Materials Letters 196 (2017) 1–3

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Contact angles of WC/WC grain boundaries with binder in cemented carbides with various carbon content

I. Konyashin [a,b], B.B. Straumal [b,c,*], B. Ries [a], M.F. Bulatov [d], K.I. Kolesnikova [b,c]

[a] Element Six GmbH, Burghaun, Germany
[b] National University of Science and Technology «MISIS», Moscow, Russia
[c] Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Russia
[d] Moscow Technological University (MIREA), Moscow, Russia

ARTICLE INFO

Article history:
Received 24 February 2017
Accepted 1 March 2017
Available online 2 March 2017

Keywords:
Nano-crystalline metals
Thermodynamics
Kinetics
Grain boundaries
Cemented carbides
Binder drift

ABSTRACT

Contact angles of WC/WC grain boundaries (GBs) with the Co-based binder were measured by use of special model alloys with 10 wt% Co, ultra-coarse grained microstructure and either a low or a high carbon content. The low-carbon sample contained significantly more low-angle WC/WC contacts with binder than the high-carbon sample. Therefore, the wettability of WC/WC GBs by the liquid Co-based binder is noticeably worse in the high-carbon sample than that in the low-carbon sample. The established worse wettability of WC/WC GBs by binders at high carbon content sheds light on the mechanism of the binder drift during sintering of functionally graded cemented carbides containing high-carbon surface layers.

1. Introduction

In recent years there was a great interest to the fabrication of functionally graded cemented carbides due to their potentially usual and high mechanical and performance properties. The majority of technologies employed for the fabrication of functionally graded WC-Co cemented carbides are based on creating significant Co drifts from a surface region of carbide article with high carbon content into an interior region with a low carbon content [1–6]. Nevertheless, the mechanism of this phenomenon is presently not fully understood. The goal of this work is to clarify the possible influence of different states of WC/WC grain boundaries (GBs) completely or incompletely wetted by the liquid Co-based binder in the WC-Co cemented carbides with different carbon content on the cobalt drifts. In the present work we suggest a new mechanism explaining the phenomenon of Co drifts from a part having a high carbon content into a part having a low carbon of cemented carbide articles during liquid-phase sintering.

2. Experimental

Special model samples with 10 wt% Co, ultra-coarse microstructure and either low or high carbon contents were made by milling, pressing and sintering of ultra-coarse WC powders with additions of either tungsten metal or carbon black. The WC powder (MAS 3000-5000, H.C. Starck) was milled with 10 wt% Co in an attritor-mill for 1 h in hexane with 2 wt% paraffin wax and sintered at 1380 °C for 75 min (45 min vacuum + 30 min HIP). Their magnetic properties and microstructure were examined by standard procedures of the cemented carbide industry. After sectioning, grinding, polishing and etching, samples were investigated by means of the scanning electron microscopy (SEM). SEM investigations have been carried out in a Tescan Vega TS5130 MM microscope equipped with the LINK energy-dispersive spectrometer produced by Oxford Instruments. A quantitative analysis of the wetting state of WC/WC GBs was performed adopting the following criterion: every WC/WC GB was considered to be completely wetted only when a layer of Co-binder had covered the whole GB (e.g. WC/WC GBs marked in the micrograph in Fig. 1 by symbol "C"). If such a layer appeared to be interrupted, the GB was regarded as a partially wetted (WC/WC GBs marked in the micrograph in Fig. 1 by symbol "P"). The contact angle between Co-binder and WC/WC GBs was also measured. At least 500 GBs were analyzed in each sample.

* Corresponding author at: Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, 142432, Russia.
E-mail address: straumal@issp.ac.ru (B.B. Straumal).

http://dx.doi.org/10.1016/j.matlet.2017.03.001
0167-577X/

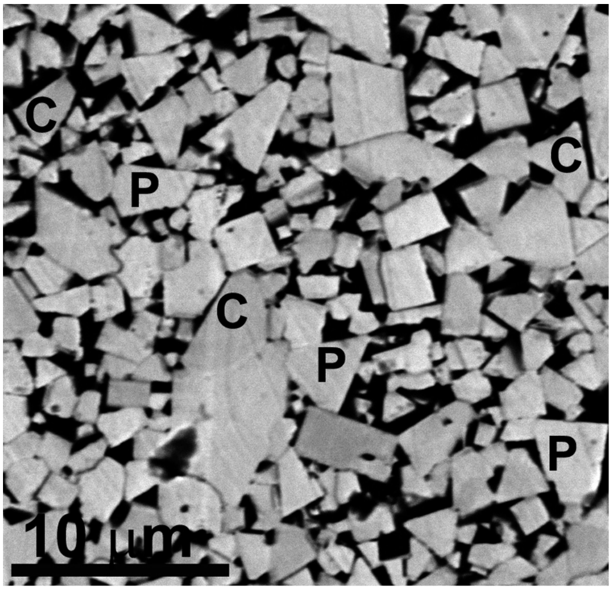

Fig. 1. SEM micrograph of the ultra-coarse cemented carbide after liquid-phase sintering at 1380 °C. WC appears bright and Co/binder appears dark. Letters indicate C: WC/WC grain boundaries completely wetted by the Co-based melt with zero contact angle; and P: WC/WC grain boundaries partially (incompletely) wetted by the melt, non-zero contact angle.

3. Results and discussion

The general viewpoint on the wettability of WC by liquid Co is that it is complete and independent on the carbon content, see e.g. Refs. [7,8]. Complete wetting means that the contact angle formed by the liquid Co-based binder on the WC surface or with the WC/WC GB is zero (like GBs in Fig. 1 marked by symbol "C") [9,10]. Special model samples with 10 wt% Co, ultra-coarse microstructure and either low or high carbon content were made in order to prove the abovementioned viewpoint on the independence of the wettability of WC by liquid binders on the carbon content. Fig. 2 shows the microstructure of these samples. The coercivity of the sample with low carbon content was 9.7 10^{-3} T and its specific magnetic saturation was 73%, so that the sample composition was close to the border line with the η-phase formation according to W–Co–C phase diagram. The coercivity of the sample with high carbon contents was 6.1 10^{-3} T and its specific magnetic saturation was 93%, so that the sample composition was close to the border line with the free carbon formation according to W–Co–C phase diagram.

Fig. 1 shows the microstructure of the cemented carbide sample with the high carbon content with letters "C" and "P" indicating different contact angles of WC/WC grain boundaries with the Co-based binder. As it can be seen in Fig. 1, some contact angles with WC/WC GBs in the microstructure are equal to 0° indicating complete wetting (marked with letter "C"). Nevertheless, Fig. 1 clearly indicates that there are some contact angles with WC/WC GBs in the microstructure that are different from 0° (marked with letter "P"). In other words, the wettability of WC/WC GBs by the Co-based liquid binder is good but still incomplete (or partial).

Fig. 3 shows the results of the contact angles' measurements indicating that the low-carbon sample contains significantly more low-angle WC/WC contacts with binder than the high-carbon sample. Therefore, the wettability of WC by the liquid Co-based binder in the low-carbon sample is noticeably better than that in the high-carbon sample. The mentioned above results on measuring WC/WC contact angles with the binder in cemented carbides with various carbon contents indicating different wetting rate of WC by Co-based binders with various carbon content were confirmed by recently published work [11].

Thus, the phenomenon of Co drifts from WC-Co regions having high carbon contents into regions having low carbon contents during liquid-phase sintering can be explained by the different wettability of WC by Co-based binders at various carbon contents. The topology (and resulting properties) of binder network are controlled by the complete and incomplete wetting of W/W grain boundaries (GBs) and GB triple junctions. The regions with the low carbon contents attract the liquid binder due to the better wettability of WC by the melted binder in comparison with those with the high carbon contents.

4. Conclusions

The contact angles of WC/WC GBs with the Co-based binder were measured by use of special model samples with either low or high carbon content. The low-carbon sample contains significantly more low-angle WC/WC contacts with the binder than the high-carbon sample. It means that the wettability of WC/WC GBs by the liquid Co-based binder in this sample is noticeably worse than that in the low-carbon sample. Different wetting values of WC/WC GBs at various carbon contents is presumably the driving force for the binder drift between WC-Co regions with various carbon contents allowing one to fabricate functionally graded cemented carbides.

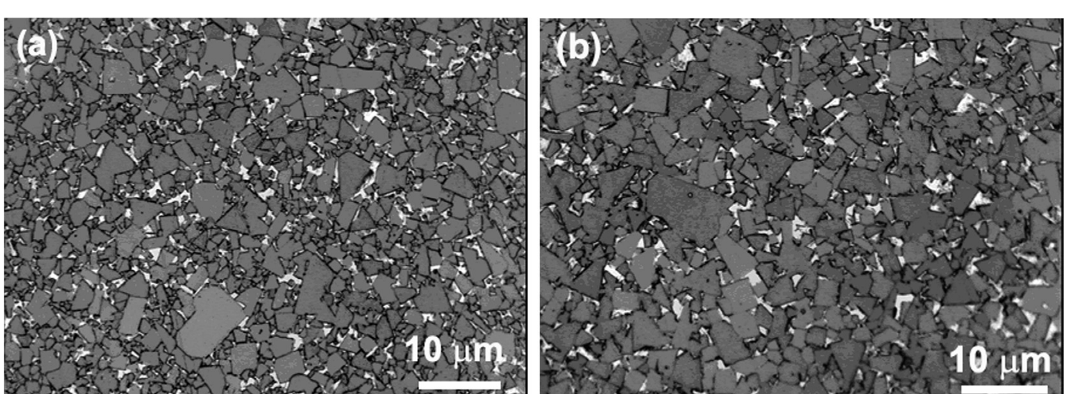

Fig. 2. SEM micrographs of the functionally graded cemented carbide with the original Co content in the WC-Co graded powder of 10 wt%: (a) surface region and (b) core region.

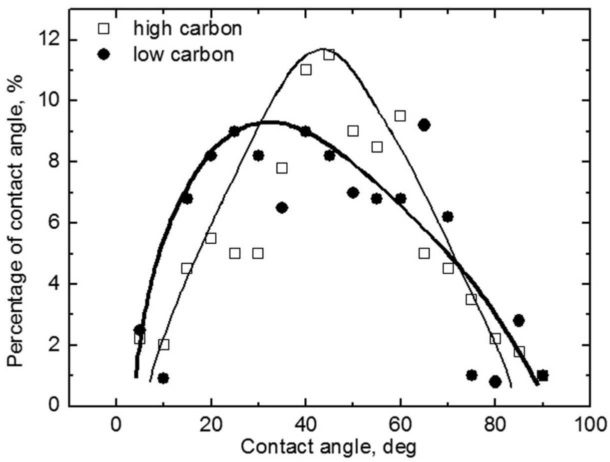

Fig. 3. Curves indicating the distribution of dihedral (contact) angles of WC/WC GBs with the Co-based binder in the cemented carbides with various carbon contents.

Acknowledgements

The work was partially supported by the Russian Foundation for Basic Research (grant 15-53-06008), Ministry of Science & Technology, Israel (grant 3-12418), and Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of MISiS.

References

[1] U. Fischer, M. Waldenstrom, T. Hartzell, Cemented carbide body with increased wear resistance, US Patent 5 856 626 (1999).
[2] U, Fischer, E, Hartzell, J, Akerman, Cemented carbide body used preferably for rock drilling and mineral cutting, US Patent 4 743 515 (1988).
[3] J. Guo, P. Fan, Z. Fang, A new method for making graded WC-Co by carburizing heat treatment of fully densified WC-Co, in: L. Sigl, P. Rödhammer, H. Wildner (Eds.), Proc. 17th Int. Plansee Seminar. Plansee corp, Reutte, vol. 2, 2009, 50/1-50/6.
[4] Z. Fang, P. Fan, J. Guo, Functionally graded cemented carbide with engineered hard surface and the methods for making the same, US Patent Application US2010/0101368A1 (2010).
[5] I. Konyashin, B. Ries, F. Lachmann, WO2010/097784A1 (2010).
[6] I. Konyashin, S. Hlawatschek, B. Ries, A. Mazilkin, Mater. Lett. 167 (2016) 270–273.
[7] J. Gurland, L. Norton, J. Metals Trans. 4 (1952) 1051–1056.
[8] L. Ramqvist, Int. J. Powder Met. 1 (1965) 2–20.
[9] E.I. Rabkin, L.S. Shvindlerman, B.B. Straumal, Int. J. Mod. Phys. B 5 (1991) 2989–3028.
[10] B.B. Straumal, B. Baretzky, O.A. Kogtenkova, A.B. Straumal, A.S. Sidorenko, J. Mater. Sci. 45 (2010) 2057–2061.
[11] I. Konyashin, A.A. Zaitsev, D. Sidorenko, E.A. Levashov, B. Ries, S.N. Konischev, M. Sorokin, A.A. Mazilkin, M. Herrmann, A. Kaiser, Int. J. Refract. Met. Hard Mater. 62 (2017) 134–148.