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Changes in Structure and Corrosion Resistance of Cryogenically Treated WC-Co Cemented Carbides

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Abstract: The aim of this study was to evaluate changes in the corrosion resistance and microstructure of deeply cryogenic treated (DCT) cemented carbides (CC). Changes in corrosion resistance were determined by potentiodynamic testing in artificial mine water. Microstructural changes were characterized using X-ray diffraction analysis. Four sorts of WC-Co cemented carbides with different WC grain sizes and volume fractions of cobalt binder were used for the experiment. Specimens were divided into two groups. The first group of specimens was deeply cryogenic treated (DCT) at -186°C in dry liquid nitrogen vapor. The second group of specimens was tempered at 450°C. The results of the experiments show that DCT increased the amount of ϵ -Co in all the types of CC compared to the tempered group of specimens. This microstructural change and a change in the micro-stresses in the surfaces of the specimens contributed to increasing the corrosion resistance of CC after DCT.

Keywords: WC-Co, Cemented carbides, Deep cryogenic treatment (DCT), Corrosion resistance, Transformation of cobalt.

1. Introduction

Cryogenic treatment is generally understood as bringing a material to a temperature deep below *its* freezing point in order to improve its properties. Temperatures this low are the subject of cryogenics. Cryogenics is a science and engineering discipline which explores temperatures lower than 120 K [1], although this temperature limit is not accepted by all researchers and a number of other temperature thresholds are mentioned in the literature.

A treatment which involves exposing a material to a temperature below freezing point was first explored using dry ice (solid carbon dioxide) at temperatures of approx. -79 °C (the sublimation temperature of dry ice is -78.5 °C). In some materials, this treatment considerably improves wear resistance. Understandably, the next step involved using liquid nitrogen at temperatures down to -196 °C (its boiling point is -195.80 °C). Treatment at the boiling point of liquid nitrogen brought further improvement in some properties. Additional improvements could be expected at -269 °C in liquid helium (boiling point: -268.9 °C). At these low temperatures, the movement of atoms is slow, and the process would thus take an extremely long time, becoming financially unviable [2].

In literature, cryogenic processes are often classified according to their temperature. Temperatures from -80 °C down to -150 °C are used in shallow cryogenic treatment (SCT), whereas the range from -



150 °C to -196 °C is called deep cryogenic treatment (DCT). However, the reported ranges vary. This concerns primarily the limit of -150 °C, with alternatives ranging from -140 °C to -160 °C [3-5]. Conventional deep freezing, such as the treatment of tool steels with CO₂, does not qualify as cryogenic treatment.

Deep cryogenic treatment (DCT) is a type of heat treatment which involves gradual cooling to very low temperatures. When liquid nitrogen is used as the cooling environment, the material is cooled close to -196 °C. This procedure, as well as the subsequent tempering which sometimes follows, causes changes in the microstructure which can improve the material's utility properties. These properties may include wear resistance, fracture toughness, hardness, and corrosion resistance [6-8]. DCT is typically used for tool steels where it can reduce the amount of metastable retained austenite in their martensitic microstructure [6]. Furthermore, DCT alters the distribution and morphology of carbides which are ordinarily found in these steels [6]. The use of DCT for treating WC-Co cemented carbides is not yet widely-known.

Cemented carbides (CC) are particle-reinforced composites. They are best known as materials for exchangeable cutting inserts. As a result, there is a body of literature on assessing the impact of DCT on the life and wear of tools used for machining various engineering materials. The DCT process is reported to improve the wear resistance of the tool flank by 21.2% and to extend the tool life by 11%, 17% and up to 38%, depending on the machining parameters [7-9]. Much like in steels, microstructure evolution is behind the changes in the properties of cemented carbides. The improvement in their wear resistance is typically attributed to martensitic transformation of cobalt. DCT causes high-temperature α -Co phase with FCC lattice to transform to ϵ -Co with HCP lattice which is stable at temperatures below 422°C [10,11]. Hence, the ultimate change in their properties which occurs after DCT depends on the ratio of α -Co to ϵ -Co. Other microstructural changes which may be induced by DCT and which alter wear resistance and other properties of cemented carbides include the precipitation of fine η -phase or changes in the morphology and the refinement of α -phase, as reported by some authors [12]. All these changes are then manifested in residual stress levels. Yong J and Ding C [13] claim that DCT affects compressive residual stress in the material, depending on the processing time.

An important property dictated by the microstructure which has not received adequate attention in earlier studies is the corrosion resistance of cemented carbides. The mechanism of corrosion in cemented carbides is often electrochemical [14]. In this process, the Co binder acts as the anode, which gradually dissolves. The carbide grains become the cathode, and the environment acts as the electrolyte. The solubility (stability) of the binder in a corrosive environment plays a decisive role in the corrosion resistance of cemented carbides. The stability of the binder depends on its chemical and phase composition. Besides the binder properties, the corrosion resistance of cemented carbides depends on the volume fraction of binder in their microstructure and on the size of the tungsten carbide grains (α -phase) [15].

This study evaluates the impact of DCT on the corrosion resistance of several types of cemented carbides with differently sized tungsten carbide (WC) grains and different volume fractions of the cobalt (Co) binder. The corrosion resistance of the cemented carbides was measured in a potentiodynamic test in artificial mine water. The specimens were examined using X-ray diffraction analysis to identify any microstructural changes caused by DCT. The results were then compared with the data for the tempered specimens. There were two reasons for this step. First, to compare the DCT-treated CC structures with those obtained by ordinary heat treatment – since ordinary heat treatment reduces residual stresses, for instance. Second, to compare the outcome of tempering alone with a combined DCT and tempering process.

2. Experimental material and parameters

Four types of WC-Co cemented carbides were chosen for the experiment, as shown in table 1. They differed in the volume fraction of the binder and in the grain size of the alpha phase.

Their corrosion resistance in artificial mine water was determined by potentiodynamic testing in a Biologic SP-150 potentiostat. The three-electrode configuration uses a calomel reference electrode and

a platinum wire. The chemical composition of this corrosion environment is summarized below, see table 2. The pH of the environment was 5, measured using a conventional pH tester.

Table 1. Structures and properties of the cemented carbides under investigation [16].

Cemented carbide	Co content (wt. %)	WC grain size (μm)	HV30	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
C15	15	$>6 \mu\text{m}$	960	22.0
C10	10	$>6 \mu\text{m}$	1120	18.0
F15	15	$0.5\text{-}0.8 \mu\text{m}$	1320	11.9
F10	10	$0.5\text{-}0.8 \mu\text{m}$	1590	10.1

Table 2. Chemical composition of the artificial mine water.

Compound	Concentration (mg/l)
Na_2SO_4	1237
CaCl_2	1038
MgSO_4	199
NaCl	1380

The specimens were examined using X-ray diffraction in an X'Pert Pro automatic powder diffractometer. The X-ray source had a copper anode and a wavelength of $\lambda_{\text{Cu}\alpha 1} = 0.15405980 \text{ nm}$. All specimens were measured using an identical procedure. The measuring range was from 30 to $125^\circ 2\theta$. The irradiated area was $20 \times 20 \text{ mm}$. The phases present in the specimens prior to heat treatment were identified based on the diffraction lines and ICDD PDF2 standards. The parameters of the treatment which was carried out after characterization of the initial condition of the specimens are summarized below in table 3. Standard test parameters which are used for processing steels were used for DCT of the CC specimens. The actual process of DCT on the samples was performed using the cryogenic chambers at the European Cryogenic Institute, s.r.o., see figure 1. The tempering process parameters were chosen to avoid significant oxidation of the surfaces of the specimens during tempering. This process was performed using a laboratory chamber furnace in the Department of Material Science and Technology at UWB. The heat treatment was followed by another series of X-ray diffraction measurements and corrosion tests to identify the differences between the initial and final conditions. The post-heat treatment X-ray analysis was performed using the same parameters as the preceding ones.



Figure 1. Equipment for cryogenic processing at the European Cryogenic Institute [17].

Table 3. Characterization of heat treatment procedures.

Heat treatment	Temperature (°C)	Holding time (min)
DCT	-186	480
Tempering (T)	450	120

3. Results and discussion

Table 4 gives a summary of the results of the potentiodynamic testing of corrosion resistance. The values given in this table are the average values from two measurements made on each of the analyzed samples. In all DCT specimens, the corrosion resistance in the testing environment increased after DCT. In the tempered specimens, this only occurred in F10 and C15 types.

Table 4. Results of potentiodynamic testing. Initial state (IS), tempered (T) post-DCT (DCT).

Sample	E _{corr} (V)	Corrosion rate (mmpy)	R _p - Polarization resistance (Ω·cm)
F10_DCT	-0.159	2.09E-06	1.54E+05
F15_DCT	-0.205	2.21E-06	1.19E+05
F10_T	-0.156	1.31E-05	1.76E+04
F10_IS	-0.276	2.78E-05	7.50E+03
C10_DCT	-0.319	2.99E-05	4.77E+03
C10_IS	-0.383	3.97E-05	4.00E+03
F15_IS	-0.311	3.98E-05	1.07E+04
F15_T	-0.363	5.37E-05	4.44E+03
C15_T	-0.406	6.12E-05	3.74E+03
C15_DCT	-0.306	6.68E-05	1.16E+04
C10_T	-0.368	7.19E-05	3.81E+03
C15_IS	-0.352	8.40E-05	2.10E+03

The data in table 4 is in agreement with other studies: fine-grained CCs with less binder exhibit a higher corrosion resistance in this particular environment [15,18]. Neither the subsequent deep cryogenic treatment nor tempering had an impact on this. However, the heat treatment did affect the microstructure of the specimens.

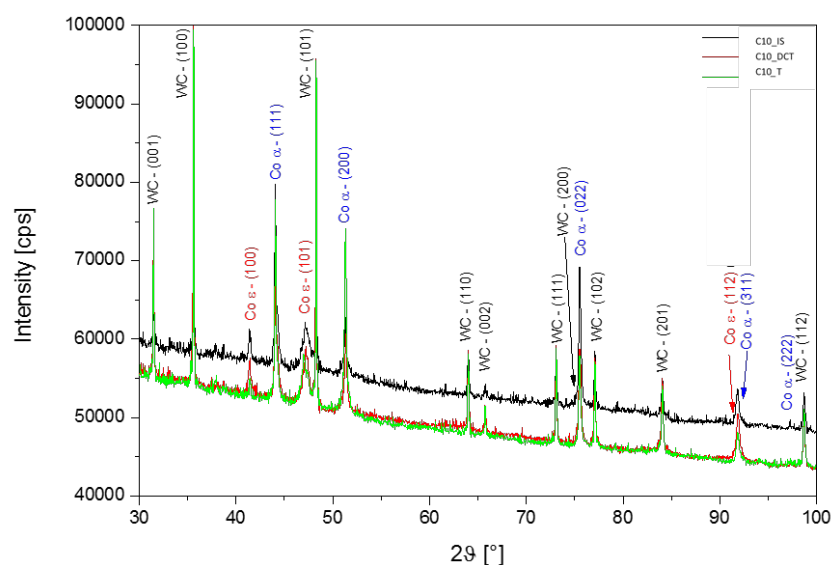
**Figure 2.** Phase composition of a coarse-grained cemented carbide with 10% Co by weight, in the initial state (IS), after tempering (T) and after deep cryogenic treatment (DCT).

Figure 2 illustrates the phase composition of a fine-grained cemented carbide (C10) with a low volume fraction of Co. Higher background readings in the IS specimen (initial state) are due to the poorer homogeneity of the material. However, the subsequent heat treatment improved homogeneity and reduced the background signal.

There are reports [19,20] that DCT, and sometimes tempering, lead to the formation of η -phase in the cemented carbide. This phase has an impact on the wear resistance, hardness and possibly on the fracture toughness of cemented carbides. In this case, as in an earlier study by the authors [21], this phase was not found in the microstructure of the cemented carbides. The fact that it did not form is probably related to the heat treatment conditions. The formation of this phase depends on both the distribution of the elements in the Co binder and the method of cooling from the heat treatment temperature. Furthermore, tempering took place at a lower temperature, which further suppressed the formation of the η -phase. However, X-ray diffraction analysis provided evidence of the changes caused by DCT in the binder, as indicated in table 5.

Table 5. Changes in the fractions of Co binder phases prior to and after heat treatment.

Specimen	Co - α (vol. %)	Co - ϵ (vol. %)
C10_IS	72.70	27.30
C15_IS	69.44	30.56
F10_IS	93.87	6.13
F15_IS	79.17	20.83
C10_DCT	43.45	56.55
C15_DCT	55.39	44.61
F10_DCT	57.23	42.77
F15_DCT	59.03	40.97
C10_T	71.40	28.60
C15_T	75.52	24.48
F10_T	94.61	5.39
F15_T	67.42	32.58

The readings show that DCT caused an increase in the amount of ϵ -Co. The largest increase was recorded for the F10 cemented carbide which had the highest corrosion resistance after DCT. In the tempered CC types, this was only detected in some specimens. The literature [22] indicates that a larger volume fraction of ϵ -Co improves wear resistance because this HCP phase has a higher hardness than α -Co with FCC structure. The reason for the relatively larger amount of α -Co in the initial cemented carbide is its stabilization during sintering. In the course of the process, the surface of the WC grains gradually dissolves in the Co binder which at that time consists of α -Co phase. Consequently, the binder (particularly in the vicinity of WC grains – and depending on their size and the binder fraction) does not consist of pure Co but comprises a multiphase system whose corrosion resistance depends on the ratios of the dissolved constituents [15]. Martensitic transformation during DCT is then governed by this ratio of constituents dissolved in α -Co. Martensitic transformation affects the micro-stresses which are generated by transformations taking place during DCT or during tempering, see figure 3.

The graphs in figure 3 show that the transformation of α -Co to ϵ -Co during DCT increases the compressive micro-stresses in the surfaces of the specimens. Their levels decrease as the distance increases from the surface. The data show that these stresses equalized greatly due to DCT. In tempered specimens, the compressive stresses declined.

Changes caused by heat treatment affected the size of the crystallites of the dominating alpha phase (WC), as seen in figure 4. DCT reduced and equalized the size of crystallites in coarse-grained specimens (C). This was due to the reduced coherence of the diffraction planes. In specimens with fine-grained WC (specimens F), the process had the opposite effect. The size of the crystallites increases in

the first half of the graph. This applies to the specimen with 10% Co. The impact on the change in the crystallites was the smallest in the specimen with 15% Co. In the tempered specimens, the size of the crystallites increased in all cases.

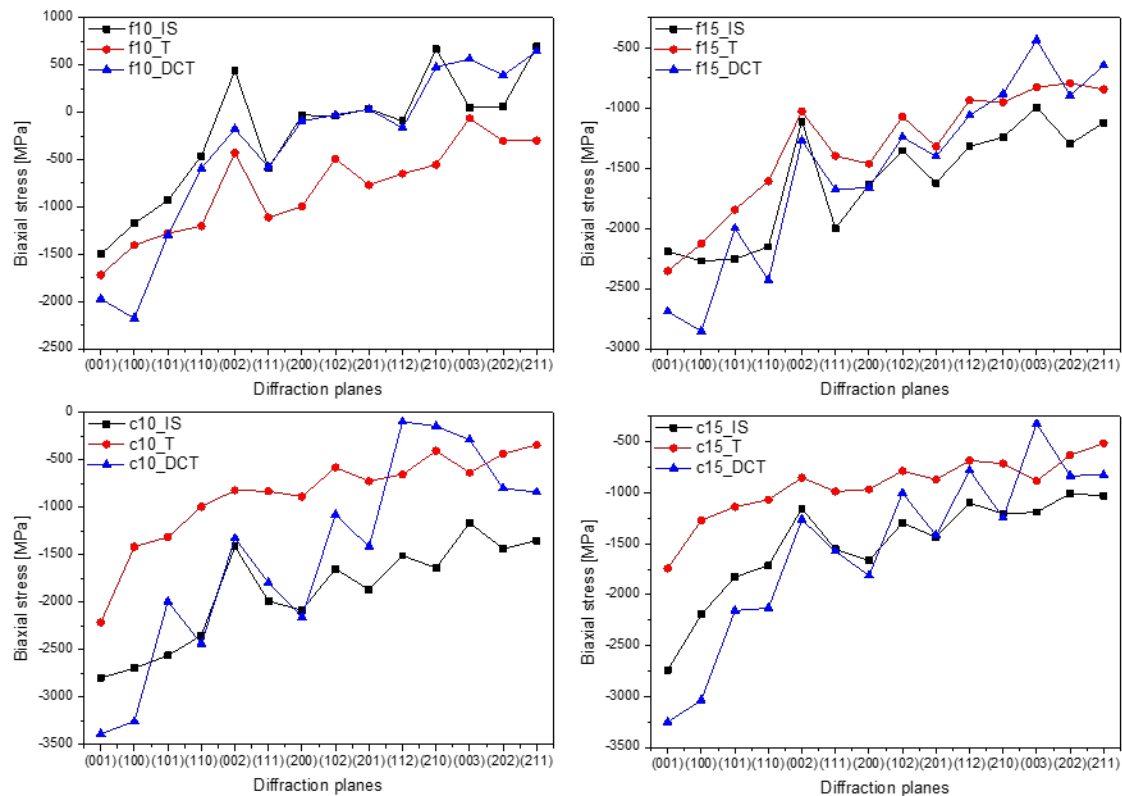


Figure 3. Micro-stresses in the initial state (IS), after tempering (T) and after deep cryogenic treatment (DCT).

4. Conclusion

The results presented in this study support the claim that DCT causes a phase transformation and an increase in the proportion of the ϵ -Co phase in the structure of CC, similar to that mentioned in [22]. Due to this transformation and the change in the size of the crystallites of the alpha phase, there is an increase in the applied pressure micro-stresses, which, as mentioned in [13], occurs during the DCT process. The change in the acting micro-stresses caused by the martensitic transformation in the Co binder then to a large extent affects the corrosion resistance of the CC structure. An increase in corrosion resistance after DCT treatment was found by potentiodynamic testing. In contrast, after tempering, a decrease in the applied micro-stresses was observed as expected. Separate tempering of samples without prior DCT processing did not cause the formation of η -phase in the structure of the samples. In samples that were tempered after the DCT process, η -phase was formed, see [20]. All the results obtained can then be summarized as follows:

- DCT improved corrosion resistance in the selected environment for all types of CCs, beyond the level found in the initial condition and after tempering.
- The slowest corrosion rate was found in specimens with fine-grained WC and a low volume fraction of cobalt.
- In post-DCT specimens and those after tempering, X-ray diffraction analysis found no η -phase.
- DCT changed the ratio of α -Co to ϵ -Co. In all specimens under analysis, the DCT-induced martensitic transformation increased the ϵ -Co volume fraction.

- After DCT, micro-stress in the surfaces of specimens increased in all the CC types, when compared to the initial condition as well as to the tempered condition (which experienced a reduction in compressive stress).
- DCT led to changes in the size of alpha-phase crystallites. In fine-grained CCs and in tempered specimens, the crystallite size increased. In coarse-grained CCs, the crystallite size decreased.

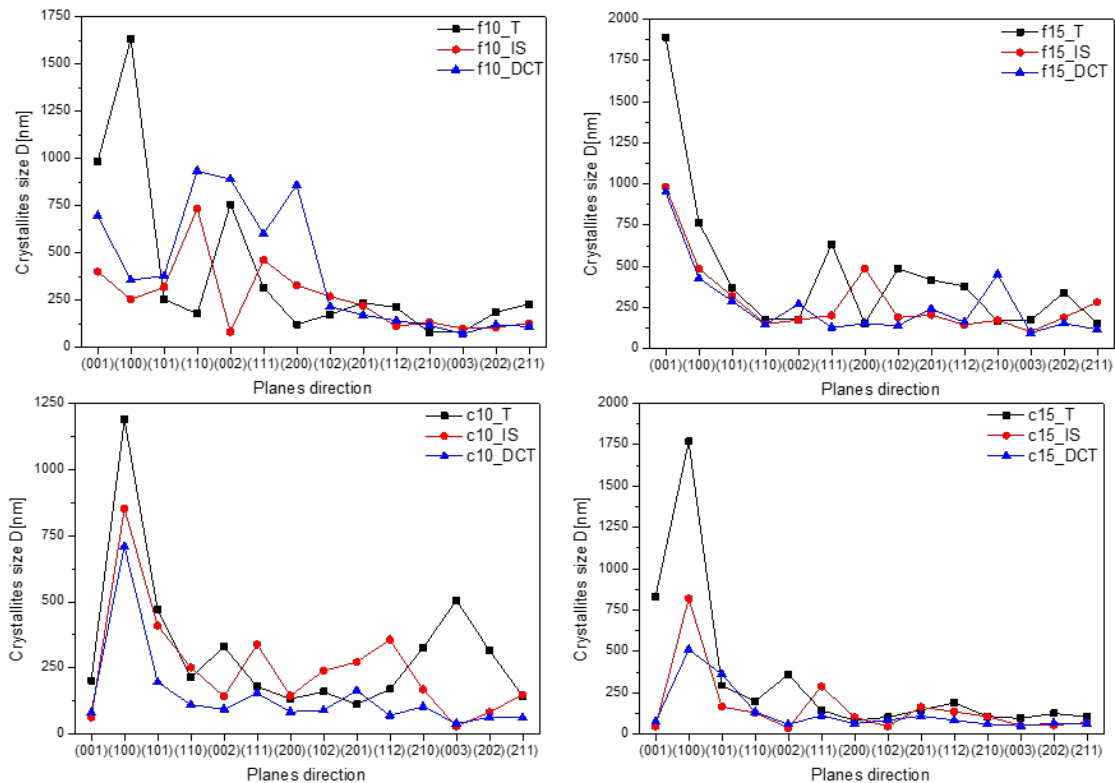


Figure 4. Changes in crystallite size of the dominating α -phase: in the initial state (IS), after tempering (T) and after DCT.

Cryogenic treatment of cemented carbides has favorable effects on their corrosion resistance, mainly due to phase transformation of the binder, and the resulting residual stress which increases the level of activation energy required for corrosion to occur. In future experiments, methods for identifying the microstructural phase in DCT-treated cemented carbides will be explored by testing various etching procedures and diffraction. Further experiments will involve tempering after DCT.

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