobalt as metal binding the hard WC phases is very interesting from technological point of view, and especially its sintering process [1, 2]. Sintering with the liquid phase, accompanying fabricating sintered carbides with cobalt matrix, may be carried out at lower temperatures, i.e., at about 1450°C, compared to tool ceramics sintered in solid phase. It is a fact that the sintering temperature of the high-speed steels does not exceed 1300°C [3-5]. However, the narrow sintering window of about 5°C, depending on steel grade, calls for using accurate heating equipment [6-8]. Moreover, hardness and wear abrasion resistance of these materials is lower compared to sintered carbides. The concept of the toollyly graded materials - FGM, pertaining to materials in which structure and properties change gradually, continuously or in a discreet way (stepwise) along with the location in it, was developed theoretically in 1972 by Bever and associated [9, 10], however it was expatiated only after 15 years within the framework of a research project started in Japan, when various methods were developed to fabricate such materials [11-16]. The goal of this project is to use the hard ceramic particles and investigate the effect of their portion on structure and properties the gradient cobalt based tool materials.

2. Materials and methods

The classical powder metallurgy, i.e., the one-side uniaxial compacting was employed for fabricating the gradient materials. Cobalt powder shown in Figure 1a with the average grain size of up to 1.5 μ m was used as the substrate. The fine-grained tungsten carbide with the grain size of 0.85 μ m and the coarse grained one with the grain size of 0.50 μ m, shown in the Figures 1b and 1c, were used as hard reinforcing phases.

Carbides and cobalt powders were mixed for an hour and next formed in a die. Powder mixes were prepared with different cobalt portions in relation to the WC carbide and with different WC carbide grain sizes for compacting the prepregs with gradient structure. Table 1 presents the detailed information on powder types and their portions in particular gradient materials. About 2% mass portion of paraffin was added to increase the tungsten carbide portion and formability of the powder mix. The maximum portion of particles reinforcing the cobalt matrix was selected experimentally based on forming criterion. This consisted in compaction examining the prepreg with the unaided eve. Defects in the form of cracks or damaged prepreg corners eliminated the possibility to use the mix with such high portion of the reinforcing powder. The reinforcing phases' portion was lowered next, up to the value making forming the prepregs possible with no surface defects. Powder mixes were weighed and were poured into the die one by one. To form the gradient material the die was filled with six layers successively with the increasing portions of reinforcing phases, levelling each time the surfaces of layers being about 1 mm thick. The first (bottom) layer is the powder mix with the maximum cobalt content. The layer with the maximum portion of the WC reinforcing particles, with poor flow was poured as the last one, using the maximum compacting pressure during the unilateral forming, in the zone directly under the pressing stamp. All layers of the gradient material were compacted simultaneously under the pressure of 700 MPa. Prepregs were sintered at temperature of 1450°C in vacuum for 1 h. The sintered prepregs' density measurements were made using the Archimedes method basing on the product mass and the apparent loss of mass during immersion in water according to standard. Moreover, the measurement of the surface pores portion was made with the image analysis method on the Leica type light microscope. Because of the lack of clear boundaries between the gradient materials layer after sintering, the specimens were examined in three areas, i.e., in the upper layer, reach in carbide phase, in the middle one, and in the bottom one with the maximum cobalt content. Portion of pores was examined in 10 areas of each layer of the gradient material and its average value and standard deviation were calculated. Hardness tests of the sintered test pieces were made with the Vickers method on Wilson Wolpert 401 MVD Microvickers device with the load of 5 N.

<u>3.Results</u>

It was found out based on compacting tests of WC carbides powders mix with grain size of 50µm and cobalt in the uniaxial unilateral die that the maximum portion of the WC carbide in the powders mix that can be compacted is 85%. Adding about 2% of the mass portion of paraffin increases significantly formability of powders mix and makes it possible to increase the WC portion by 10%. In case of the WC carbide with the grain size of $0.85\mu m$, addition of paraffin makes it possible to increase the WC carbide portion by 7%. Addition of paraffin as a lubricant lowers friction significantly between powder particles and between the powder and the die.



Fig. 1. Powder of cobalt a) WC 0,85µm b) WC 50µm c)

Number of layer	Number of sample											
	I ^a		II ^a		III^{a}		IV^b		V ^b			
	Mass portion of powder in every layers*, %											
	WC	Со	WC	Со	WC	Со	WC	Со	WC	Со		
1	93	5	95	3	97	1	93	5	95	3		
2	88	10	93	5	96	2	88	10	93	5		
3	78	20	88	10	95	3	78	20	88	10		
4	68	30	83	15	93	5	68	30	83	15		
5	58	40	78	20	88	10	58	40	78	20		
6	48	50	-	-	83	15	48	50	-	-		

Table 1. Type and portion of powders used to manufacturing of TGM

*In every case added 2% of paraffin wax

^{a)} Grain size of tungsten carbides (WC $- 0.85 \mu m$)

^{b)} Grain size of tungsten carbides WC $- 0.50 \mu m$

This makes it possible to decrease the compacting pressure which is important because of lowering the stresses in the prepreg. Stresses are often the cause of cracks and defects during demoulding. Moreover, paraffin makes demoulding easier and decreases the density difference between areas of green compact. Porosity examined with image analysis method on the light microscope in areas with the lowest and highest density, of the compacted cobalt powder, was 6.5 and 7.9% respectively. Distribution of pores portion in the prepreg formed from cobalt powder under a pressure of 500 MPa. Density values of gradient materials, depending on the employed carbide powders after compacting and sintering are shown in Table 2. Density of gradient materials is dependant on the extent of compaction during sintering, but also in cobalt and WC carbide portions, whose density values are 8.8 and 15.5g/cm³ respectively. Therefore, gradient materials with the higher cobalt portion, regardless of the extent of compaction during sintering will have lower density compared to materials with a lower cobalt portion. Therefore, density measurement does not provide complete information about the extent of compaction of the gradient materials. Examination of the test pieces porosity made on the light microscope may yield more information about consolidation of the material during sintering; this way we can determine the portion of pores in the particular layer of gradient materials. Test pieces shape was deformed significantly in the sintering process, as shown in Fig. 2 connected with the bigger contraction of the cobalt rich layer and lower contraction the layer with the high carbide portion.



Fig. 2. View of sintered sample number I

The excessive cobalt portion, reaching up to 50% in the lower layer, may even lead to visible partial melting and to the necessity to lower the sintering temperature. A lower temperature will not ensure, on the other hand, the relevant compaction of the upper layer with the high WC content. Moreover, carbides grain size also affects contraction. Test pieces with carbides of the size of 50µm were subjected to smaller contraction than those with the grain size of 0.85µm. Regrettably, gradient test pieces with the coarser grain demonstrate big porosity. Bigger shape deformation was observed in materials in which carbide was used with grain size of 0.85µm and in which the WC phase portion difference between the upper and bottom layer was higher and was 45%; this deformation consisted in bending the prepreg in the direction to the lower layer in case of the smaller carbide portion difference value of 17% this prepreg bending was not that big. Test pieces in which coarse grained carbides were used, i.e., 50µm were characteristic of higher porosity especially in surface layers with the high carbide content. Portion of pores was more than 10% and reached about 30% in certain places, which disqualifies this material as the tool material. This is caused by the big grain size difference between the WC – about $50\mu m$, and cobalt – $1.5\mu m$. Such big imbalance of the powders grain sizes reduced the possibility of obtaining the homogeneous mix and made thickening of the prepreg more difficult during sintering. Also in test pieces in which the WC carbide with 0.85µm grain size was used occurrence of single big pores was revealed; however they did occurred at certain locations only and did not feature the big percentage. This is undoubtedly the effect of bad preparation of the powder mix, mostly paraffin, which makes local agglomeration, is subjected to degradation during heating to sintering temperature and created a big pore, which is not compacted during sintering. The results of pore portion measurement are presented in Table 2. The high porosity of test pieces with the WC carbide with the grain size of 50µm made it impossible to make hardness tests of these materials. Areas making hardness test possible occur locally, and their hardness is about 850 HV.

Table 2.Density and porosity of sintered gradient materials

Number o	f sample	Ι	II	III	IV	V
Density	, g/cm ³	13.8	14.4	14.3	9.7	9.5
	Layer 1	1.4	9.3	1.48	17.9	36.9
Porosity, %	Layer 2	0.1	5.5	1.22	15.2	22.8
	Layer 3	0.29	4.8	0.71	10.15	18.35

The maximum hardness values of the surface layers of all gradient materials for which the WC powder was used with the grain size of 0.85µm. The cobalt portion increase in the surface layer reduces its hardness from about 1600HV for the test piece with the maximum WC portion (97%) to about 1000HV for the one with the carbide portion of 93%. Structure examinations on the scanning microscope and analysis of the surface distribution in the micro-areas have revealed that the most homogeneous structure is characteristic for gradient materials reinforced with tungsten carbide with the grain size of 0.85µm.

4.Conclusions

It was demonstrated in the paper that in gradient materials formed from layers with the increasing portions of the reinforcing phases no delaminations occur in the cobalt matrix and there are no clear boundaries between the particular layers compacted in the die in the sintered state.

The essential information for further investigation of the gradient materials is that the big imbalance of the hard carbide phases between the upper wear resistant layer and the lower one with high impact strength results in deformation of the carbides' shape during their free sintering. The only feasible solution of this problem is the hot isostatic sintering, which, however, rises significantly the manufacturing cost of this type of tools.

Gradient materials in which the WC carbide grains were used with the size of 0.85μ m are characteristic for their low porosity and high hardness. The maximum hardness of the abrasion wear resistant upper layer, which reaches about 1600HV is higher than hardness of the commercially available carbides of the K20, K30 or B25 types, and comparable with hardness of the commercially available carbides of the K10 and P10 types. The TiC carbide was used in addition in the last one, which was not used in gradient materials.

Acknowledgements

Research was financed partially within the framework of the Polish State Committee for Scientific Research Project KBN PBZ-100/4/T08/2004 headed by Prof. L.A. Dobrzański.

<u>References</u>

- K.J. Brooks, Half a century of Hardmetals, Met. Pow. Rep. 50 (1995) 22-28.
- [2] L. Stobierski, Carbide ceramics, AGH, Kraków 2005.
- [3] B. Šuštaršic, L. Kosec, M. Kosec, B. Podgornik, S. Dolinšek, The influence of MoS₂ additions on the densification of water-atomized HSS powders, Journal of Materials Processing Technology. Vol. 173 (2006) 291-300.
- [4] P. Romano, O. Lyckfeldt, N. Candela, F. Velasco, Waterbased processing of high-speed steel utilising starch consolidation, Journal of Materials Processing Technology Vol. 143-144 (2003) 752-757.
- [5] L.A. Dobrzański, G. Matula, G. Herranz, A. Várez, B. Levenfeld, J.M. Torralba, Metal Injection Moulding of HS12-1-5-5 high-speed steel using a PW-HDPE based binder, Journal of Materials Processing Technology, Vol. 175 (2006) 173 – 178.
- [6] G. Matula, L.A. Dobrzański, A. Várez, B. Levenfeld, J.M. Torralba, Comparison of structure and mechanical properties of HS12-1-5-5 type high-speed steels produced by Powder Injection Moulding and Pressureless Forming method, Journal of Materials Processing Technology, Vol. 162-163 (2005) 230-235.
- [7] L.A. Dobrzański, G. Matula, A. Várez, B. Levenfeld, J.M. Torralba, Structure and mechanical properties of HSS HS6-5-2 and HS12-1-5-5-type steel produced by modified powder injection moulding process, Journal of Materials Processing Technology, Vol.157-158 (2004) 658-668.
- [8] G. Matula L.A. Dobrzański, Structure and properties of FGM manufactured on the basic of HS6-5-2, Worldwide Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 101 – 104.
- [9] M.B. Bever, P.F. Duwez, Mater. Sci. Eng., 10, 1972,1-8.
- [10] Shen M., Bever M.B., J. Mater. Sci. 7, 1972, 741-746.
- [11] H. Wan, S. Yao, Matsumura, Electrochemical preparation and characterization of Ni/SiC gradient deposit, Journal of Materials Processing Technology 145 (2004) 299–302.
- [12] S. Put, J. Vleugels, O. Van der Biest, Microstructural engineering of functionally graded materials by electrophoretic deposition, Journal of Materials Processing Technology 143–144 (2003) 572–577.
- [13] J. L. Johnson, R. M. German, Liquid Phase Sintering of Functionally Graded W-Cu Composites, 16th International Plansee Seminar, vol.2, 2005,116-130.
- [14] M. Collin, S. Norgren, Hardness gradients in WC-Co created by Local addition of Cr₃C₂16th International Plansee Seminar, vol.2, 2005, 227-241.
- [15] A. Eder, W. Lengauer, K. Dreyer, H. Van Den Berg, H.-W. Daub, D. Kassel, Phase Formation During Sintering of Functionally Graded Hardmetals, Plansee Seminar, vol.3 81-94, 2005.
- [16] A. Delanoe, J.M. Missiaen, C.H. Allibert, S. Lay, E. Pauty, Effects of the C potential and Cr doping on the densification of alloys WC-Co, 16th International Plansee Seminar, vol. 2, 2005, 642-653.