International Journal of Refractory Metals & Hard Materials 72 (2018) 135–140

Contents lists available at ScienceDirect

International Journal of Refractory Metals & Hard Materials

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

High resolution STEM investigation of interface layers in cemented carbides

Arno Meingast[a], Ernesto Coronel[a,*], Andreas Blomqvist[a], Susanne Norgren[a,b], Göran Wahnström[c], Martina Lattemann[a]

[a] Sandvik Coromant R&D, 126 80 Stockholm, Sweden
[b] Ångström Tribomaterials Group, Applied Materials Science, Uppsala University, Uppsala, Sweden
[c] Department of Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

ARTICLE INFO

Keywords:
STEM
SEM
EDXS
WC
Co
Ti

ABSTRACT

Cemented carbides with sub-micron grain size have increased the need to restrict grain growth during sintering. Commonly used inhibitors like V, Ti, and Cr have been observed to form interface layers in the interfaces between WC grains and the Co binder. Atomistic modeling has predicted the composition and thickness of the interface layers.

Earlier, the interface layers have been characterized qualitatively using high resolution transmission electron microscopy (TEM). To get more information about the structure and composition of the interface layers in a Ti containing cemented carbide in this work, Z contrast imaging and spectroscopy using scanning transmission electron microscopy (STEM) have been combined. Elemental maps revealing the structure of the interface layers will be presented.

1. Introduction

WC-Co cemented carbides are used in a variety of different applications and their mechanical properties need to be taylored to different requirements. One important area is the control of as-sintered WC grain size and morphology. WC grain size can be controlled by the addition of grain growth inhibitors such as V, Cr, Nb, Ta, Ti, Zr, Hf [1,2]. Both grain growth and grain morphology are affected by segregation of inhibitors to certain WC planes. Ultrathin Cr layers, for example, were reported on both basal and prismatic planes in a Cr containing WC-Co [3] whereas Ti was only reported to be found on basal WC planes [4] and the addition of TiC has been observed to affect the WC grain morphology in WC-Ni [5]. Further on, a cubic ultrathin layer, possibly $(Ti,W)C_X$, was observed in a WC grain in Ti doped WC-Co [6].

To assess the propensity of transition metals to form thin layers of cubic carbide structures in WC/Co interfaces first-principles calculations in the framework of density functional theory (DFT) have been performed [7]. It was found that ultra-thin cubic layers of TiC are formed on the basal WC/Co interface, while on the corresponding prismatic WC/Co interfaces no films are predicted to segregate. The films on the basal WC/Co interface are predicted to form also for values of the Ti potential μ_{Ti} for which the TiC bulk phase is thermodynamically unstable. However, the margin is small, so the films are expected to form where the local Ti potential μ_{Ti} is close to that of TiC.

The aim of this work is to determine whether Ti segregates to basal or prismatic WC crystallographic planes at inhibitor levels above the Ti solubility limit in the liquid Co binder as well as the structure of the WC/Co interface planes to which Ti segregated.

2. Experimental and theoretical details

2.1. Materials design

2.1.1. Compositional design

The required Ti content was calculated such that the fcc (Ti,W,)C, i.e. γ-phase, would be thermodynamically stable at all temperatures and that the system is saturated with Ti. The chosen composition was 0.185 wt% Ti (0.35 at.%), 10.13 wt% Co (15.6at.%), 5.63 wt%C (42.5 at.%) rest W. The mole fractions of binder, γ-phase and liquid versus temperature are given in Fig. 1. The volume fraction of γ-phase at the sintering temperature of 1410 °C is 0.007 (0.7 vol.%). The calculations were performed using the Thermocalc software [8] with the TCFE7 database [9].

Raw materials were carefully selected with regards to particle size, composition and homogeneity. WC (Wolfram Bergbau und Hütten AG) with a Fisher Sub-Sieve Sizer (FSSS) value of 5.8 μm and a total carbon level of 6.138 wt% (of which 0.03 wt% is free carbon), Co (Freeport Cobalt) with a FSSS value of 1.4 μm and a purity of 99.99 wt% (excluding carbon and oxygen), and TiC (Treibacher Industrie AG) with a purity of 99.98 wt% and a grain size of 1.5 μm were used.

* Corresponding author.
E-mail address: ernesto.coronel@sandvik.com (E. Coronel).

https://doi.org/10.1016/j.ijrmhm.2017.12.028
Received 17 October 2017; Received in revised form 17 December 2017; Accepted 18 December 2017
Available online 18 December 2017

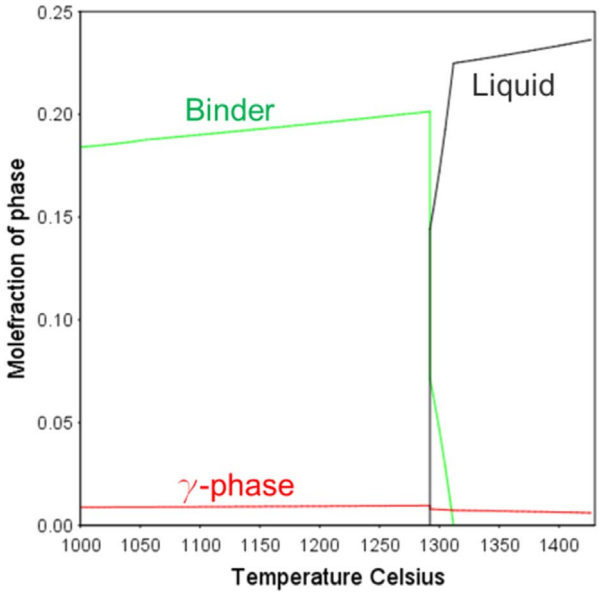

Fig. 1. Mole fractions of binder, γ-phase and liquid versus temperature.

The carbon loss due to reduction of stable oxides during the open porosity sintering stage was compensated for by adding the excess carbon. The raw materials were weighed together with a pressing agent, polyethylene glycol (PEG), and milling liquid resulting in a wet slurry ready for milling. In order to reduce contamination during the process, a WC–lined mill and pure WC-Co milling bodies were used. The powder was milled in a 0.25 l mill for 9 h, to ensure a homogeneous powder, using 900 g of milling bodies and ethanol as milling fluid to prevent oxidation. Thereafter, the powder was pan dried in protective atmoshpere and pressed into the SNUN ISO geometry and sintered.

2.1.2. Sintering details

Debinding of the pressing agent was performed in hydrogen atmosphere at temperatures up to 450 °C. Thereafter sintering continued in vacuum with a temperature ramp rate of 8 °C/min up to 1380 °C where the furnace was kept for 20 min to adjust for the thermal lag before increasing the temperature to 1410 °C with a ramp rate of 5 °C/min. An isothermal dwell was applied for 60 min at 1410 °C controlling the atmosphere using 25 mbar of CO and 25 mbar of Ar keeping the oxygen partial pressure below the stability point of titanium oxides.

2.2. Theoretical predictions

For detailed prediction of film formation, a technique to determine the corresponding “interfacial phase diagrams”, i.e. diagrams that describe the composition and structure of the ultrathin films, the interfacial “phases” appearing at the interfaces, was developed [10]. The developed technique combines first-principles DFT calculations together with thermodynamic modeling of the adjoining bulk phases [11]. For Ti containing material it was then found that at basal WC/Co interfaces a two monolayer thick cubic film is formed. The topmost metal layer, i.e. the layer next to the Co phase, contained mainly W atoms, while the second cubic metal layer contained essentially only Ti atoms [12].

2.3. Characterization methods

For the microstructural observation secondary electron (SE) images of a diamond polished surface of the Ti containing WC-Co were recorded using a Supra 40 (Zeiss) scanning electron microscope (SEM) equipped with an Everhart-Thornley SE detector.

A Helios NanoLab 650 DualBeam (Thermo Fisher Scientific, former FEI Company) equipped with an energy dispersive X-ray spectroscopy (EDXS) detector X-MaxN 80mm^2 silicon drift detector (SDD) (Oxford Instruments) and an ion conversion and electron (ICE) detector was used for the acquisition of SE SEM images and elemental distribution maps using EDXS.

A transmission electron microscopy (TEM) specimen of the Ti containing WC-Co sample was prepared by means of conventional TEM specimen preparation. A 3 mm disc was cut from the bulk sample using a diamond saw (Buehler IsoMet 5000) and an ultrasonic disc cutter (Gatan Inc.). The disc was polished on both sides using diamond particles dispersed in oil with grain sizes of 9 µm and 1 µm down to a thickness of about 80 µm. A dimple grinder (Gatan Inc.) using diamond pastes of 6 µm, 3 µm and 1 µm was used for thinning the specimen to a thickness of 17 µm in the central region of the disc. Final thinning to electron transparency was performed by argon etching using a precision ion polishing system (PIPS II, Gatan Inc.).

Scanning (S)TEM and EDXS were applied for acquiring elemental distribution maps of WC and Co interfaces. A C_S-probe- and C_S-image corrected TEM (Titan^3 60–300, Thermo Fisher Scientific, former FEI Company) operated at 200 kV and equipped with a high brightness electron source (X-FEG), imaging filter (GIF Quantum ERS, Gatan Inc.) and four SDD EDXS detectors (Super-X) was used for the EDXS and STEM analysis. For STEM imaging a high angle annular dark field (HAADF) detector (E.A: Fischione Instruments Inc.) with a collection semi-angle of 63.8 mrad to 200 mrad was used with a nominal camera length of 91 mm. The convergence semi-angle was set to 21.4 mrad and EDX spectrum images (SIs) were acquired using the DigiScan engine in the Gatan Microscopy Suite. A pixel time of 10 or 20 ms and an energy dispersion of 10 eV per pixel were used. WC grains were oriented such that either $\{0, 0, 0, 1\}_{WC}$ basal or $\{1, -1, 0, 0\}_{WC}$ prismatic planes were parallel to the electron beam allowing for characterization of possible ultrathinTi rich layers.

3. Results

A SE SEM image of a diamond polished surface of the sintered microstructure is shown in Fig. 2 where the light grey phase is the WC phase, darker areas corresponds to Co rich binder phase areas. The γ-phase is indicated with arrows in the SE SEM image.

Elemental distribution maps retrieved from SEM EDXS map acquisitions are shown in Fig. 3. Two regions with high Ti signal were observed which overlaps with C signal confirming the formation of Ti containing carbide, i.e. γ-phase.

For the detailed characterization of the interface regions between

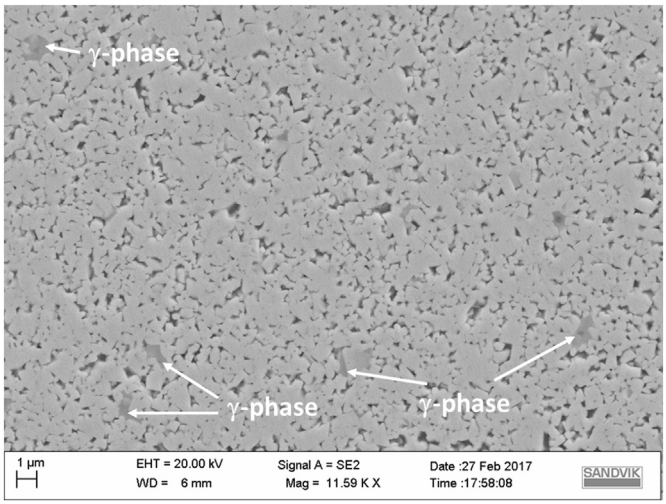

Fig. 2. SE SEM image of the Ti containing WC-Co revealing grey regions assumed to be γ-phase beside WC grains (light grey), Co rich binder phase areas (darker areas).