



# WC-Co-Re cemented carbides: Structure, properties and potential applications

I. Konyashin<sup>a,b,\*</sup>, S. Farag<sup>a</sup>, B. Ries<sup>a</sup>, B. Roebuck<sup>c</sup>

<sup>a</sup> Element Six GmbH, Burghaun D-36151, Germany

<sup>b</sup> National University of Science and Technology MISiS, Moscow 119049, Russia

<sup>c</sup> National Physical Laboratory, Teddington TW11 0LW, United Kingdom

## ARTICLE INFO

### Keywords:

Cemented carbides

Co-Re binders

Microstructure

High-temperature properties

## ABSTRACT

Cemented carbides of the WC-Co-Re system represent a new class of hard materials having a significantly increased Young's modulus, hot hardness and high temperature creep resistance. The WC-Co-Re phase diagram was evaluated and compared with the corresponding WC-Co phase diagram. Physical and mechanical properties of such composites were measured at room and elevated temperatures and compared with those of conventional WC-Co cemented carbides. Microstructures of the WC-Co-Re cemented carbides at different carbon contents, binder contents and WC grain sizes were examined. Rhenium being dissolved in the Co-based binder is found to be a very strong grain growth inhibitor with respect to WC coarsening during liquid-phase sintering. The Young's modulus, hot hardness and high temperature creep resistance of the WC-Co-Re cemented carbides are greater than those of conventional WC-Co cemented carbides. Due to their unique properties the WC-Co-Re materials can find applications in use in high-pressure high-temperature components for synthesis of diamond and c-BN and cutting Ni-based super alloys and other heat-generating workpiece materials.

## 1. Introduction

It is well known that high-pressure high-temperature (HPHT) components such as anvils and dies employed for the synthesis of diamond, polycrystalline diamond (PCD) or cubic boron nitride (c-BN) are subjected to harsh operation conditions. They include ultra-high pressures (above 5 GPa) and relatively high temperatures (of above 1400 °C). Presently, there is a general trend to fabricate diamond and c-BN by so-called direct conversion, which enables the synthesis of diamond or c-BN out of graphite or hexagonal boron nitride without employing catalysts [1,2]. As a result, nano-structured diamonds and c-BN with exceptionally high hardness values can be obtained. However, direct conversion is only achievable at extremely higher pressures exceeding 12 GPa. Such unfavorable conditions inevitably lead to the deformation of HPHT components and, if the deformation exceeds a certain level, the components fail. Currently, the large-scale fabrication of superhard materials at pressures above 12 GPa is limited by relatively short lives of HPHT components made of conventional WC-Co materials. Therefore, the development and research of novel cemented carbides with improved high temperature properties currently can be considered as a topic of great interest. Prolonging the lifetime of HPHT components can generally be achieved by improving the deformation

resistance of the composite materials, which in turn is dependent on its Young's modulus and high-temperature creep resistance.

It is well understood that additions of Re to binders of WC-based cemented carbides allows improvement of their high-temperature properties [4–10].

Cemented carbides containing rhenium were first patented in 1949 [3]; however, at this time no information regarding potential advantages of partial substitution of Co by Re in the cemented carbide binder for high temperature applications was available.

WC-Co-Re cemented carbides characterized by particular Re to Co ratios were developed for fabricating cutting tools in the Soviet Union [4–8]. Although, it was established that such cemented carbides are characterized by significantly higher hot hardness and improved performance at elevated temperatures in comparison with conventional WC-Co materials, such composites were not applied in HPHT applications.

Cemented carbides containing Co-Re binders and mixed (W,Re)C carbides were examined in refs. [9, 10]. It was found that rhenium added to the Co-based binder phase forms a solid solution with cobalt decreasing the stacking fault energy of the binder phase, which leads to the stabilization of the hcp Co modification. Tungsten and rhenium were found to form mixed carbides having different compositions.

\* Corresponding author at: Element Six GmbH, Burghaun D-36151, Germany.

E-mail address: [igor.konyashin@e6.com](mailto:igor.konyashin@e6.com) (I. Konyashin).

<https://doi.org/10.1016/j.ijrmhm.2018.10.001>

Received 24 July 2018; Received in revised form 12 September 2018; Accepted 3 October 2018

Available online 05 October 2018

0263-4368/© 2018 Elsevier Ltd. All rights reserved.

Waldorf et al. examined the performance of WC-Co-Re cemented carbides in machining Ni-based superalloys and established that their tool lifetime is prolonged by up to 150% in comparison with conventional WC-Co carbide grades [11].

The major objective of this work was to optimize fabrication conditions of WC-Co-Re cemented carbides, produce such cemented carbides with different compositions and WC mean grain sizes, and examine their physical and mechanical properties at room temperature and elevated temperatures.

## 2. Experimental procedure

A number of laboratory batches of WC-Co-Re cemented carbides with different carbon contents, WC mean grain sizes, binder contents and ratios between Re and Co were produced and examined. WC powders with mean grain sizes of 3  $\mu\text{m}$  and 0.8  $\mu\text{m}$ , a Co powder with a grain size of about 1  $\mu\text{m}$  and a Re powder with a grain size of 1–3  $\mu\text{m}$  were milled in hexane with different amounts of carbon black and 1.8% paraffin wax by use of attritor-mills and ball-mills. The batches produced from the medium-coarse WC powder with a mean particle size of 1.7  $\mu\text{m}$  were designated as “medium-grain cemented carbides” and those obtained from the fine-grain WC powder with a particle size of 0.6  $\mu\text{m}$  were designated as “submicron cemented carbides”. After drying a slurry obtained in such a way, carbide samples were pressed and sintered in a laboratory Sinter-HIP furnace at a temperature of 1520 °C for 1 h followed by cooling at rates varying from 0.5 degrees/min to 4 degrees/min. The Vickers hardness was measured according to the ISO 3878 standard at a load of 300 N. The transverse rupture strength (TRS) was measured according to the ISO 3327 standard. The compression strength was measured according to the ISO 4506 standard at room and elevated temperatures. The hot hardness and length of the Palmqvist cracks were measured at a load of 300 N at temperatures of 300 °C, 500 °C and 800 °C in an Ar atmosphere. The Young's modulus was measured with the aid of the ultrasonic method by means of measuring the transverse and longitudinal components of the speed of sound through the material. The high temperature creep resistance was examined at a temperature of 800 °C according to the procedure described in Ref. [12]. The XRD measurements were carried out on a Bruker D8 Advance instrument using a Co anode.

## 3. Results and discussion

Fig. 1 schematically shows the W-Co-Re-C phase diagram at 9 wt% Re + 6 wt% Co, which was elaborated based on the results obtained in the literature (Ref. [6]) and experimental results of the present work, in comparison with the corresponding WC-Co diagram at 10 wt% Co redrawn from Ref. [13]. When taking into account that Re has a significantly higher density than Co, the WC-Co Re cemented carbide with the binder containing 9 wt% Re and 6 wt% Co is characterized by nearly the same percentage of the binder phase by volume in comparison with a WC-Co material containing 10 wt% Co.

It can be seen in Fig. 1 that the W-Co-Re-C phase diagram differs from the W-Co-C phase diagram. The following special features of the W-Co-Re-C phase diagram should be mentioned.

First, all the melting points in the W-Co-Re-C diagram are shifted towards higher temperatures. Therefore, WC-Co-Re cemented carbides have to be sintered at significantly higher temperatures in comparison with conventional WC-Co materials.

Second, to the two-phase region not comprising  $\eta$ -phase and free carbon for WC-Co-Re cemented carbides is slightly shifted towards higher carbon contents. The shift is relatively insignificant, but still should be taken into account when fabricating the WC-Co-Re cemented carbides. Note that the width of the two-phase region in the W-Co-Re-C phase diagram is close to that in the W-Co-C phase diagram.

Third, additions of Re to the binder noticeably broaden the region, where WC +  $\eta$ -phase + liquid are in equilibrium at temperatures of

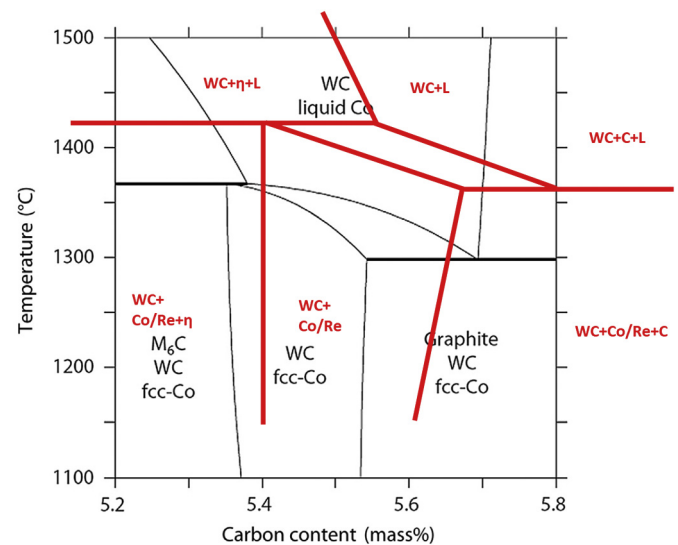


Fig. 1. Vertical sections of the W-Co-Re-C phase diagram (red lines) at 9 wt% Re + 6 wt% Co in comparison with the W-Co-C phase diagram at 10 wt% Co (black lines). The WC-Co diagram is redrawn from Ref. [13]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

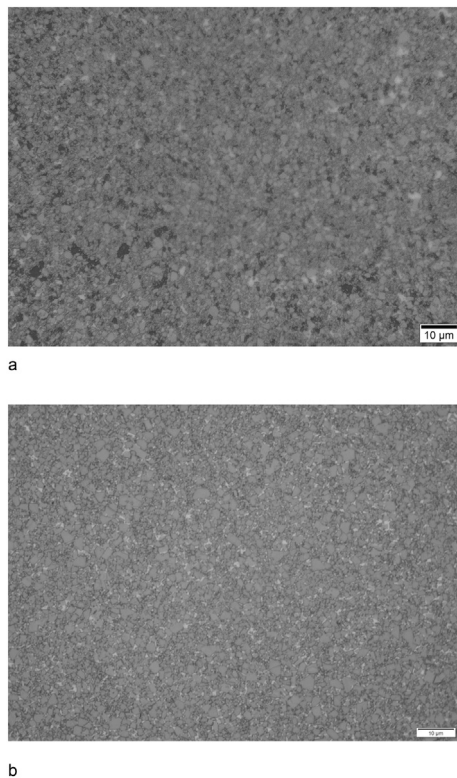
above approx. 1430 °C. This means that if the WC-Co-Re cemented carbides with medium-low and low carbon contents are fast cooled from sintering temperatures, they could contain  $\eta$ -phase, which did not decompose to the thermodynamically stable mixture of WC + Co/Re. Therefore, after sintering WC-Co-Re cemented carbides have to be cooled down at relatively low rates to ensure a full decomposition of the  $\eta$ -phase, which co-exists with WC and liquid phase at temperatures of above 1420 °C. This is illustrated in Fig. 2, which shows that the microstructure of the WC-Co-Re batch with a medium-low carbon content comprises inclusions of  $\eta$ -phase after fast cooling and is free of  $\eta$ -phase as a result of slow cooling.

The special features of the W-Co-Re-C phase diagram and the presence of large amounts of Re dissolved in the binder of WC-Co-Re cemented carbides lead to some peculiarities of their microstructure and properties.

Figs. 3 and 4 show the typical microstructure of the medium-grain WC-Co-Re cemented carbide in comparison with that of a conventional WC-Co material obtained from the same grade of WC powder. As one can see in Fig. 3, the microstructure of the WC-Co-Re cemented carbide is significantly finer than that of the conventional WC-Co cemented carbide. Therefore, Re acts as a strong WC grain growth inhibitor suppressing the WC coarsening process. According to the results of Ref. [14] Re segregates at WC/binder grain boundaries of WC-Co-Re cemented carbides. It can therefore be supposed that the phenomenon of suppressing the WC grain growth in WC-Co-Re materials is similar to the well-known inhibition effect of conventional grain growth inhibitors segregating at WC-Co grain boundaries [15,16].

The grain growth inhibiting effect of Re is quite important with respect to fabricating submicron cemented carbides usually employed for HPHT components, as there is no need for adding conventional grain growth inhibitors to the fine-grained WC-Co-Re cemented carbides. Figs. 4 and 5 show microstructures of the submicron WC-Co-Re cemented carbide not containing grain growth inhibitors, which are quite fine and uniform, and do not comprise abnormally large WC grains. Note that this cemented carbide was sintered at a temperature of 1520 °C, which is noticeably higher than temperatures usually employed for sintering submicron WC-Co grades.

Another unusual microstructural feature can be observed when fast cooling WC-Co-Re composites at medium-low carbon contents. The  $\eta$ -phase inclusions that formed as a result of fast cooling after sintering



**Fig. 2.** Microstructures of the medium-grain WC-Co-Re cemented carbides containing 9 wt% Re + 6 wt% Co with the total carbon content of 5.45 wt% cooled at different rates from the sintering temperature (1520 °C) down to 1300 °C: a – cooling rate of 4 degrees per minute and b – cooling rate of 0.5 degrees per minute (light microscopy after etching in the Murakami reagent).

are not fully etched by the Murakami reagent and exhibit a brown color after long etching (Fig. 6). As Co and Re form a solid solution as well as Re and W form mixed (W,Re)C carbides [11], not only the binder but also inclusions of the  $\eta$ -phase will comprise Re (see EDX measurements in Fig. 6a), resulting in an improved corrosion resistance of both phases in different aggressive media including the Murakami reagent. It was clearly established that the large inclusions shown in Fig. 6a comprise just the  $\eta$ -phase, as they become dark after etching in the Murakami reagent for 5 min. Numerous EDX measurements of different large inclusions of the  $\eta$ -phase in the WC-Co-Re samples indicated that they contain roughly 40 to 50 at.% Co, 10 to 20 at.% W and 30 to 40 at.% Re. Based on these results it can be supposed that the  $\eta_1$ -phase is present in the samples with the approximate composition of  $\text{Co}_3(\text{W,Re})_3\text{C}$ , so that tungsten atoms in the  $\eta$ -phase are partially substituted by Re atoms. This can be expected when taking into account that both W and Re form

mixed (W,Re)C carbides according to Ref. [10]. Nevertheless, the exact composition and stoichiometry of the  $\eta$ -phases forming in the WC-Co-Re cemented carbides are subjects of a separate study.

Results XRD analysis of the WC-Co-Re cemented carbide shown in Fig. 7 indicate the absence of fcc Co. The peaks corresponding to the binder phase lie between those of hcp-Co and hcp-Re. Thus, it can be assumed that the binder consists of a Co-Re solid solution having a hexagonal crystal lattice, as Co and Re are known to form an uninterrupted series of solid solutions.

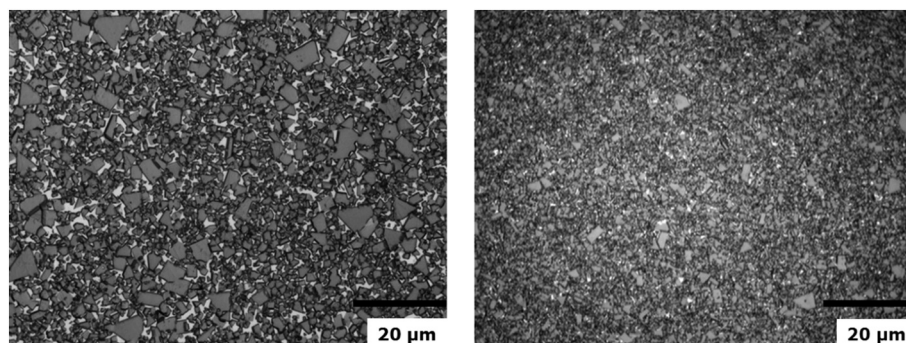
Large amounts of Re dissolved in the Co-based binder of WC-Co-Re cemented carbides have a strong influence of their magnetic properties. Fig. 8 indicates the dependence of the coercive force and the magnetic moment on the carbon content in the WC-Co-Re cemented carbides. Both the coercivity and the magnetic moment are almost independent on the carbon content unlike conventional WC-Co materials, which makes it difficult to determine the phase composition and WC mean grain size of WC-Co-Re cemented carbides based on their magnetic properties.

WC-Co-Re cemented carbides are characterized by a high combination of hardness, fracture toughness and TRS at room temperature, which is comparable with that of conventional WC-Co cemented carbides. As it can be seen in Fig. 9, a point indicating the combination of hardness and fracture toughness of the medium-grain carbide grade containing 9 wt% Re + 6 wt% Co lies on the baseline for conventional WC-Co cemented carbides. Its TRS (2920 MPa) is also comparable with that of a medium-coarse WC-Co mining grade with 10 wt% Co (2800 MPa, see Ref. [18]).

It was found that the WC-Co-Re cemented carbides have significantly improved physico-mechanical properties at elevated temperatures. The curves shown in Fig. 10 provide evidence that the hardness reduction as a function of temperature (20–800 °C) of the WC-Co-Re material is less significant than that for conventional WC-Co cemented carbides. The hardness reduction of the WC-Co-Re cemented carbide is nearly two times smaller in comparison with the conventional WC-Co material at temperatures of 300 °C and 500 °C, which are typical for the operation of HPHT components. The improved hot hardness is thought to be decisive for the fabrication of machining tools for Ni-super alloys or other heat generating materials that require a high degree of thermal and mechanical stability of cutting edges.

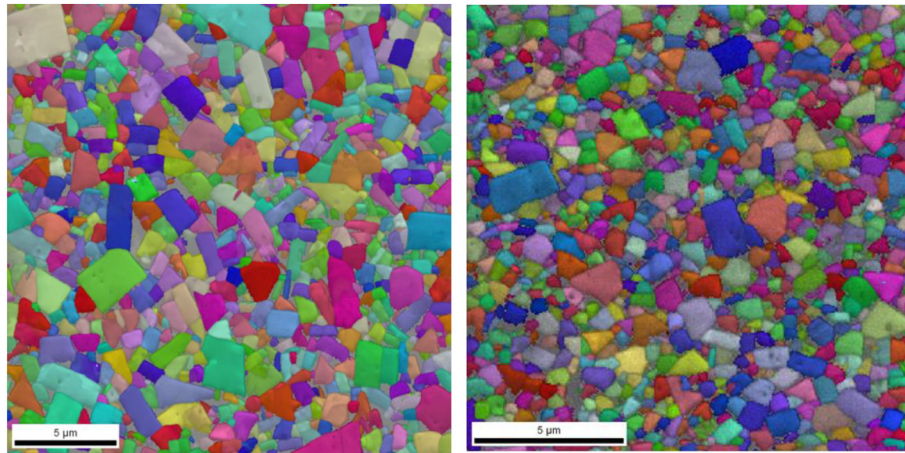
Results on the compression strength, which plays an important role when operating HPHT components, of the submicron WC-Co-Re cemented carbide and conventional WC-Co material shown in Fig. 11 indicate that the difference in the compression strength values is marginal.

Fig. 12 shows the temperature dependence of the Palmqvist crack lengths for the submicron WC-Co-Re cemented carbide. It can be seen that the WC-Co-Re carbide is characterized by only slightly longer Palmqvist cracks at elevated temperatures compared to room temperature. The Palmqvist crack measurement is thought to be influenced by the elasto-plastic behavior of the WC-Co-Re cemented carbides,

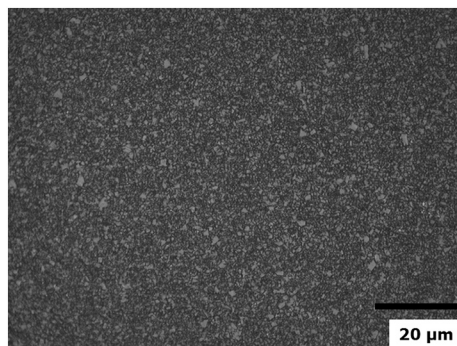


**Fig. 3.** Microstructures of the medium-grain WC-10%Co cemented carbide (left) and medium-grain WC-Co-Re cemented carbide containing 9 wt% Re + 6 wt% Co (right). Sintering at 1520 °C followed by slow cooling down to 1250 °C. (light microscopy after etching in the Murakami reagent).





**Fig. 4.** Microstructure of the medium-grain WC-Co-Re cemented carbide containing 9 wt% Re + 6 wt% Co (left) and the submicron WC-Co-Re cemented carbide containing 5.5 wt% Re + 3.7 wt% Co (right) (EBSD).



**Fig. 5.** Microstructure of the submicron WC-Co-Re cemented carbide containing 5.5 wt% Re + 3.7 wt% Co (light microcopy after etching in the Murakami reagent).

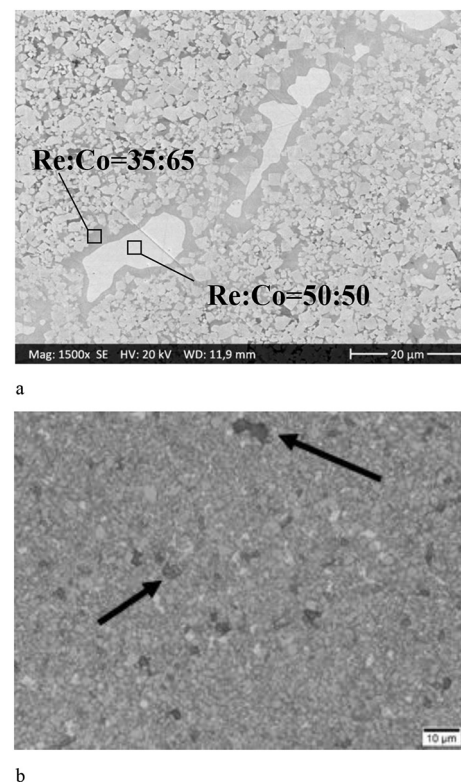
resulting in shorter cracks when increasing temperature; this phenomenon is also observed in WC-Co cemented carbides.

One of the most important parameters affecting the performance of HPHT components is Young's modulus of cemented carbides indicating their stiffness. As shown in Fig. 13, the Young's modulus of the WC-Co-Re materials increases as a result of the partial substitution of Co by Re, while keeping the volume percentage of the binder constant.

When taking into account the noticeably higher hot hardness of WC-Co-Re cemented carbides in comparison with conventional WC-Co materials mentioned above it can be supposed that the Re-containing cemented carbides are characterized by improved high temperature creep resistance. Indeed, as it can be seen in Fig. 14 the same values of compression strain rates are obtained for WC-Co-Re cemented carbides at noticeably higher loads than for the conventional WC-Co material, indicating that the Co-Re binders have a significantly improved high-temperature creep resistance.

In spite of high prices of Re powders and consequently higher production costs of the WC-Co-Re cemented carbides they can find applications in fields, where their unique high temperature properties, namely significantly improved creep resistance, increased and hot hardness, play a decisive role. These are primarily HPHT components for diamond and c-BN synthesis and cutting tools for machining superalloys and other heat-generating workpiece materials.

In HPHT applications, the increased Young's modulus of the WC-Co-Re cemented carbides should also play an important role. It is well known that HPHT components are completely recycled after operation. It was reported in ref. [19] that WC-Co-Re cemented carbides can be recycled in a similar way as conventional WC-Co materials, therefore, Re contained in the WC-Co-Re cemented carbides can be recycled and



**Fig. 6.** Microstructure of the WC-Co-Re cemented carbide (13.5 wt% Re + 9 wt% Co) containing inclusions of  $\eta$ -phase at a low carbon content: a– HRSEM image indicating a Co pool comprising round inclusions of  $\eta$ -phase and the corresponding Re:Co ratios (at.%) obtained by EDX, and b - light microscopy image with inclusions of  $\eta$ -phase (marked by arrows) having a yellow-brown color after etching in the Murakami reagent for 5 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

re-used many times. Thus, when taking into account the high price of Re, only an initial large investment is needed for the fabrication of HPHT components made of WC-Co-Re cemented carbides, which is thought to make their employment in the field of diamond and c-BN synthesis feasible. It is expected that using WC-Co-Re cemented carbides in HPHT components operating at extremely high pressures of the order of 15 GPa needed for obtaining diamond and c-BN by direct conversion without employing catalysts might be essential.

It should be noted that the Re to Co ratio of 60 wt% Re to 40 wt% Co

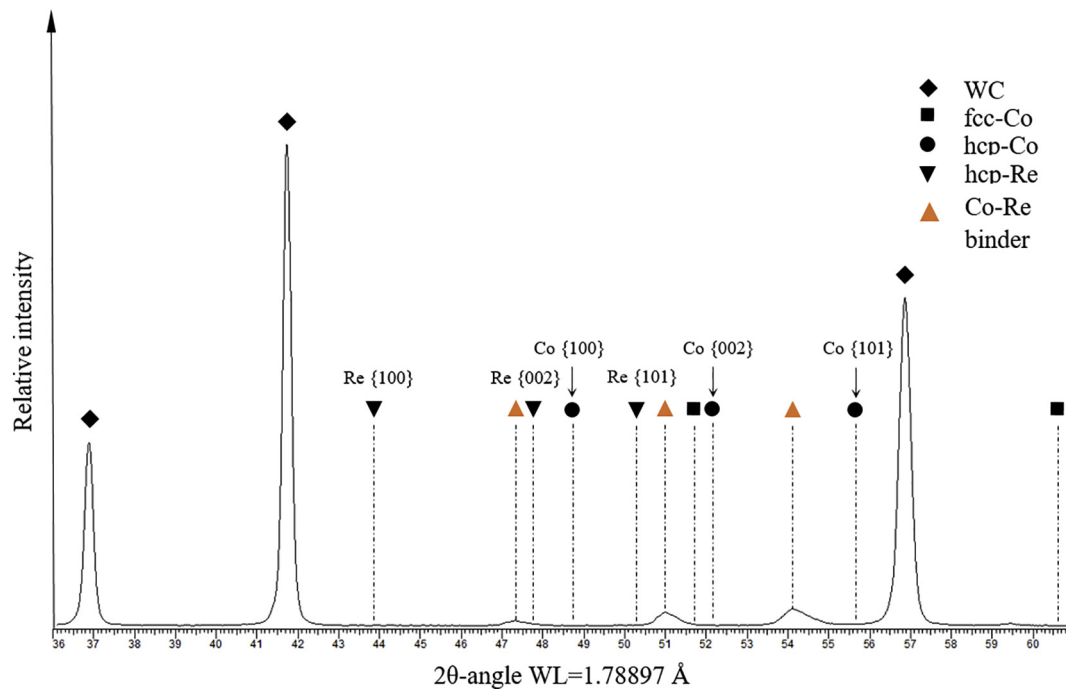


Fig. 7. Diffraction pattern of the WC-9wt%Co-13.5wt%Re cemented carbide.

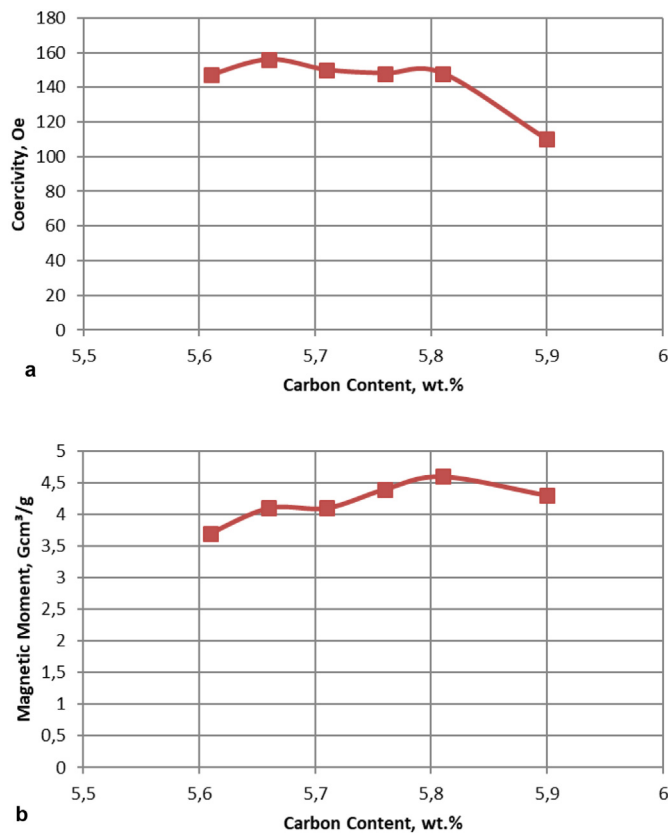


Fig. 8. Dependencies of a – magnetic coercivity and b - magnetic moment on the carbon content for the medium-grain WC-Co-Re cemented carbide containing 9 wt% Re and 6 wt% Co.

was mainly used in this study based on the results of Refs. [7, 8], in which different compositions of the binder phase (the Re to Co ratios) were examined. In particular, in Refs. [7, 8] it was established that at the Re to Co ratio of 60:40 the binder comprises only the hcp phase and

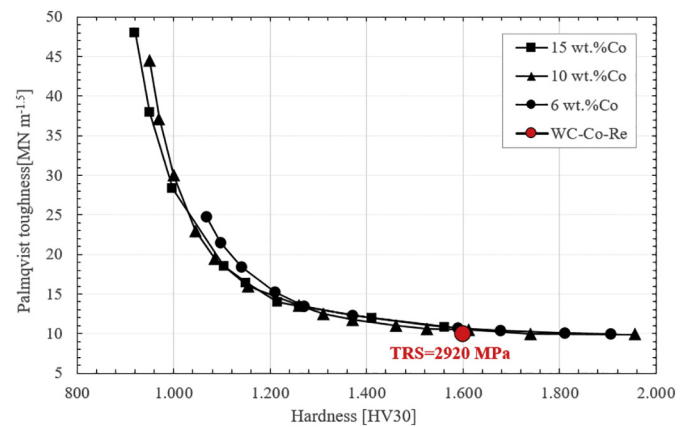


Fig. 9. The combination of hardness and fracture toughness of the WC-Co-Re cemented carbide (9 wt% Re + 6 wt% Co) in comparison with the baseline for conventional WC-Co cemented carbides according to ref. [17].

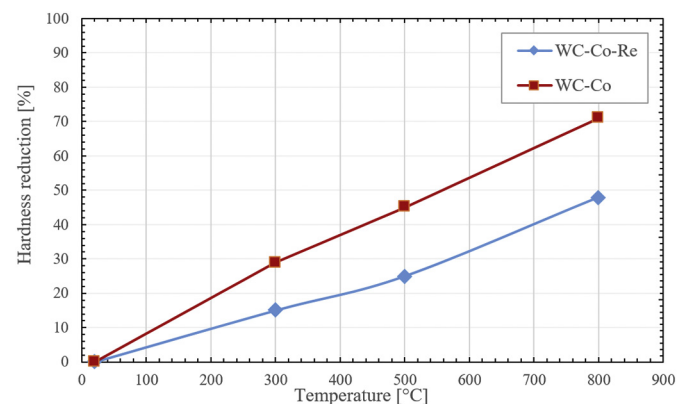
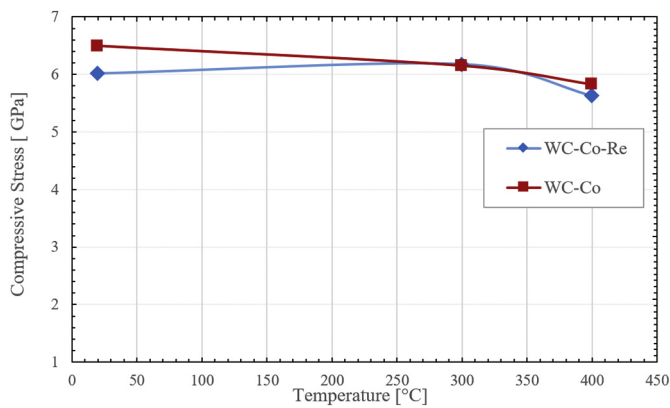
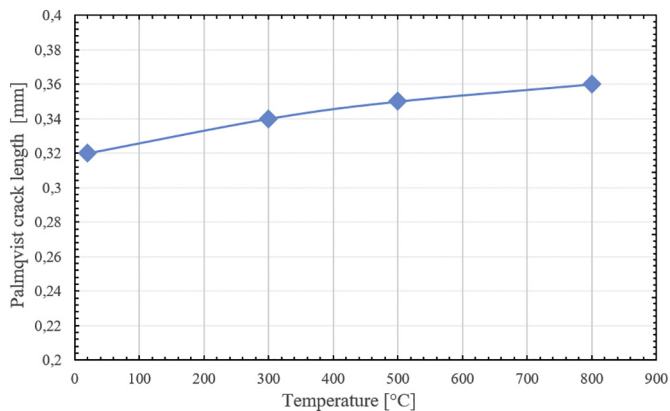


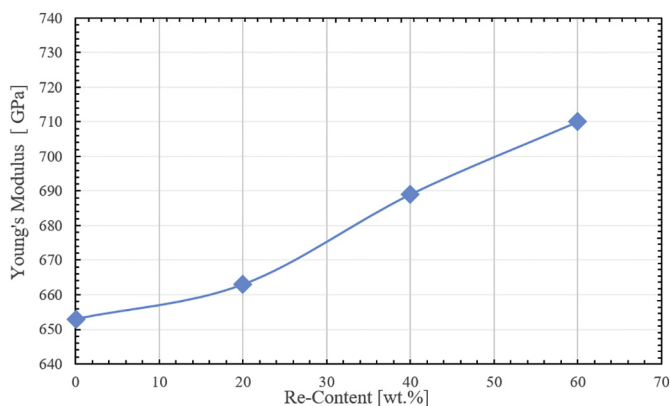
Fig. 10. Hardness reduction as a function of temperature of sub-micron WC-Co-Re cemented carbide containing 5.5 wt% Co and 3.7 wt% Re in comparison with conventional submicron cemented carbide with 6 wt% Co.



**Fig. 11.** Compression strength of the ultrafine WC-Co Re cemented carbide containing 5.5 wt% Co and 3.7 wt% Re in comparison with the conventional submicron grade with 6 wt% Co at room temperature and elevated temperatures.

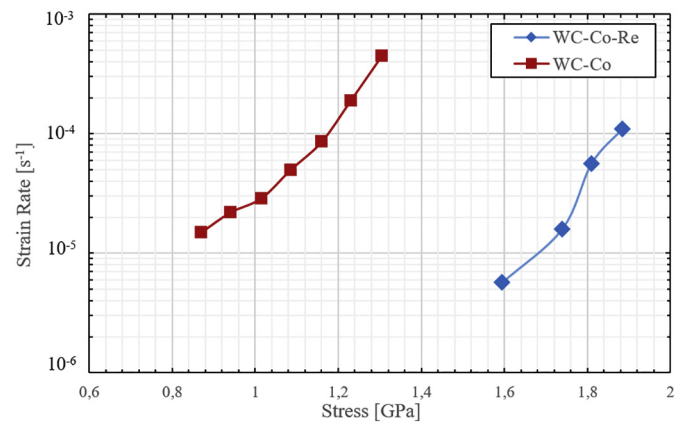


**Fig. 12.** Temperature dependence of the Palmqvist cracks' length for the sub-micron WC-Co-Re cemented carbide containing 5.5 wt% Co and 3.7 wt% Re.



**Fig. 13.** Young's modulus of WC-Co-Re cemented carbides as a function of the Re percentage in the binder phase.

the corresponding WC-Co-Re cemented carbides are characterized by the best combination of high-temperature TRS, hot hardness and performance in metal-cutting. The high Re additions of 60 wt% was found to be mandatory for the optimized high-temperature properties and performance in metal cutting. At lower Re to Co ratios the martensitic fcc to hcp transformation also occurs, but its rate is significantly lower. A solid-solution hardening effect is thought to be the major mechanism explaining the established improved high-temperature creep resistance. The other mechanism can be the suppression of grain boundaries' sliding at elevated temperatures, as Re is known to segregate at WC/Co



**Fig. 14.** Dependences of strain rates for the WC-Co-Re and WC-Co cemented carbides on the compression stress at a temperature of 800 °C.

grain boundaries [14]. The W solubility in the binder is not significantly influenced by Re additions, as the tungsten content measured in large Co-Re pools by EDX was found to be about 5 to 10 at.% at low carbon contents. This tungsten content is close to that in WC-Co cemented carbides with low carbon contents, so that the impact of carbon activity on the tungsten solubility in the Co-Re binders appears not to be significant.

It should be noted that another addition to WC-Co cemented carbides is known to be ruthenium (see e.g. [20,21]). The hardness of WC-Co materials with Ru additions is found to increase and toughness is found to decrease when increasing the ruthenium content leading to improved abrasion resistance of cemented carbides containing Ru. Nevertheless, there is no information in the literature on high temperature properties of cemented carbides containing Ru additions, so that it is not possible to evaluate whether additions of Ru would be useful for fabricating HPHT components. Also, it was established in Ref. [20] that adding even relatively insignificant amounts of Ru (3 wt% Ru to WC-10 wt% Co) resulted in a noticeable decrease of fracture toughness (up to 30%). Therefore, mechanical properties of cemented carbides containing Ru at room temperature appear to be inferior in comparison with those of cemented carbides containing large additions of Re.

It is well known that cutting tools for machining superalloys and other heat-generating workpiece materials are subjected to extremely high cutting temperatures [11]. When taking into account the significantly increased hot hardness of WC-Co-Re carbide grades, they can be effectively employed in machining Ni- and Co-based superalloys, which was established in Refs. [7, 11]. Another advantage of WC-Co-Re cemented carbides in this application is the possibility of their fabrication as submicron and ultra-fine grades without employing conventional WC grain growth inhibitors, as Re acts as a very strong grain growth inhibitor, which ensures obtaining cutting inserts with extremely fine and uniform microstructure.

#### 4. Conclusions

1. The W-Co-Re-C phase diagram noticeably differs from the W-Co-C phase diagram, which requires the need for the elaboration and optimization of special fabrication conditions for obtaining WC-Co-Re cemented carbides with suitable microstructure and properties.
2. Rhenium acts as a strong WC grain growth inhibitor suppressing the WC coarsening process, so that no additions of conventional grain growth inhibitors are needed in the fabrication of submicron WC-Co-Re grades with fine and uniform microstructure.
3. The Young's modulus, hot hardness and high-temperature creep resistance of the WC-Co-Re cemented carbides are noticeably greater than those of conventional WC-Co cemented carbides.

4. Potential applications of the WC-Co-Re cemented carbides are related to their significantly improved high-temperatures properties. Therefore, the cemented carbides with Co-Re binders can arguably be employed for HPHT components for diamond and c-BN synthesis, and cutting tools for machining superalloys and other heat-generating workpiece materials.

## Acknowledgment

This work was financially supported by the European Union's Horizon 2020 Research and Innovation Programme under the Flintstone2020 project (Grant Agreement No. 689279).

## References

- [1] T. Irifune, et al., Ultrahard polycrystalline diamond from graphite, *Nature* 421 (2003) 599.
- [2] N. Dubrovinskaya, et al., Superhard nanocomposite of dense polymorph of boron nitride: noncarbon material has reached diamond hardness, *Appl. Phys. Lett.* 90 (2007) 101912.
- [3] Mallory Metallurgical Products LTD, UK patent 622041, (1949).
- [4] I.N. Chaporova, V. Kudryavtzeva, Z. Sapronova, Sintered Cemented Carbide, SU616814, (1975).
- [5] Z. Sapronova, K. Chernjavskij, V. Zanozin, et al., Burden for Obtaining Sintered Hard Alloys, SU1783853, (1990).
- [6] I.N. Chaporova, Z.N. Sapronova, Investigation of the W-C-Re-Co System, Theory and Practice of Cemented Carbide Application, Moscow, 1991, pp. 12–15.
- [7] I.N. Chaporova, Z.N. Sapronova, et al., Mechanical and Performance Properties of the WC-Re-Co Cemented Carbides, Properties and Application of Cemented Carbides, Moscow, 1991, pp. 30–34.
- [8] I.N. Chaporova, V.N. Kudryavtzeva, Z.N. Sapronova, Investigation of Structure and Properties of Alloys of the W-C-Re-Co System, Quality and Effectiveness of Cemented Carbide Application, Moscow, 1984, pp. 7–9.
- [9] A.F. Lisovsky, N.V. Tkachenko, V. Kebko, Structure of a binding phase in Re-alloyed WC-Co cemented carbides, *Int. J. Refractory Met. Hard Mater.* 10 (1991) 33–36.
- [10] R.F. Havell, Y. Baskin, Rhenium-carbon-tungsten interactions, *J. Electrochem. Soc.* (108) (1961) 1068–1069.
- [11] D. Waldorf, M. Stender, S. Liu, D. Norgan, Alternative Binder Carbide Tools for Machining Superalloys, Proceedings of the International Conference on Manufacturing Science and Engineering, October 7–10, Evanston, Illinois, USA, 2008, pp. 1–9.
- [12] B. Roebuck, S. Moseley, Tensile and compressive asymmetry in creep and monotonic deformation of WC/Co hardmetals at high temperature, *Int. J. Refract. Met. Hard Mater.* 48 (2015) 126–133.
- [13] A. Petersson, Cemented carbide Sintering: Constitutive Relations and Microstructural Evolution, Royal Institute of Technology, Sweden, Stockholm, 2004 Ph.D thesis.
- [14] Yamaguchi Ryosuke, Okada Kazuki, Daito Masanori, Akiyama Kazuhiro, Cutting Tool Made from WC Based Cemented Carbide and Cutting Tool Made from Surface Coating WC Based Cemented Carbide which Exhibit Excellent Chipping Resistance in Cutting Work of Heat Resistant Alloy, JP2011–235410, (2011).
- [15] S. Lay, S. Hamar-Thibault, A. Lackner, Location of VC in VC, Cr<sub>3</sub>C<sub>2</sub> codoped WC-Co cermets by HRTEM and EELS, *Int. J. Refract. Met. Hard Mater.* 20 (2002) 61–69.
- [16] Xingwei Liu, Xiaoyan Song, Haibin Wang, Xuemei Liu, Fawei Tang, Hao Lu, Complexions in WC-Co cemented carbides, *Acta Mater.* 149 (2018) 164–178.
- [17] B. Roebuck, M.G. Gee, R. Morrell, Hardmetals – microstructural design, testing and property maps, in: G. Kneringer, P. Rödhammer, H. Wildner (Eds.), Proceedings of the 15th International Plansee Seminar, vol. 4, Plansee Group Reutte, Austria, 2001, pp. 245–266.
- [18] I. Konyashin, Cemented carbides for mining, construction and wear parts, in: V. Sarin (Ed.), Comprehensive Hard Materials, Elsevier Science and Technology, 2014 Editor-in-Chief.
- [19] I. Konyashin, B. Ries, Cemented Carbide Material and Method of Making Same, PCT Patent Applications, (2014) (WO2014/122306A2).
- [20] T.L. Shing, S. Luyckx, I.T. Northrop, I. Wolff, The effect of ruthenium additions on hardness, toughness and grain size of WC-Co, *Int. J. Refractory Met. Hard Mater.* 19 (2001) 41–44.
- [21] J.H. Potgieter, N. Thanjekwayo, P. Olubambi, et al., Influence of Ru additions on the corrosion behaviour of WC-Co cemented carbide alloys in sulphuric acid, *Int. J. Refractory Met. Hard Mater.* 29 (2011) 478–487.