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Effects of Cr_3C_2 Addition on Wear Behaviour of WC-Co Based Cemented Carbides

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Abstract: Microstructure, hardness, transverse rupture strength, and abrasion resistance of WC-10 wt% Co cemented carbides modified with the addition of different mass fraction of Cr_3C_2 , in the range of 0–3 wt%, are studied. The influence of the microstructure, composition and hardness on the mechanical properties and wear resistance is analysed. Considering that the material under investigation can be used as die for the extrusion process of hard ceramic materials, the tribological behaviour was evaluated by performing sliding wear tests in wet conditions using a block-on-ring tribometer. Wear mechanism principally based on binder removal and subsequent fragmentation and microabrasion of the WC grains is proposed. Carbide grain size and bulk hardness can be tuned as function of specific applications by adding different amounts of Cr_3C_2 . In particular, increasing hardness and reducing grain size by the addition of Cr_3C_2 are demonstrated to considerably enhance the wear performance of these carbides.

Keywords: cemented carbides; binder modification; hardness; transverse rupture strength; wear resistance

1. Introduction

WC-Co cemented carbides are known for their excellent properties and extraordinary resistance to heat even after long-term exposure to high temperatures [1–4]. Their outstanding mix of strength, wear resistance, hardness and toughness is the result of the combination of the hard carbides and the ductile metallic binder [5–7]. For these reasons, WC-Co carbides are extensively employed in applications requiring exceptional mechanical properties and wear resistance [8], e.g., cutting tools [9,10], bearings, drilling and mining equipment [5], dies and punches [11].

The material characteristics of the WC-Co hardmetals are strictly related to their chemical composition and microstructure, which in turn is influenced by the process parameters. In particular, it is known that it is possible to adjust the final properties of WC-Co alloys to fit each specific application by varying the binder content [12], the grain size, or by using additives as: chromium carbide (Cr_3C_2) [13,14], nickel or vanadium carbide (VC) [9,14,15]. For example, it was demonstrated that the wear resistance of WC-Co cemented carbides generally increases as the volume fraction of cobalt and the WC grain size are reduced [9,16]. Almond and Roebuck [17] found that the wear performance of the WC-Co hardmetal increases dramatically as the grain size is reduced to nanometre scale.

Cr_3C_2 has been used in small amounts in WC-Co cemented carbides as an inhibitor of grain growth [16]. However, other properties, such as hardness, magnetic coercivity and transverse rupture strength (TRS), have been found to be affected by the addition of Cr_3C_2 [15,18]. Mostly the above cited works studied the tribological and wear behaviour in dried conditions, however considering that WC-10 wt% Co can be used as material of the die for the extrusion processes of hard ceramic materials, it could be interesting to test this material in wet conditions.

Therefore, in the present work, the tribological behaviour of WC-10Co grades containing different mass fraction of Cr_3C_2 , ranging from 0 to 3 wt% was studied in wet conditions by using a block-on-ring tribometer. The structure, density, hardness, and TRS of the different grades were studied as function of Cr_3C_2 content. The volume losses of the different grades were measured and compared. The wear surfaces were analyzed to identify the wear mechanisms. Correlations between volume loss, microstructure, hardness, and TRS were determined.

2. Materials and Methods

The WC-10Co specimens were fabricated using conventional production routes. The average particle size of the WC powder, before the sintering process, was 5 μm . The binder and the WC were mixed firstly by dry ball milling and then by wet milling with acetone. The Cr_3C_2 was previously mixed into the binder and, subsequently, the carbide was added. A 1–2 wt% of powder wax was added to the charge three hours before the end of the milling. The whole mixing stage went on for 20 hours. Green compacts were obtained pressing the powder premix in a die under 180 MPa. A green density of 55% of the theoretical value was obtained for all specimens. The green compacts were first dewaxed in a furnace at 350 °C for 2 h in hydrogen and then sintered in the same furnace for 1 h at 1400 °C under vacuum. Afterwards, the samples were finished by grinding to obtain the final dimensions and tolerances according to ASTM B611-13, which was applied in the following tribological tests [19]. The average roughness, R_a , of the samples' surfaces was measured to be 0.7 μm . The test-pieces were 25 mm $\times$ 76 mm $\times$ 12 mm in size. Seven alloys based on WC-10 wt% Co with additions of 0–3 wt% Cr_3C_2 partly replacing the WC were studied. Alloy compositions are given in Table 1.

Table 1. Compositions in wt% of the seven alloys.

Alloy	WC	Cr_3C_2	Co
0 wt% Cr_3C_2	90	0	10
0.5 wt% Cr_3C_2	89.5	0.5	10
1 wt% Cr_3C_2	89	1	10
1.5 wt% Cr_3C_2	88.5	1.5	10
2 wt% Cr_3C_2	88	2	10
2.5 wt% Cr_3C_2	87.5	2.5	10
3 wt% Cr_3C_2	87	3	10

The density of the samples was determined by hydrostatic weighing using Archimedes' principle. The porosity was obtained knowing the measured density and the theoretical density of each composition calculated from the rule of mixtures ($\text{WC} = 15.77 \text{ g/cm}^3$, $\text{Cr}_3\text{C}_2 = 6.74 \text{ g/cm}^3$, and $\text{Co} = 8.85 \text{ g/cm}^3$).

Selected compacts representative of the seven experimental alloys were polished firstly using 7 μm diamond pastes and then colloidal silica (0.05 μm) suspension. The polished specimens were eventually etched using the Murakami reagent for 80 s. The microstructure of the prepared samples was investigated with optical microscopy (Zeiss Axioplan 2 imaging, Zeiss, Germany) and a scanning electron microscopy (SEM, Hitachi TM 3000, Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray analyser (EDX, Hitachi TM 3000, Hitachi, Tokyo, Japan). The grain size distribution was measured using the linear intercept method. At least 1000 grains from four photomicrographs taken arbitrarily from different specimen locations were measured for each grade.

The hardness of the sintered compacts was measured on the polished surfaces of the samples according to ISO 6507-1:2018 using an indentation load of 30 kg [20].

The transverse rupture strength of the sintered specimens was measured according to ASTM B406-76 under three-point loading [21].

Abrasion tests were performed according to ASTM B611–13 in a specially built block-on-ring tribometer [5,19]. The blocks were pressed against the steel disk ($\varnothing$ 169 mm) with a normal load ($F_n = 200 \text{ N}$) and at a constant sliding speed (50 rpm). Wear tests were conducted under wet conditions

at room temperature in accordance to the adopted standard. Wear loss of the hardmetal samples was measured by weighing the block before and after the sliding using a digital balance. The volume loss was calculated from the mass loss and the density of each sample.

For each of the above tests, five repetitions were performed for each alloy grade. The average values with the ± 2 sigma error bars ($\sim 95\%$ confidence intervals) are reported in the following figures.

3. Results and Discussion

For the sake of comparison, Figure 1 reports the microstructures of the sinterized hardmetal without Cr_3C_2 addition and of the one with 1.5 wt% of Cr_3C_2 . The main effect of the Cr_3C_2 addition is the refinement of the WC grain size. The arrows in Figure 1a points to some very large WC grains which are not observed in the materials sintered with the addition of Cr_3C_2 . It was already demonstrated that small addition of Cr_3C_2 restricts the grain growth of the WC due to the slower grain boundary migration and hence limited coalescence of WC grains caused by the Cr segregation to the WC grain boundaries [22,23].

Figure 1. Optical micrographs of the microstructure: (a) 0 wt% of Cr_3C_2 and (b) 1.5 wt% of Cr_3C_2 .

The inverse relation between WC grain size and Cr_3C_2 content is further evidenced by the quantitative metallographic study in Figure 2. The WC grain size decreases with the increase of the Cr_3C_2 content. Actually, it seems that a minimum grain size is reached for Cr_3C_2 values around 1.5 wt%, since with higher values of the Cr_3C_2 substitution the average grain size slightly increases. The existence of this minimum cannot be statistically proved considering the overlap of the confidence interval at 1.5 wt% with those measured for larger Cr_3C_2 content. It can be concluded then that the grain size decreases from a starting value of 2.1 μm , observed without the addition of the additive, to 1.6–1.8 μm when the Cr_3C_2 content reaches 1–1.5 wt%; this corresponds to a 20% decrease. Further addition of Cr_3C_2 above 1.5 wt% does not seem to have any effect on decreasing the grain size.

Figure 2. Effect of the Cr_3C_2 addition on the WC grain size of the WC-10Co cemented carbide.

The EDX analyses showed that no trace of Cr_3C_2 is present in the alloys and hence the additive was completely dissolved during the sintering. The added Cr is entirely present into the Co binder, while the carbide grains do not contain any Cr. The chromium content of the binder was measured to

vary between 4 and 7 at% at higher level of Cr_3C_2 addition, whereas the W content of the binder was roughly equal to 1 at% despite the added amount of Cr_3C_2 , see Figure 3a.

At Cr_3C_2 contents higher than 2 wt% a Cr-rich phase was observed. Figure 3b shows an area of this chromium-rich phase observed with the SEM. The composition of this chromium-rich phase is compatible to the presence of a M_7C_3 carbide, whose chromium and cobalt contents have been demonstrated to depend on the amount of Cr_3C_2 added to the starting powder, see [12,22,24,25]. The phase diagram calculated by Zackrisson et al. [22] shows that some M_7C_3 can precipitate from the liquid for Cr_3C_2 contents higher than 1 wt%, although there is a primary precipitation of the solid binder for Cr_3C_2 contents lower than 3.5 wt%. M_7C_3 is not stable at room temperature and there is a driving force which promotes its transformation into M_3C_2 . However, the kinetics of this transformation is expected to be very slow due the slow rate of diffusion of the involved species [26]. The volume fraction of this chromium-rich phase is expected to increase with the addition of Cr_3C_2 . This was indeed observed since the volume fraction of M_7C_3 rises to 2% with the 3 wt% of Cr_3C_2 substitution.

Figure 3. SEM microstructure and EDX analysis: (a) the binder phase and (b) the M_7C_3 carbide observed at 3 wt% addition of Cr_3C_2 (concentrations are in at%).

The addition of Cr_3C_2 does not have any effect on the densification of the WC-10Co cemented carbides. The decrease in the measured densities of the studied alloys is perfectly compatible with the added amount of chromium carbide at the same level of porosity, see Figure 4. All the samples were measured to have an equal porosity of ~2% in average without regard to the amount of Cr_3C_2 . This is expected considering the consistency of the applied manufacturing process. The measured porosity is in agreement with the values of the porosity showed by sintered WC-10Co carbides in similar conditions [15].

Figure 4. Effect of the Cr_3C_2 addition on the density of the WC-10Co cemented carbide.

The hardness of the WC-10Co cemented carbides increases with the addition of Cr_3C_2 . The total registered increase is equal to 200 HV, Figure 5. Considering the constancy of the porosity with the Cr_3C_2 content, the following conclusions can be drawn about the causes of hardness increment. Up to 1.5 wt% addition of Cr_3C_2 , the hardness increase is mainly related to the refinement of the WC grain size. This is responsible of an increase of 140 HV, which corresponds to 70% of the total observed increase of 200 HV.

Figure 5. Effect of the Cr_3C_2 addition on the hardness of the WC-10Co cemented carbide.

On the other hand, the remaining 30% portion of the total hardness increment of 200 HV is due to the gradual increase of the weight fraction of the hard and brittle chromium-rich M_7C_3 carbide into the binder [27]. The effect of solid solution hardening due to the increased presence of Cr in the binder when the Cr_3C_2 addition increases can be easily discarded according to the Hume–Rothery rules [28].

As shown in Figure 6, the addition of up to 1.5 wt% of Cr_3C_2 increases the TRS of the hardmetal. However, larger amounts of such additions have the reverse effect due to the increased presence of the brittle M_7C_3 carbide into the binder. Indeed, the first strong decrease of the TRS is visible at 2 wt% of Cr_3C_2 . This is the lowest value of Cr_3C_2 content at which the M_7C_3 was firstly observed.

Figure 6. Effect of the Cr₃C₂ addition on the transverse rupture strength of the WC-10Co cemented carbide.

Figure 7 reports the volume loss during the tribological tests by each tested sample as function of the Cr₃C₂ substitution level. The addition of the hard phase has a quite positive effect on the resulting wear resistance of the cemented carbide. The wear volume decreases with the increase of the Cr₃C₂ substitution level, but with different laws at low and high Cr₃C₂ content. The addition of Cr₃C₂ up to 1.5 wt% brings about a strong decrease of the wear volume with the Cr₃C₂ content.

Figure 7. Volume loss of the WC-10Co cemented carbides vs. the Cr₃C₂ content. The two regression lines fitted to the data at low (≤ 1 wt%) and high (≥ 1.5 wt%) Cr₃C₂ content are reported.

A regression analysis of the data in this interval indicates a good linear relationship between the volume loss and the Cr₃C₂ content ($r^2 = 0.973$ with $p < 0.001$). The slope coefficient of the fitted line was calculated to be $-0.025 \text{ cm}^3/(\text{wt}\% \text{ of Cr}_3\text{C}_2)$. Above 1.5 wt%, the wear volume drops more lightly with the Cr₃C₂ content. In this case the linear regression ($r^2 = 0.915$ with $p < 0.001$) predicts a slope coefficient of the fitted line equal to $-0.003 \text{ cm}^3/(\text{wt}\% \text{ of Cr}_3\text{C}_2)$, which is one order of magnitude lower than the value previously observed.

The microscopic analysis of the wear track shows that all samples underwent the same wear mechanism. The profile of the wear tracks is macroscopically smooth and shallow. This indicates that plastic deformations of the asperities occurred during the test. Ploughing grooves running longitudinally to the sliding direction are also visible, Figure 8. Fractured material and traces of binder removed from the surface were found along these grooves. The pits visible on the surface of Figure 8 are left by the carbide particles that were pulled out from the materials.

Figure 8. Optical micrograph of the of the worn surfaces.

Based on the above results, it is fair to propose a wear mechanism mainly based on binder extrusion and microabrasion. During the initial phase of the process, the ductile Co matrix in between the hard WC particles is plastically deformed by the compressive coupling force. This causes the extrusion of the binder and its subsequent removal, which occurs by a combination of plastic deformation and microabrasion [29]. When sufficient binder has been removed, the WC particles are no longer adequately supported, so that they become loose and can develop a motion relative to the binder. This triggers the microcracking and then the fragmentation of the WC grains, until their partial or complete pull-out from the material.

It is well known that the abrasive wear resistance of coarse-grained cemented carbides is usually lower than that of fine grain size [5,9]. Furthermore, it is fair to infer that the initial phase of the wear process, namely the binder extrusion, is easier the more ductile the binder is. Indeed, Pirso et al. [5] correlated the bulk hardness of these composites with their abrasive wear resistance demonstrating that the wear coefficient is inversely proportional to the bulk hardness for WC–Co alloys.

The above experimental observations confirm the proposed wear mechanism and furthermore are in full agreement with what previously reported in literature [5,9]. Figure 9 shows the average volume loss versus the average hardness. It clearly demonstrates that the wear volume loss is inversely related to the hardness of the cemented carbides. However, a bimodal dependence, as the one previously observed in Figure 7, is evident. For low Cr_3C_2 content, there is a strong decrease of the volume loss with the hardness. This happens in the composition range for which the Cr_3C_2 addition generates a decrease of the grain size. Above the 1.5 wt% of Cr_3C_2 , the slight decrease in wear loss is due to the increase of the bulk hardness caused by the presence of the new M_7C_3 hard phase.

Figure 9. Wear volume vs. the hardness of the WC-10Co cemented carbides.

4. Conclusions

The addition of Cr_3C_2 to WC-10Co cemented carbides has a double effect on their properties. Up to 1.5 wt%, it determines a decrease of the grain size. For addition of Cr_3C_2 larger than 1.5 wt%, a hard and brittle phase, the chromium-rich M_7C_3 carbide, is formed into the microstructure. Its chromium content and volume fraction increase as the amount of Cr_3C_2 added to the starting powder increases. The M_7C_3 carbide produces a modification of the binder which becomes harder and then more brittle. These two effects control the resulting properties of the cemented carbide.

- Addition of up to 1.5 wt% of Cr_3C_2 greatly increases the hardness of the WC-10Co hardmetal due to the effect of grain size refinement. The slight increase in hardness observed beyond 1.5 wt% addition is caused only by the increased presence of M_7C_3 .
- The addition of Cr_3C_2 , up to 1.5 wt%, greatly improves the TRS of the WC-10Co hardmetal. However, larger amounts of such additions have the reverse effect due to the embrittlement of the binder.
- Wear performance is significantly enhanced by the addition of Cr_3C_2 due to the hardness increase and reduction of the grain size. However, addition of Cr_3C_2 above 1.5 wt% brings about a moderate increase of the wear performance which is produced just by the progressively increasing presence of the M_7C_3 carbide and not by a further decrease of grain size. Aiming at the combined optimization of the wear resistance and the mechanical properties of the WC-10Co cemented carbides, to add amounts of Cr_3C_2 higher than 1.5 wt% is then detrimental.

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Conflicts of Interest: The authors declare no conflict of interest.

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