Effect of sintering temperature on microstructural evolution of M48 high speed tool steel bonded NbC matrix cemented carbides sintered in inert atmosphere

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Abstract

This work presents the results on microstructure and hardness evaluation of NbC-12wt% M48 high speed steel (HSS) cemented carbides, pressureless sintered at different temperatures in argon atmosphere. To evaluate the effect of sintering process on the microstructure, sintering was performed in the range of 1260 °C to 1420 °C according to dilatometer analysis. The sintered samples were characterized using several techniques, including determination of density by Archimedes, measurement of hardness and fracture resistance, microstructural analysis by scanning electron microscope (SEM), phase analysis using X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). As expected, microstructural results indicated higher NbC grain growth at elevated sintering temperatures. The high speed steel wetted the NbC particles at high temperature (> 1340 °C). As a result, the metallic binder spread and a homogenous distribution between the NbC grains could be achieved. Mechanical analysis showed a dependence of mechanical properties on NbC grain size and the state of the microstructure. A maximum hardness of 14.91 ± 0.14 GPa was measured for cemented carbide samples sintered at 1300 °C, while the highest fracture resistance (1.56 ± 0.3 MPa.m^{1/2}) was associated with the sample sintered at 1380 °C

Keywords: Niobium carbide, cemented carbide, sintering, high speed steel, microstructure, Cryogenic milling

1. Introduction

WC-Co cemented carbides materials have excellent mechanical and wear properties to be used for cutting tool and wear applications. Due to the proven toxic nature of WO₃, researches have been taking place during the past decade to substitute WC with non-toxic materials [1,2]. Nowadays, Niobium carbide (NbC) has received particular attention as a replace candidate, due to its mechanical properties being comparable to WC [3,4]. Pure NbC has high melting point (3600°C), high hardness (19.6 GPa) and low density (7.79 gr/cm³) [5]. Compared to WC, It not only shows higher oxidation resistance in air, but also the Nb₂O₅ is more stable than WO₃ at elevated temperatures. Combining the as mentioned advantages with lower dissolution rate in Iron, NbC has better stability when getting in contact with Fe based steels at high temperatures [6]. Moreover, NbC and Nb₂O₂ are not water soluble and so far no report has been published on their toxicity to human contrary to WO₃ [7–9]. Recent studies on wear properties of NbC cemented carbides shows their promising tribo-active characteristic due to the formation of stable Nb₂O₅ in the contact area [3,4].

In recent years, different metallic components used as binder for NbC matrix cemented carbides. Earlier efforts on using pure Iron binder resulted in products with low density values and poor mechanical properties. Inferior mechanical properties of Iron as the binder along with the presence of Fe₂Nb intermetallic phase results in poor mechanical performance of the final cermet [10]. Enhanced tribological and mechanical behavior were observed in Co bonded NbC cemented carbides [4]. Remarkable wear properties were related to intrinsic wear resistance of pure NbC. Wear behavior of binderless NbC (hot-pressed) was benchmarked with different ceramics and hardmetals revealing the strong position of

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NbC materials under tribological considerations [3]. However, Co bonded NbC revealed even better wear properties at high sliding velocities than pure NbC. Comparable mechanical properties with WC-Co hardmetals was observed in spark plasma sintered NbC-12Co containing 5wt% of Mo₂C as grain growth inhibitor [11]. It has to be mentioned that Co, similar to WC, is a toxic material [12,13]. Despite the outstanding properties of Co bonded NbC materials, efforts are promoted to substitute Co by more environmental friendly binders like Ni and Fe [14–16]. Iron can be a better candidate because of nontoxicity and resources abundance (leading to lower cost). However, with pure Fe as a binder, as already mentioned, poor densification and mechanical properties are exhibited in the final cermet [10]. Huang et. al [11] results indicated the great potential of steel to be substitute the Co binder without providing an explanation on this phenomenon. It is well known that the mechanical properties of the binder phase significantly effects the performance of the hardmetal. Addition of elements like C, Ni, Cr, Co to pure Iron improves the mechanical properties of Iron by forming solid solutions resulting in better performance as the binder [17,18]. Moreover, these additives in the steel based binders could help to increase the sintering performance due to higher solubility of NbC in these elements at sintering temperature [6]. Further investigations by Huang et al. [14] on 316L and 430L stainless steel binders indicated the better mechanical properties of the hardmetal with 430L as the binder due to the difference in the binders crystal structure. Based on these studies, it can be concluded that steel and stainless steel binder will directly influence the liquid phase sintering behavior which will result in different microstructure and mechanical properties of the cemented NbC.

In the present work, the M48 high speed steel (HSS) was selected as binder for NbC matrix hardmetals. To compare the so far used stainless steel binders with M48 HSS, it is necessary to look deeper into the alloying elements which are presented in table 1. In 316L high amount of Ni (10-14 wt%) increases toughness of the steel as well as functioning as a wetting agent due to favorable wetting properties of NbC with Ni. Also, high chromium content (16-18 wt%) improves the mechanical properties and high temperature oxidation resistance in 316L and 430L steels [19]. The same effect also applies to M48 HSS but to some extent due to lower content of Cr in this steel. However better wetting properties and sintering performance are expected from M48 HSS due to the presence of Co as an alloying element and higher solubility of NbC in Co compared to Ni [6,11]. Moreover, Co improves the mechanical properties of the tool steel making it superior to 316 and 430 stainless steels [20]. The other benefit of using M48 as the binder is the presence of W, V, Mo in the form of cubic carbides in the structure. Earlier reports indicate the important role of these carbides in inhibiting the NbC grain growth during sintering [11]. According to the presents of Co, W, V and Mo as-mentioned behavior, it is expected that M48 HSS can be a good candidate as the binder for the NbC cermets.

Table 1. Comparison on alloying composition of 316L and 430L stainless steel and M48 high speed steel [19]

Steel	wt% of alloying elements										
	C	Si	Mn	Cr	Mo	Ni	Co	Cu	V	W	Fe
M48 HSS	1.2 – 1.5	0.15-0.4	0.15-0.4	3.4-4	4 – 5.5	0-0.3	8-10	0.13	2.75-3.25	9.5-10.5	Balance
316L	0.03	0-1	0-2	16-18	2-3	10-14	-	-	-	-	Balance
430L	0.03	0-1	0-1	16-18	-	-	-	-	-	-	Balance

Sintering atmosphere has a great impact on the final properties of NbC-HSS cemented carbides. Typically in the hardmetal industry, vacuum is used as sintering atmosphere until almost near full density of the compacts is achieved. At the final stage of consolidation, an overpressure (1-10 MPa) of an inert gas (usually argon) is applied to eliminate bulk residual porosities [21]. The mentioned practice is not applicable to NbC-HSS hardmetals. Previous studies on melted steels under vacuum condition, indicates the high probability of elimination of important alloying components with low vapor pressure (Cr, Co) due to evaporation [21]. Therefore sintering in atmospheric pressure is suggested for this material. However, sintering in nitrogen atmosphere causes loss of ductility due to nitrogen intake by molten steel binder. Based on the mentioned remarks, in the current study argon was selected as the sintering atmosphere.

2. Materials and Methods

2.1. Preparation of HSS powder

Commercially available PM M48 HSS 19 mm rod (China) was used as the raw material to produce metal binder for liquid sintering. In a first step, the bulk material was mechanically grinded to coarse chips (below 100 micron) by a metal rasp. An attritor based cryogenic milling machine has been developed. The man made milling device was cooled with liquid nitrogen, to mill down the metal powder. In order to prevent the direct contact of liquid nitrogen with metallic powder, a liquid nitrogen jacket was used to cool down the main milling metal chamber. The milling was carried out using stainless steel balls (d: 10 mm) and impeller with a ball to powder ratio of 25:1. Milling continued for 6 hours at 400 rpm in ethanol. The milling chamber temperature was kept constant at - 90°C by adjusting the flow of liquid nitrogen inside the jacket chamber. The as-milled powders were first sieved then dried for 24 hours at 50°C

2.2. NbC cemented carbide sample preparation

Commercially available NbC powder with a mean grain size of 1.02 μm (Langfeng Metallic, China) was used as the starting material. The powder was wet - mixed with 12 wt% of M48 HSS powder and 1 wt% of paraffin wax as lubricant in toluene on a roll mill for 24 hours using stainless steel balls with a diameter of 8, 6, and 4 mm. The solvent was removed from the suspension using a rotary evaporator (R-134, Buchi, Switzerland) at 40 °C and kept for 24 hours in an oven at 110 °C to get fully dried. Cylindrical green compacts with diameter of 9 mm were prepared using hydraulic compaction press (PW 20, P/O/Weber, Germany) at 50 kN force which resulted in a pressure of 780 MPa on the sample. Dewaxing and sintering of the green samples was performed in a Carbolite tube furnace with SiC tube and heating elements under flowing argon atmosphere. Dewaxing was carried out by heating at 10 °C/min up to 280°C and a dwell time of 1h. Subsequent heating of dewaxed samples was carried out at 15°C/min up to 900 °C and continued at 10 °C up to sintering temperature. Fig. 1 represents a schematic illustration of the 3 step sintering process in a typical temperature/time cycle.

Fig. 1. Schematic diagram featuring the classical sintering cycle. Typical conditions are: debinding in 280 °C for 1h , heating to 900 °C with 15 °C/min, heating to sintering temperature with 10 °C/min, sintering in 1280 °C -1420 °C for 1 h.

2.3. Characterization

Chemical composition of the initial M48 bar was measured using optical emission spectroscopy (Foundry Master, Oxford Instruments, UK). The morphology and particle size distribution of the powder obtained from cryomilling and the NbC

powder was studied using scanning electron microscope (VEGA3, TESCAN Co., Czech Republic) and laser diffraction particle size analyzer (LS13 320, Beckman Coulter, USA).

Bulk density of the sintered cemented carbides was measured using Archimedes method in water. Microstructural observations on polished surface of the sintered samples were performed by SEM, equipped with an energy dispersive spectrometer (EDS, Xflash 610, Bruker Nano GmbH, Germany). The average linear NbC grain size was measured by line intercept method using Gatan image analysis software [22]. The densification behavior was also studied using a thermo mechanical analyzer (TMA 402 F3, NETZSCH, Germany) in argon atmosphere.

Mechanical properties, including Vickers hardness (HV2) and Vickers indentation fracture (VIF) were assessed with an indentation load of 19.6 N (, Leitz microhardness, Leitz wetzlar Germany). The fracture resistance was also evaluated from the length of the radial cracks originating in the corners of the Vickers indentations and calculated by the formula proposed by Shetty [23].

3. Results and discussion

3.1. Characterization of the starting powders

The element analysis of the starting M48 HSS material is presented in table 2. As expected for this grade, high values of W, Co are presented in this material along with moderate values of Cr, Mo, and V. To study the effect of cryomilling on the morphology of the steel particles, SEM observations were done prior and after cryomilling with optimized condition (fig. 2). As can be observed, the cryomilling process has led to particle size reduction and morphology change to flake like particles with high aspect ratio. Fig. 3 shows the particle size distribution (PSD) of the as-milled steel powder. The wide PSD is due to the high aspect ratio of the powders resulting in both low values as for the thickness and high values for the length of particles. According to particle size analysis, the mean particle size of the steel powder after cryogenic milling is 42.18 micron. In order to have an estimate on the aspect ratio of the treated powders, thickness of random particles were measured using SEM micrographs and an average of 3.07 ± 1.36 micron was calculated. Combining the two results, an aspect ratio of 13-14 can be calculated for the as-milled powders.

The microstructural characteristics of the starting NbC was also studied and presented in Fig. 3 and 4.

Table2. Chemical composition of M48 HSS

wt%										
C	Si	Mn	Cr	Mo	Ni	Co	Cu	V	W	Fe
1.17	0.3	0.3	4.01	3.71	0.2	9.53	0.13	3.02	9.66	Balance

Fig. 2. SEM morphology of the M48 HSS powder: (a) after mechanical grinding by metal rasp and (b) cryomilled powder

Fig. 3. SEM micrograph of the NbC powder

Fig. 4. Particle size distribution of: (a) steel powder after cryogenic milling and (b) NbC powder.

3.2. Densification behavior

The dilatometry data of green compacts heated from debinding temperature up to 1420 °C with a constant heating rate of 5 °C/min under flowing argon is reported in fig. 5. In order to obtain a better understanding on the densification behavior, the first derivate of densification curve with respect to time was calculated and used to define the points of interest in the graph. The calculations were performed using NETSCH Proteus thermal analysis software.

As indicated in fig. 5, the onset of the densification is at 855 °C and the beginning of high shrinkage rate is at 1055 °C. Analysis on the derivate of linear shrinkage revealed the occurrence of two high shrinkage rate points with an inflection point at 1270 °C in the dilatometry plot. It is assumed that different sintering mechanisms are contributed in these temperatures. To further explore the influence of different sintering regimes on density, microstructure, and mechanical properties of the final cermet, sintering temperatures were selected according to defined points of interest in the dilatometer results. Therefore, as presented in red circles in fig. 5, sintering was done at 5 different temperatures as follow: (1) 1260 °C (before the inflection point), 1300 °C (after the inflection point with higher shrinkage rate), 1340 °C (end of high shrinkage rate area), 1380 °C, and 1420 °C.

At the final stage of the densification curve, a slight expansion could be observed from 1340 °C to 1380 °C. SEM micrographs showing the edge of samples sintered before (1300 °C) and on the peak of expansion (1380 °C) are presented in fig. 5. Rejected liquid droplets can be noted on the side of the sample sintered at 1300 °C while this feature cannot be detected in sample sintered at 1380 °C. According to Washburn's equation [24] for capillary flow:

$$l^2 = \frac{r\gamma \cos \theta}{2\eta}$$

Where t is the time and η is the viscosity of a liquid with γ as the surface tension that penetrates through a capillary with radius of r and contact angle of θ , the expansion in the densification curve could be interpreted. It is proposed that poor wetting behavior at low sintering temperature results in low contact angle that limits the penetration of liquid inside the sample. As the sintering temperature rises, improved wetting properties results in better penetration of liquid phase inside the sample causing a slight expansion in the densification behavior.

Fig. 5. Shrinkage behavior of green NbC-12wt% M48 HSS samples after debinding

3.3. Microstructure

As expected, the microstructure of the sintered samples was strongly influenced by the sintering temperature. The results are presented in fig. 6. Using EDS analysis, a bright NbC and a grey metallic binder phase was identified in the micrographs. In addition, a bright phase (indicated by arrows) mostly consisting of Mo, Cr and W was presented along some NbC grain boundaries in the sample sintered at 1420 °C (fig. 6(e)). At Sintering temperatures below 1340 °C, the microstructure still show the flaky structure of the cryomilled HSS binder particles (fig. 6(a) and (b)).

Above 1340 °C the sintering experiments resulted in a more homogeneous distribution of metallic binder with the drawback of having higher NbC grain growth. The solubility of NbC increases with temperature reaching to a maximum

Fig. 6. SEM micrograph of NbC-12%M48 HSS sintered at: (a) 1260 °C, (b) 1300 °C, (c) 1340 °C, (d) 1380 °C, and (e) 1420 °C

value of 0.98 wt% at 1310 °C [25]. It is known that wetting is significantly influenced by the solid solubility in the liquid. Therefore, higher solid solubility improves wetting behavior which induces liquid spreading to fill pores. With reference to low solubility of NbC in Iron at low temperatures, high contact angle and poor wetting behavior is expected resulting in high dihedral angle. This will limit the penetration of liquid phase between the solid particles resulting in undistributed

binder phase along with high contiguity in the microstructure [26]. Higher porosity and lower relative density is another consequence of limited solubility which can be noted in Fig. 5(a).

In addition, the formation of a eutectic alloy at 1310 °C between Fe and NbC increases the liquid portion in the binder on one hand and improves the wetting performance on the other hand [25]. Meanwhile, transformation of ferrite to liquid phase in the HSS binder results in higher liquid portion when the temperature is getting close to the liquidus region [27]. Higher portion of liquid in the binder phase helps the followability and boosts the spreading of the binder phase resulting in lower porosity and even binder distribution in final microstructure [26]. This phenomenon can be traced from coarse undistributed binder particles in Fig. 6 (a) to even distribution of binder phase in Fig. 6 (e).

Microstructural alteration from well-faceted NbC grains to faceted grains with slight rounding on the edges was another feature in these samples. The formation of this microstructure defines the presence of solution-precipitation mechanism in densification. During sintering, solid dissolution into the liquid occurs preferentially from small grains and convex points. The dissolved solid then diffuses through the liquid, precipitating onto larger grains or concave regions resulting in rounded grains [26].

Table 3 shows the average NbC grain size measured using line intercept technique. A constant increase in the mean grain size is observed as the sintering temperatures increases up to 1380 °C followed by a marked increase at 1420 °C. The pronounced grain growth implies higher contribution of solution-precipitation mechanism due to higher solid solubility and liquid amount at this temperature. High densification level was observed in samples sintered above 1300 °C due to active liquid phase sintering mechanism. However, pore elimination is limited as sintering temperature rises above 1380 °C due to rapid NbC grain growth leading to trapped porosities inside the grains. Comparably lower density values were obtained for samples sintered at lower temperatures revealing the effect of sintering mechanism on pore elimination.

Table 3. Average NbC grain size of samples sintered at different temperatures.

Sample name	Sintering Temperature (°C)	R.D. (%)	NbC grain Size (μm)
S 1260	1260	94.9	2.9
S 1300	1300	97.3	3.8
S 1340	1340	99.5	4.9
S 1380	1380	99.1	6.1
S 1420	1420	98.3	10

3.4. Phase analysis

X-ray diffraction pattern of the sample sintered at 1420 °C is presented in Fig. 7. Two main phases can be detected from X-ray spectrum. The high and low intensity peaks correspond to NbC and Fe phases respectively. Unfortunately, no sign of secondary carbides in the metal binder appears in the X-ray pattern due to the scant amount of these species in the sample.

In order to trace the alloying elements inside the steel binder in the final microstructure, EDS elemental distribution maps of Fe, Cr, C, Co, Nb, W, and V were examined as presented in Fig. 8. Due to higher solubility of NbC in Co than Fe [25], more uniform distribution of Co can be noted in the microstructure while Fe is mostly located in the binder phase. Similar mapping result was noted for Nb distribution indicating the limited solubility of NbC in Fe. Considering the carbides in the microstructure, an even distribution of V was observed due to complete mutual solubility of VC and NbC. In the case of W and Cr, however, the distribution was less uniform with higher concentration in the binder phase due to lower solubility of their carbides in NbC [5].

Fig. 7. XRD result for the cermet sintered at 1420 °C.

EDS point analysis of the samples sintered at 1420 °C shows that the bright phase (mentioned earlier) is rich in Mo, W, and Cr. It is assumed that decrease in solubility of molybdenum, tungsten, and chromium carbides in niobium carbide at lower temperatures results in precipitation of these carbides along NbC grain boundary during cooling cycle.

Fig. 8. EDS elemental mapping of the sample sintered at 1420 °C: (a) SEM image, (b) Fe, (c) Cr, (d) C, (e) Co, (f) Nb, (g) W, (h) V.

3.5. Mechanical properties

Fig. 9 represents the dependence of hardness and fracture resistance on sintering temperature. A sharp increase to high hardness values can be observed followed by a steady drop as the sintering temperature increases in the hardness graph. However, moderately low values were obtained for the fracture resistance with a drop at 1300 °C. According to previous reports on VIF technique, the method is not suitable for measuring the fracture toughness, K_{IC} , of brittle materials [28]. Therefore in this study, it was used only to make a comparison on toughness of different samples and the values may differ from the real fracture toughness (K_{IC}) of the cermet.

It is well known that hardness and fracture toughness in hardmetals are mainly affected by porosity, binder distribution and carbide grain size [29] High amount of porosity is the key factor for poor hardness values obtained for sample

sintered at 1260 °C. A pronounced increase in hardness (up to 14.91 ± 0.14 GPa) can be monitored when sintering temperature is raised to 1300 °C. Referring to the measured density value (table 2), it can be noted that higher density (i.e. lower porosity) achieved at 1300 °C results in better hardness performance. Meanwhile, increased contiguity in the structure with interconnected small carbide particles network also has an explicit role in this growth [30]. Up to 1380°C no significant decrease in hardness value could be observed. The plateau is followed by a slight decrease at 1420 °C. As stated earlier, the drop could be associated with higher porosity measured for samples sintered above 1380 °C due to abnormal grain growth of NbC which could deteriorate the hardness of hardmetal[30].

Fig. 9. Variation of hardness and fracture resistance of the cemented carbides with sintering temperatures

Regarding the fracture resistance, comparably high value was measured with broad deviation for the sample sintered at 1260 °C. Referring to microstructural analysis (fig. 6. a), undistributed large binder particles is the prominent feature of this sintering condition. The presence of these particles in the vicinity of indentation mark effectively suppresses the palmqvist crack growth leading to higher fracture resistance measured values. Also considering the possibility of having large binder particles under Vickers indenter, it is probable that at some points the fracture resistance value is more influenced by the properties of the HSS binder than the hardmetal. As the occurrence of these phenomena is not consistence in all indentation spots, high deviation in measured values could be observed. From 1300 °C to 1380°C increase in fracture resistance is mainly due to the NbC grain growth [31]. Highest fracture resistance which valued 1.56

MPa.m^{1/2} was obtained in the sample sintered at 1380 °C. A drop in fracture resistance at 1420 °C is connected to higher porosity levels at this temperature.

With reference to Huang's [11] work, a hardness value of 13.92 GPa was obtained for NbC-12 wt% stainless steel 316L cermet. Higher hardness values obtained in this study at same sintering temperature and binder content is directly associated with higher hardness of the HSS as the binder. Previous studies confirms the crucial role of binder phase on mechanical properties of the cermet [14]. Regarding the fracture resistance, inferior values was measured compared to Huang's work [11]. It should be noted that the morphology and distribution of eutectic carbides in HSS after solidification has great impact on the mechanical properties. Coarse undistributed carbides results in low toughness [27]. It is assumed that low cooling rates inside the furnace leads to formation of coarse eutectic carbides inside the steel binder which may be a reason for low fracture resistance values.

In order to gain better understanding on the fracture resistance behavior, propagation of palmqvist cracks induced by Vickers indentation was studied using SEM (Fig. 10). As shown in Fig. 10 (a-c), the metal binder has preclude the crack propagation in many indent marks. It is known from previous reports that the metal binder in hardmetals has a key role in shielding the stress field in front of a crack tip to improve the toughness [30]. Inhomogeneous binder distribution at low sintering temperatures together with arbitrary occurrence of indentation mark at high and low binder concentration sites in the sample resulted in high deviation in the fracture resistance values observed in this range.

Fig. 10. SEM micrograph of crack propagation in cermets sintered at: (a), (b) 1260 °C and (c), (d) 1420 °C

According to Fig. 10 (d), some indentation marks in samples sintered at higher temperatures, indicated poor hindering effect of steel binder allowing the crack to propagate. It is supposed that poor ductility of the metal binder in cermets sintered at elevated temperatures is responsible for this behavior. In fact, this phenomenon could be also the key factor in low fracture resistance values obtained in M48 HSS cemented niobium carbides. As reported elsewhere, several factors including the carbon content, cooling rate, type of secondary carbides, etc. determine the final mechanical properties in high speed steels [27]. Therefore, further studies on the effect of these parameters on the mechanical properties of the steel binder and final hardmetal are suggested.

4. Conclusion

Using liquid phase sintering, NbC-M48 HSS steel cemented carbides can be sintered at temperatures higher than 1300 °C in argon atmosphere successfully. Because of non-wetting behavior of the HSS steel on NbC surface and low flowability of liquid phase, sintering below 1300°C resulted in an inhomogeneous non sintered microstructure. Above 1300 °C, higher NbC solubility and lower dihedral angle at these temperatures enhanced the liquid penetration between NbC grains resulting in more homogenous microstructure.

The hardness value increased from 11.15 GPa to 14.91 GPa as the sintering temperature raised from 1260 °C to 1300 °C expressing a significant dependence on sintering temperature. No significant decrease in hardness values at sintering temperatures up to 1380°C could be observed. In this study low fracture resistance was obtained in all sintering temperatures. Optimal combination of the hardness and fracture toughness was achieved in the sample sintered at 1380 °C with 14.87 ± 0.11 GPa and 1.56 ± 0.3 MPa.m^{1/2} values respectively.

It is assumed that further improvement on the ductility of the steel binder could greatly enhance the mechanical properties of the final product. Therefore, additional investigation on this area could be suggested.

References

- [1] T. Kraus, P. Schramel, K.H. Schaller, P. Zöbelein, A. Weber, J. Angerer, Exposure assessment in the hard metal manufacturing industry with special regard to tungsten and its compounds, *Occup. Environ. Med.* 58 (2001) 631–634. doi:10.1136/oem.58.10.631.
- [2] P. Leanderson, W. Sahle, Formation of hydroxyl radicals and toxicity of tungsten oxide fibres, *Toxicol. Vitro* 9 (1995). doi:10.1016/0887-2333(94)00197-3.
- [3] M. Woydt, H. Mohrbacher, The use of niobium carbide (NbC) as cutting tools and for wear resistant tribosystems, *Int. J. Refract. Met. Hard Mater.* 49 (2015) 212–218. doi:10.1016/j.ijrmhm.2014.07.002.
- [4] M. Woydt, H. Mohrbacher, The tribological and mechanical properties of niobium carbides (NbC) bonded with cobalt or Fe₃Al, *Wear* 321 (2014) 1–7. doi:10.1016/j.wear.2014.09.007.
- [5] H.O. Pierson, Handbook of refractory carbides and nitrides : properties, characteristics, processing, and applications, *Handb. Refract. Carbides Nitrides*. (1996) 362. doi:10.1016/B978-081551392-6.50005-2.
- [6] B.M. Kramer, N.P. Suh, Tool Wear by Solution: A Quantitative Understanding, *J. Manuf. Sci. Eng.* 102 (1980) 303–309. doi:10.1115/1.3183869.
- [7] M. Woydt, H. Mohrbacher, J. Vleugels, S. Huang, Niobium carbide for wear protection - tailoring its properties by processing and stoichiometry, *Met. Powder Rep.* 0 (2016). doi:10.1016/j.mprp.2015.12.010.
- [8] G. Ramírez, S.E. Rodil, H. Arzate, S. Muhl, J.J. Olaya, Niobium based coatings for dental implants, *Appl. Surf.*

- Sci. 257 (2011) 2555–2559. doi:10.1016/j.apsusc.2010.10.021.
- [9] M. Braic, V. Braic, M. Balaceanu, A. Vladescu, C.N. Zoita, I. Titorencu, V. Jinga, F. Miculescu, Preparation and characterization of biocompatible Nb-C coatings, *Thin Solid Films*. 519 (2011) 4064–4068. doi:10.1016/j.tsf.2011.01.193.
- [10] P.G. Esteban, E. Gordo, Development of Fe–NbC cermet from powder obtained by self-propagating high temperature synthesis, *Powder Metall.* 49 (2006) 153–159. doi:10.1179/174329006X102825.
- [11] S.G. Huang, K. Vanmeensel, H. Mohrbacher, M. Woydt, J. Vleugels, Microstructure and mechanical properties of NbC-matrix hardmetals with secondary carbide addition and different metal binders, *Int. J. Refract. Met. Hard Mater.* 48 (2015) 418–426. doi:10.1016/j.ijrmhm.2014.10.014.
- [12] R. Lauwerys, D. Lison, Health risks associated with cobalt exposure--an overview., *Sci. Total Environ.* 150 (1994) 1–6. <http://www.ncbi.nlm.nih.gov/pubmed/7939580>.
- [13] A.. Bech, M.. Kipling, J.. Heather, Hard Metal Disease, *Br. J. Industrial Med.* 19 (1962) 239–252. doi:10.1001/jama.1963.03700050155123.
- [14] S.G. Huang, J. Vleugels, H. Mohrbacher, Stainless steel bonded NbC matrix cermets using a submicron NbC starting powder, *Int. J. Refract. Met. Hard Mater.* 63 (2017) 26–31. doi:10.1016/j.ijrmhm.2016.04.021.
- [15] S.G. Huang, J. Vleugels, H. Mohrbacher, M. Woydt, Microstructure and tribological performance of NbC-Ni cermets modified by VC and Mo₂C, *Int. J. Refract. Met. Hard Mater.* 66 (2017) 188–197. doi:10.1016/j.ijrmhm.2017.03.012.
- [16] S.G. Huang, J. Vleugels, H. Mohrbacher, M. Woydt, Microstructure and mechanical properties of NbC matrix cermets using Ni containing metal binder, *Met. Powder Rep.* 71 (2016) 349–355. doi:10.1016/j.mprp.2016.05.009.
- [17] R.. Fleischer, Substitutional solution hardening, *Acta Metall.* 11 (1963) 203–209. doi:10.1016/0001-6160(63)90213-X.
- [18] H. Gleiter, *Fundamentals of Strengthening Mechanisms*, Pergamon Press Ltd, 1982. doi:10.1016/B978-1-4832-8423-1.50162-0.
- [19] A.S.M. Handbook, Volume 1: Properties and Selection: Irons, Steels, and High Performance Alloys, 2005.
- [20] A.P. Gulyaev, I.K. Kupalova, Effect of cobalt on the structure and properties of high-speed steels, *Met. Sci. Heat Treat.* 12 (1970) 666–671. doi:10.1007/BF00654791.
- [21] V.K. Sarin, *Comprehensive Hard Materials*, 2014. doi:10.1016/C2009-1-61070-4.
- [22] Gatan Inc., Gatan Microscopy Suite Software, (2015). doi:10.1002/jbm.a.3549.
- [23] D.K. Shetty, I.G. Wright, P.N. Mincer, A.H. Clauer, Indentation fracture of WC-Co cermets, *J. Mater. Sci.* 20 (1985) 1873–1882. doi:10.1007/BF00555296.
- [24] E.W. Washburn, The dynamics of capillary flow, *Phys. Rev.* 17 (1921) 273–283. doi:10.1103/PhysRev.17.273.
- [25] J.P. Guha, D. Kolar, Systems of niobium monocarbide with transition metals, *J. Less-Common Met.* 29 (1972) 33–40. doi:10.1016/0022-5088(72)90145-2.
- [26] R.M. German, *Liquid Phase Sintering*, Springer Science+Business Media, New York, 1985.
- [27] M. Boccalini, H. Goldenstein, Solidification of high speed steels, *Int. Mater. Rev.* 46 (2001) 92–115. doi:10.1179/095066001101528411.
- [28] G.D. Quinn, R.C. Bradt, On the vickers indentation fracture toughness Test, *J. Am. Ceram. Soc.* 90 (2007) 673–680. doi:10.1111/j.1551-2916.2006.01482.x.

- [29] I. Azcona, A. Ordóñez, J.M. Sánchez, F. Castro, Hot isostatic pressing of ultrafine tungsten carbide-cobalt hardmetals, *J. Mater. Sci.* 37 (2002) 4189–4195. doi:10.1023/A:1020048105585.
- [30] H.C. Lee, G. J, Hardness and Deformation of Cemented Tungsten Carbide, *Mater. Sci. Eng.* 33 (1978) 125–133.
- [31] V. Richter, M. Ruthendorf, On hardness and toughness of ultrafine and nanocrystalline hard materials, *Int. J. Refract. Met. Hard Mater.* 17 (2000) 141–152.

Highlights

- Significant microstructural revolution was observed at sintering temperatures higher than 1300 °C
- Improved wetting performance and increased liquid portion in the binder at high sintering temperatures are proposed as the main reasons.
- Using M48 HSS as the binder improved the hardness up to 14.91 ± 0.14 GPa compared to previous studies.
- Low fracture resistance was obtained when using M48 HSS as the binder.