



T DEPENDENCE OF THE MECHANICAL PROPERTIES ON THE MICROSTRUCTURAL PARAMETERS OF WC-Co

L. Emanuelli, A. Molinari, G. Arrighetti, G. Garoli

Abstract

The effect of binder content and WC grain size on the mechanical properties is widely investigated in literature. An increase in binder amount and WC grain size leads to a decrease in hardness and an increase in fracture toughness. Actually, these correlations are related to the influence of binder content and WC grain size through the contiguity and mean binder free path, which are the microstructural parameters that affect the mechanical properties. The aim of this study is to verify the dependence of the two microstructural parameters that govern the WC-Co mechanical behaviour, namely the contiguity and mean binder free path, on the mechanical properties of an extended range of WC-Co samples, which differ in terms of Co content and tungsten carbide grain size.

Keywords: WC-Co, mechanical properties, microstructure

INTRODUCTION

Mechanical properties of WC-Co are strongly related to chemical composition and microstructure. Increasing the metallic binder amount and the WC grain size (D_{WC}) , hardness decreases and fracture toughness increases [1-3]. For this reason, by varying the two parameters it is possible to tailor the mechanical properties to the requirements of the specific application.

The methods used for the determination of WC-Co mechanical properties are defined by industry or national standards. Hardness, which is one of the most important properties being correlated to wear resistance of the material, is measured according to the ASTM B294 and ISO 3878 standards, using Rockwell A and Vickers as scales [1,4-6]. The fracture toughness, which is the resistance to crack propagation and is ideally independent on specimen dimension, geometry and surface finish, is usually correlated with KIC which refers only to plain strain fracture toughness. The measure of fracture toughness according to ASTM B771 and ASTM E399 standards is rather difficult, since pre-cracking stress is very similar to the critical stress intensity factor KIC [3] and therefore the introduction of the pre-crack by fatigue is quite a critical issue. A lot of works tried to define a new method for the determination of fracture toughness without any attractive effect by the industry because of the large size and complex geometry of the test samples. For this reason, the most common method for the determination of the fracture toughness has become the Palmqvist method [1, 3-8]. It is used for brittle materials and consists of the measurement of the length of the cracks formed at the four corners of a Vickers indentation.

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Considering the microstructure, the grain size of WC DWC in the sintered material, it is important to evaluate the quality of the sintering process and the effective role of the grain growth inhibitors (Cr3C2, VC and NbC) [3, 9-11]. The most common method used for the measurement of DWC is through quantitative metallography. As an example, the so called "linear intercept method" is used to quantify the grain size distribution and the mean DWC [12]. Another technique is the Jefferies method that calculates the WC average area and the equivalent diameter for the two-dimensional size of WC, without the possibility to define the size distribution [13]. Engqvist et al. proposed a new method to consider the three-dimensionality of the grain size [14].

The correlations between hardness and fracture toughness and cobalt content and carbide grain size are mostly due to the effect of two microstructural parameters that affect the mechanical behaviour:

- the carbide contiguity, which is a measure of the contacts between carbide particles and is defined as the surface area of carbide-carbide contacts as a fraction of the total contact area [3,5,15];
- the mean binder free path, which is the thickness of the binder layer between the carbides [3,5].

It is clear that on increasing the cobalt content contiguity decreases and the mean binder free path increases, increasing the fracture toughness but decreasing hardness [3]. The same effect on mechanical properties is obtained by an increase in carbide grain size, since contiguity still decreases and the mean binder free path increases.

The carbide contiguity and the mean binder free path are measured through the intercept method.

In this study, the correlations here described are investigated on several WC-Co wire drawing dies taken from industrial production. The cobalt content and WC particle size vary within small intervals, since the range of hardness/toughness combination required by this application, depending on the characteristics of the wire and of the process, is quite narrow. The aim of the work is to verify if even with small variations of the cobalt content and of the carbide grain size, hardness and Palmqvist fracture toughness may be correlated to the two microstructural parameters described above.

MATERIALS AND EXPERIMENTAL PROCEDURE

The cemented carbides investigated in this work are reported in Table 1.

A complete microstructural characterization was carried out. Murakami's reagent, which consists of 100 ml distilled water, 7g KOH and 7g K3[Fe(CN)6] [16], was used for selective etching of WC particles. The microstructure parameters, such as the mean linear intercept carbide size lav, DWC, contiguity (C) and mean binder free path (\square), were measured by means of the linear intercept method [12] (Figure 1). They are defined by Eq. (1), (2), (3) and (4) [3, 5, 12, 14]

$$l_{av} = \frac{\sum l_i}{n} \tag{1}$$

$$D_{WC} = \frac{\sum l_i^4}{\sum l_i^3} \tag{2}$$

$$C = \frac{2 \cdot N_{LWC-WC}}{2 \cdot N_{LWC-WC} + N_{LWC-Co}}$$
(3)

$$\lambda_{Co} = \frac{2 \cdot V_{Co}}{N_{L_{WC-Co}}} \tag{4}$$

Where li is the measured intercept length, n is the number of WC grains intercepted, NL is the number of WC-WC grain boundaries or WC-Co interfaces intercepted per unit length and VCo is the Co volumetric fraction.

Tab.1. Chemical composition and starting WC powder size of the studied industrial WC-Co.

Camples	WC Co Grain		Grain growth inhibitor	WC powder size
Samples	(%)	(%)	(%)	(µm)
A	93.7	6.0	$0.3 \text{ Cr}_3\text{C}_2$	0.8
В	93.8	6.0	$0.2 \text{ Cr}_3\text{C}_2$	0.8
C	93.5	6.0	$0.5 \text{ Cr}_3\text{C}_2$	0.8
D	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.8
E	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.8
F	93.2	6.5	0.3 Cr ₃ C ₂	0.8
G	93.2	6.5	0.3 Cr ₃ C ₂	0.8
Н	93.2	6.5	0.3 Cr ₃ C ₂	0.8
I	93.3	6.5	0.3 Cr ₃ C ₂	0.8
L	92.7	7.0	0.3 (W,Nb)C	1.1
M	92.7	7.0	0.3 VC	1.2
N	90.7	9.0	0.3 Cr ₃ C ₂	0.8
О	91.0	9.0	-	1.0
P	90.7	9.0	0.3 Cr ₃ C ₂	0.8
Q	91.0	9.0	-	1.0
R	88.0	12.0	-	1.0
S	88.0	12.0	-	1.0

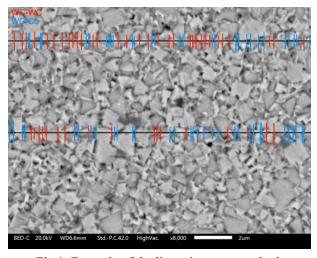


Fig.1. Example of the linear intercept method.

To get a statistically significant result, the test line has to intercept at least 20 grains and a minimum of 200 grains must be considered. C and λ were measured for each line and mean C and mean λ along with the respective standard deviations were calculated.

Vickers indentations with a load of 30 Kg were used in order to measure the hardness (HV) and the fracture toughness (K_{IC}) of parts. Eq. (5) is used to determine hardness according to ISO 3878.

$$HV = 1.854 \cdot \frac{\bar{F}}{\left(\frac{d_1 + d_2}{2}\right)^2} \tag{5}$$

Where d_1 and d_2 , in mm, are the two indentation diagonals and F is the load in Kg. HV is expressed in Kg/mm².

The fracture toughness KIC (MPa $m^{1/2}$) is determined by the Eq. (6), according to Palmqvist [1, 3-8].

$$K_{IC} = 0.0028 \cdot \sqrt{H} \cdot \sqrt{\frac{P}{\sum l_i}}$$
(6)

Where H is the Vickers hardness in N/mm^2 , P is the load in N, and l_i are the crack lengths in mm.

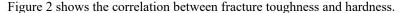
RESULTS AND DISCUSSION

The D_{WC} and the mechanical properties of the investigated hardmetals are summarized in Table 2.

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Samples	WC	Co	Other	$\mathbf{D}_{\mathbf{WC}}$	$\mathbf{l_{av}}$	HV30	K _{IC}
Sumpres	(%)	(%)	carbide (%)	(µm)	(μm)	(Kg/mm ²)	(MPa m ^{1/2})
A	93.7	6.0	$0.3 \text{ Cr}_3\text{C}_2$	0.95	0.49 ± 0.25	1836 ± 16	9.95 ± 0.10
В	93.8	6.0	$0.2 \text{ Cr}_3\text{C}_2$	0.74	0.44 ± 0.20	1887 ± 23	9.60 ± 0.12
C	93.5	6.0	$0.5 \text{ Cr}_3\text{C}_2$	0.69	0.40 ± 0.19	1916 ± 12	9.70 ± 0.12
D	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.82	0.44 ± 0.22	1912 ± 5	9.85 ± 0.03
Е	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.85	0.44 ± 0.23	1882 ± 17	9.73 ± 0.12
F	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.83	0.47 ± 0.22	1844 ± 12	9.69 ± 0.12
G	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.77	0.45 ± 0.22	1835 ± 23	9.82 ± 0.14
Н	93.2	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.70	0.43 ± 0.19	1864 ± 15	10.08 ± 0.08
I	93.3	6.5	$0.3 \text{ Cr}_3\text{C}_2$	0.71	0.41 ± 0.20	1861 ± 7	9.77 ± 0.14
L	92.7	7.0	0.3 (W,Nb)C	1.07	0.53 ± 0.30	1691 ± 16	10.31 ± 0.08
M	92.7	7.0	0.3 VC	0.71	0.42 ± 0.21	1790 ± 17	9.95 ± 0.11
N	90.7	9.0	$0.3 \text{ Cr}_3\text{C}_2$	0.83	0.44 ± 0.23	1653 ± 35	11.38 ± 0.55
О	91.0	9.0	-	1.27	0.61 ± 0.35	1534 ± 14	13.21 ± 0.39
P	90.7	9.0	$0.3 \text{ Cr}_3\text{C}_2$	0.86	0.41 ± 0.22	1686 ± 11	11.23 ± 0.14
Q	91.0	9.0	-	0.97	0.50 ± 0.26	1607 ± 10	11.27 ± 0.26
R	88.0	12.0	-	1.60	0.58 ± 0.33	1404 ± 8	15.16 ± 1.55
S	88.0	12.0	-	1.45	0.54 ± 0.34	1404 ± 13	13.41 ± 0.70

The standard deviation of DWC is not reported in Table 2 since the 3D correction obtained by Eq. (2) does not imply a distribution and the associated scatter. For this reason it is also reported the lav that is the 2D evaluation of the grain size with its standard deviation.



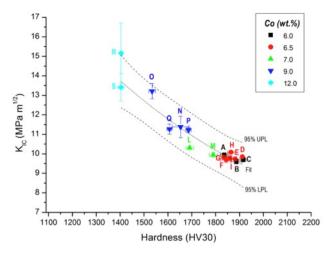


Fig.2. K_{IC} vs hardness.

As was expected [3-8], hardness and fracture toughness are inversely proportional. Figures 3a and 3b show the influence of the Co content on the hardness and on the fracture toughness, respectively.

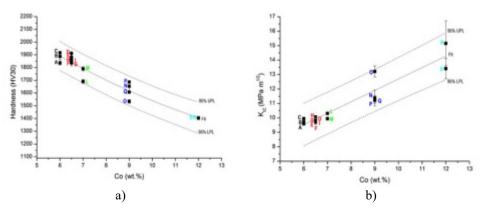


Fig.3. (a) Hardness and (b) KIC vs Co content.

Both HV30 and $K_{\rm IC}$ are very similar for Co contents in the interval between 6 and 7 wt.% Co. Differently, increasing Co content up to 9% and 12% leads to a continuously decreasing hardness and an increasing fracture toughness, with a large scatter. The different properties of materials with the same amount of binder (6, 7 and 9%) are due to the influence of D_{WC} and that is shown in Fig.4.

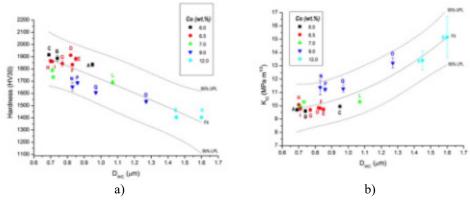


Fig.4. (a) Hardness and (b) KIC vs DWC.

The Figure displays a general trend whereby the increase in D_{WC} decreases hardness and increases fracture toughness. Such a trend may be also recognized in specimens with 6.0, 7.0 and 9.0 wt.% Co, where the difference in D_{WC} is of the order of 0.4-0.5 μ m. When the difference is smaller, as in specimens with 6.5 and 12.0 wt.% Co, the effect is not observed, because of the impossibility to define the D_{WC} standard deviation with the Eq. (2). Indeed, information regarding the grain size distribution homogeneity is given by the mean linear intercept grain size (l_{av}) obtained with the 2D Eq. (1) that presents a high standard deviation, as shown in Table 2. For this reason it is better to consider the l_{av} with its standard deviation in order to highlight the real influence of the grain size on the mechanical properties, as shown in Fig.5.

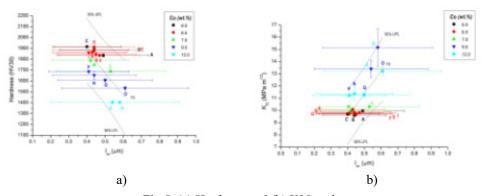


Fig. 5. (a) Hardness and (b) KIC vs lav.

It is evident that the high standard deviation of the l_{av} gives a difficult interpretation of the data. Considering grades with 6.5 and 12.0 wt.% of Co, the specimens present the same l_{av} leading to no differences in terms of mechanical properties. Otherwise, considering the material A respect to material B and C in grade with 6 wt.%, it is clear that the lower hardness and higher fracture toughness is due to a slightly higher l_{av} . The same consideration holds for grade with 9.0 wt.% of Co.

The contiguity and mean binder free path of the investigated cemented carbides are reported in Table 3.

Samples	WC (%)	Co (%)	Other carbide (%)	D _{WC} (μm)	C (-)	λ _{Co} (μm)
A	93.7	6.0	0.3 Cr ₃ C ₂	0.95	0.56 ± 0.08	0.15±0.02
В	93.8	6.0	0.2 Cr ₃ C ₂	0.74	0.56 ± 0.04	0.13 ± 0.01
C	93.5	6.0	0.5 Cr ₃ C ₂	0.69	0.53±0.05	0.11±0.01
D	93.2	6.5	0.3 Cr ₃ C ₂	0.82	0.62±0.12	0.16 ± 0.04
Е	93.2	6.5	0.3 Cr ₃ C ₂	0.85	0.61±0.09	0.15±0.03
F	93.2	6.5	0.3 Cr ₃ C ₂	0.83	0.53±0.09	0.14 ± 0.03
G	93.2	6.5	0.3 Cr ₃ C ₂	0.77	0.56 ± 0.06	0.14 ± 0.01
Н	93.2	6.5	0.3 Cr ₃ C ₂	0.70	0.52 ± 0.06	0.13±0.02
I	93.3	6.5	0.3 Cr ₃ C ₂	0.71	0.55±0.09	0.13±0.02
L	92.7	7.0	0.3 (W,Nb)C	1.07	0.50 ± 0.09	0.16 ± 0.03
M	92.7	7.0	0.3 VC	0.71	0.56 ± 0.05	0.14 ± 0.01
N	90.7	9.0	0.3 Cr ₃ C ₂	0.83	0.54 ± 0.13	0.18 ± 0.06
О	91.0	9.0	-	1.27	0.51±0.11	0.24±0.05
P	90.7	9.0	0.3 Cr ₃ C ₂	0.86	0.55±0.05	0.17 ± 0.02
Q	91.0	9.0	-	0.97	0.54±0.11	0.21±0.05
R	88.0	12.0	-	1.60	0.44±0.11	0.26±0.06
S	88.0	12.0	-	1.45	0.48 ± 0.06	0.29±0.4

Tab.3. Microstructure parameters of the different commercial WC-Co.

The standard deviation of contiguity and mean binder free path is quite high for all the materials in comparison to the mean values. This may be attributed to the microstructure heterogeneity and to the microscope resolution that does not allow highly precise information about the distribution of binder between the carbides [3] to be obtained, as shown in Figure 5.

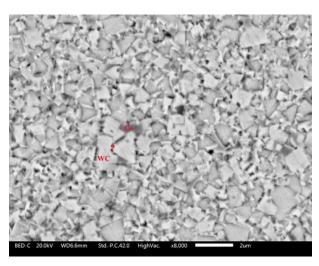


Fig.5. Example of the difficulties that occur in the measurement of the WC-WC grain boundaries and WC-Co interface.

The effect of the Co amount on contiguity and mean binder free path is reported in Fig.6. $\,$

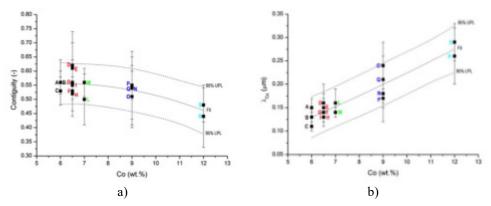


Fig.6. (a) Contiguity and (b) mean binder free path vs Co content.

Figure 6a does not show a sharp influence of cobalt content on the contiguity since the difference between the mean values of materials with the lowest and the highest %Co is comparable to standard deviation. Otherwise, Figure 6b shows that the mean binder free path increases by increasing the Co content. Again, specimens with the same cobalt content display different contiguity and mean binder free path values because of the different D_{WC} .

Figures 7a and 7b show the dependence of contiguity and mean binder free path on $D_{\text{\tiny WC}}.$

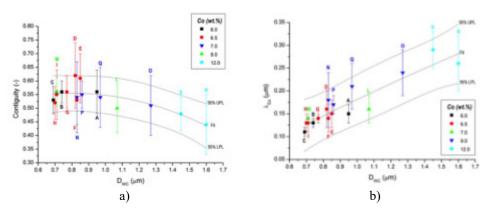


Fig. 7. (a) Contiguity and (b) mean binder free path vs DWC.

Figure 7a highlights that the effect of D_{WC} on the contiguity is significant only above 1 μ m, again because of its high standard deviation. Analogously, as shown in Figure 7b, the increase of the mean binder free path with D_{WC} is significant above 1 μ m.

From these results it is evident that the contiguity is characterized by a too high standard deviation that makes it impossible to define a clear dependence on Co content and D_{WC} . Otherwise, the influence of the Co content and D_{WC} on the mean binder free path is evident: a higher mean binder free path is obtained upon increasing the Co content and the D_{WC} .

It is now possible to correlate the two microstructural parameters that govern the WC-Co mechanical behaviour, namely the contiguity and mean binder free path, to the WC-Co mechanical properties.

Figure 8a and 8b show the influence of contiguity on hardness and fracture toughness, respectively.

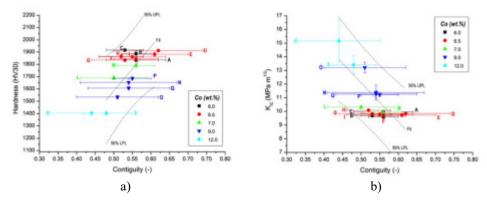


Fig.8. (a) Hardness and (b) KIC vs contiguity.

The high standard deviation of the contiguity of the analyzed materials does not allow a clear correlation to be defined. The prediction lines with a 95% of confidence describe a trend, but the hardness and fracture toughness differences between specimens with the same contiguity are very large.

The influence of the mean binder free path on the hardness and the fracture toughness is visible in Fig.9.

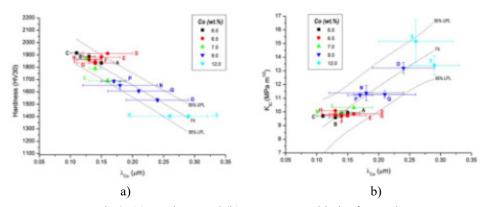


Fig.9. (a) Hardness and (b) KIC vs mean binder free path.

The prediction lines up with 95% confidence to describe a sharp trend: a higher mean binder free path leads to a lower hardness and a higher fracture toughness. In general, there is a correspondence between hardness and λ_{Co} and between fracture toughness and λ_{Co} .

CONCLUSION

In this study, the influence of the contiguity and the mean binder free path on the hardness and the Palmqvist fracture toughness of a wide range of WC-Co samples were investigated on hardmetals applied to the production of wire drawing dies. The aim of the study is to verify if even materials having small differences of cobalt content and of carbide grain size, the hardness and Palmqvist fracture toughness may be clearly correlated to the two microstructural parameters described above.

The conclusion of this study may be summarized as follows:

- 1. The dependence of the carbide contiguity on Co content and D_{WC} results is weak because of the too large standard deviation of the contiguity values;
- 2. The correlation between the hardness and fracture toughness and the contiguity is therefore ambiguous.
- 3. The dependence of the mean binder free path on the Co content and D_{WC} is evident: the mean binder free path increases by increasing Co content and D_{WC} ;
- 4. The effect of the mean binder free path on the mechanical properties was therefore verified.

Among the two microstructural parameters investigated, only the mean binder free path displays the known correlation with hardness and fracture toughness. It increases upon increasing the cobalt content and the carbide particle size. The carbide contiguity does not display the known correlation with mechanical properties, since it is within ranges in a too narrow interval in the investigated materials, and the large scatter of data the expected trends are overwhelmed.

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