INFLUENCE OF CHROMIUM AS CARBIDE FORMING DOPING ELEMENT ON THE DIAMOND RETENTION IN DIAMOND TOOLS

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ABSTRACT

Diamond tools are widely used in drill tools, wire saws or circular saws to machine very hard materials such as concrete or natural stone in the construction as well as extractive industries. The mechanical and physical properties, such of these materials call for high requirements concerning the diamond tools. In particular, the bonding between the diamond particles and the metallic binder is an essential criterion for the tool quality. It is known that the type and strength of bonding is influenced by the diamond-metal interaction that occurs during the sintering process. Depending on the element used as a metallic binder, different thermally induced chemical reactions between the diamond and the metallic matrix take place. These reactions are (1) carbide formation, (2) graphite formation, and (3) inert behavior. However, there is still a high demand concerning the research of the diamond-metal interaction influenced by a carbide forming element.

In this work, chromium as a carbide-forming element was used as a doping agent in order to increase the diamond retention in diamond tools. The elements iron, cobalt and nickel were selected as single metallic components due to their catalytic influence on the graphitization of diamonds; whereas three metallic matrix systems were additionally doped with 15% chromium. The samples were sintered by hot pressing. Furthermore, half of the samples were thermally treated in order to ensure a stronger thermal induction of the interfacial reactions. In order to analyze the bonding behavior of the diamonds in the metal matrix, the samples were broken and the interfacial area was analyzed by means scanning of electron microscopy. These experimental studies show an influence of the carbide-forming doping agent on the diamond-metal interaction.

KEYWORDS

Diamond tools, interface reactions, diamond retention, diamond-metal composites, metal diamond interface, SEM - analyses

1. INTRODUCTION

The unique combination of properties makes diamonds attractive for numerous applications. Besides their extreme hardness, diamonds are also characterized by their high thermal conductivity and low thermal expansion as well as by their chemical resistance to most materials. Due to these properties, diamonds are a popular cutting material and widely used for materials processing in the industry [1]. The machining of concrete or natural stone places high demands on the cutting tool. These demands are fulfilled by diamond impregnated cutting tools on the basis of metal matrix composites such as drill bits, wire saws or circular saws [2] [3]. Thus, diamonds provide an abrasive effect on the workpiece, while the metal matrix ensures an optimal diamond bonding and assures an ideal grain protrusion [4]. Furthermore, diamond impregnated tools provide a self-sharpening behavior as new diamonds are gradually exposed to the surface of the segment simultaneously to the metal matrix wear [5].

Generally, powder metallurgical production techniques are used and well established to fabricate diamond grinding segments. Vacuum sintering and hot pressing processes belong to these procedures and are mainly used for the batch production of diamond impregnated cutting tools. The vacuum sintering process consists of two successive steps: cold pressing and sintering, while the hot pressing process combines compaction and sintering in one step at lower temperatures. Furthermore, hot pressing requires a shorter process time and achieves higher density values and is therefore the widely used technique to manufacture diamond segments in the diamond tool industry [3].

However, tool performance strongly depends on the bonding between the diamond particles and the metallic binder, which in turn is influenced by the sintering parameters as well as by the alloying system of the metal matrix. On the one hand, the sintering parameters, in particular the temperature and time influence the bonding between the diamond particles and the metal matrix component negatively as the degradation of the diamonds into the graphite is thermally induced. However, the degradation can be inhibited by hot pressing due to the lower temperature and shorter process time required. On the other hand, the metallic binder has an influence on the diamond-metal interaction because of the carbon reactivity of its components. Furthermore, the chemical composition of the metallic binder has an influence on the interface between the diamond and the metal matrix. It is known that the carbon reactivity of transition metals in the 4th period of the periodic table increases with its number of electron vacancies in d-orbitals. Elements with fully assigned d-orbitals (e.g. Cu, Zn) are inert to carbon, while elements with minor occupied d-orbitals (e.g. Cr, Ti) are carbide formers. However, elements with medium occupied d-orbitals (e.g. Co, Fe) show a catalytic effect on carbon [7] [8]. In addition, carbon reactivity of binder metals in diamond-metal composites has been verified by means of scanning electron microscopy and X-ray diffraction in a recent work [9]. It was observed that diamond degradation is linked with the formation of graphite and can be reduced by using elements with minor occupied d-orbitals. Furthermore, the formation of a carbide layer on the diamond surface was only induced by chromium.

As a consequence of the chemical reactivity of the metal matrix composites, three different bonding behaviors between diamond and metal were observed in previous investigations: (1) carbide formers induce a carbide formation and cause a strong bonding between carbon and metal; (2) elements with a catalytic effect on carbon lead to graphitization and diamond degradation occurs. The diamond retention is debilitated due to the graphite layer on the diamond surface; (3) an inert behavior takes place when no chemical reaction occurs, leading to a mechanical bonding of the diamond within the metallic binder.

It is therefore expected that the tool performance improves and the diamond retention is strengthened when doping the metal matrix with carbide forming metals. It was already observed that a reduction of the graphitization and an intensification of the carbide formation take place when metallic binders such as Fe, Co or Ni were doped with the carbide-forming element Cr [10]. This behavior is influenced by the formation of the chromium carbide structures Cr_3C_2 and Cr_7C_3 [9, 10]. In Fe or Co metallic binders, the amount of graphite decreases with an increasing Cr content, while a reduction of the graphitization in Ni matrix systems only occurs with a 15 % Cr content [10]. However, a correlation between the diamond-metal-interaction and the diamond bonding has not been investigated yet, although the diamond retention is an important criterion for the tool performance. For this reason, it was the aim of this work to analyze the influence of the metal matrix components on the bonding behavior of diamonds.

2. EXPERIMENTAL PART

2.1 Hot pressing of diamond impregnated segments

In order to investigate the influence of the metal matrix composition on the diamond bonding behavior, four diamond-metal powder mixtures were used. The elements Fe, Co, as well as Ni were selected as single metallic components due to their catalytic influence on the graphitization of diamonds. Furthermore, the three metallic components were additionally doped with 15 mass% of Cr as carbide forming element. The metal matrix compositions were pre-mixed with 10 vol-% synthetic diamonds (SDB1055: 40-50 mesh). An overview of all diamond-metal-composites used in this work is listed in Table 1.

Table 1: Composition of diamond-metal-composites used

Matrix system	Metallic element [mass%] (grain size) Fe (2,5 µm)	Co (0,9 µm)	Ni (5 µm)	Cr (45 µm)	Diamond content [vol.%]
Fe	100	-	-	-	10
FeCr	85	-	-	15	10
Co	-	100	-	-	10
CoCr	-	85	-	15	10
Ni	-	-	100	-	10
NiCr	-	-	85	15	10

The diamond-powder-mixtures were sintered by the use of a hot press (Dr. Fritsch CSP 100, Germany). All diamond segments were sintered at a pressure of 136 bar for 180 s at a maximum temperature of 1100 °C in an atmosphere consisting of nitrogen. The two component metal matrices were sintered at the same temperature in order to analyze the effect of the carbide forming element on the diamond retention with the same conditions as the single component metal matrices.

2.2 Thermal post-treatment

A thermally induced graphitization as well as a correlated degradation of diamonds might not occur due to the short processing time during hot pressing according to the Arrhenius equation which describes the temperature dependencies of chemical reactions. In order to ensure a thermally induced chemical reaction between the diamond-metal-interface, half of the hot pressed diamond segments were subsequently thermally post-treated. For this purpose, all diamond segments were heated in a vacuum furnace (Leybold Torvac, Germany) at 1100 °C for 120 min. The heating process with its heating rates and holding periods are visualized in Fig. 1.

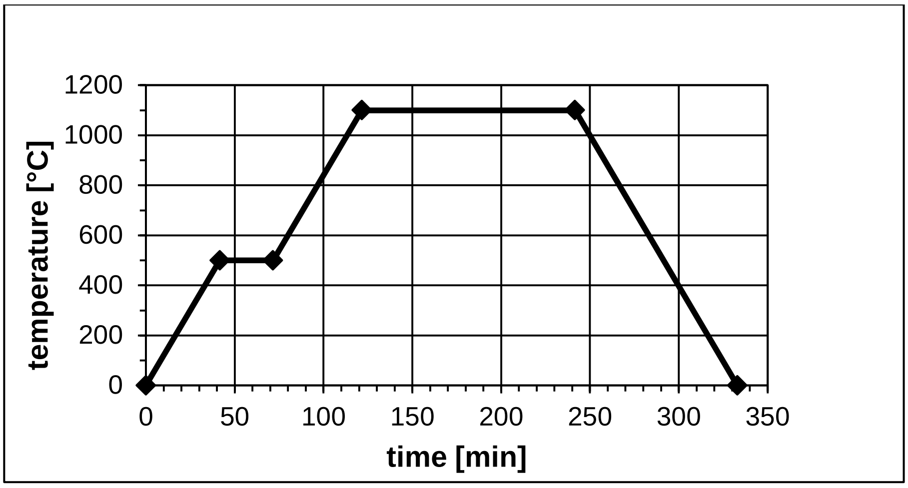

Fig. 1: Heating process of the post-treatment

2.3 SEM investigations

In order to analyze the diamond retention, the diamond segments were mechanically broken and SEM investigations of the both fractured surfaces were performed. All samples were coated with a thin layer of gold to ensure a good image quality of the electrically nonconductive diamonds. Scanning electron micrographs were realized by means of a field emission SEM (Jeol JSM-7001F, Japan). Fig. 2 shows exemplary both fractured surfaces of a Fe diamond segment after being mechanically broken.

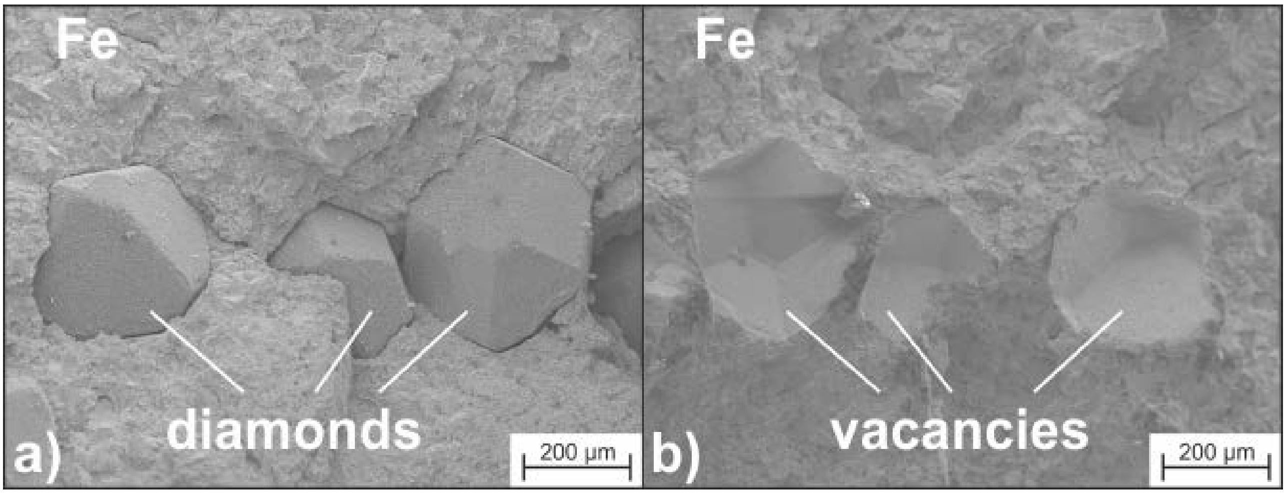

Fig. 2: Fractured surfaces of hot-pressed Fe-based diamond segments

3. RESULTS AND DISCUSSION

3.1 Hot pressed diamond segments

Fig. 2 and Fig. 3 show the fractured surfaces of Fe- and Co-based diamond segments. The diamonds are completely pulled out of the matrix and remain bonded on one site of the fragment. The counterpart shows the vacancies where the diamonds were bonded before. Furthermore, the diamond particles are not fully embedded as they are partially unattached due to a small gap between the diamond and the matrix. The reason for this behavior can be explained by a slight diamond degradation, which is clearly visible on the close up of the diamond surface as presented in Fig. 4 (a) and (b) for both metallic matrices. The damage to the diamond structure is mainly observed at the corners and edges of the diamonds.

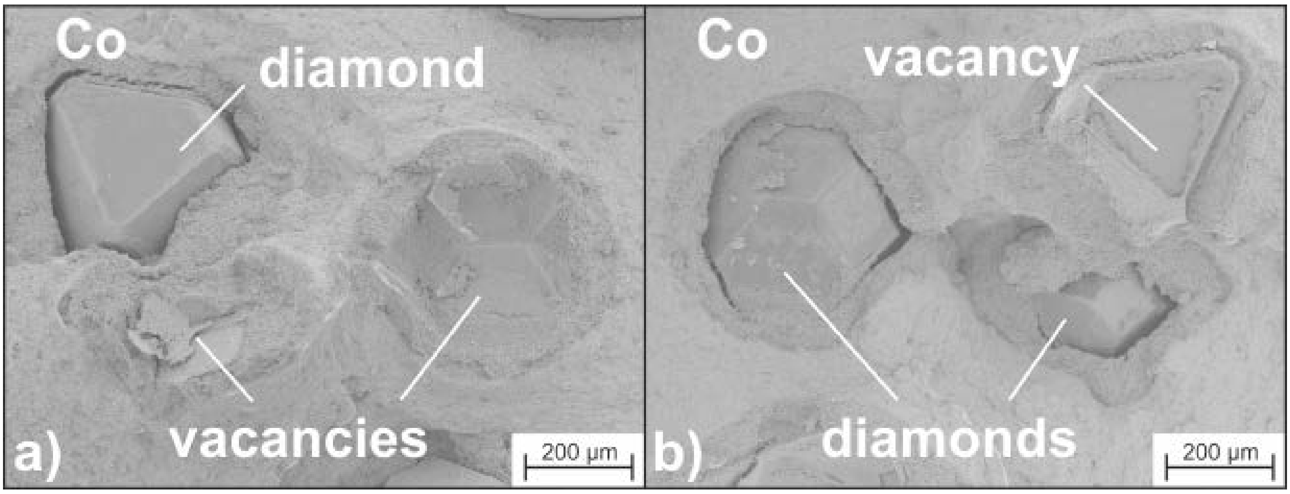

Fig. 3: Fractured surfaces of hot pressed Co-based diamond segments

The hot pressed Ni diamond segments expose a similar bonding behavior as the Fe- and Co-based samples. After being mechanically broken, the diamonds remain entirely embedded on one side of the fragment while the vacancies are visible in the counterpart. A slight formation of graphite on the diamond surface can also be observed in Fig. 4 (c). As a consequence, diamond grains are not completely mechanically bonded due to the graphite layer and a small gap between the diamond-metal-interface.

Even if the short process time of the hot pressing process should inhibit a diamond degradation, a slight diamond degradation occurred by using Fe-, Co- and Ni-based metal matrices due to their catalytic effect on carbon. Besides a minor degradation on the diamond surface, mainly the corners and edges were damaged. Therefore, the diamond particles are not fully embedded into the metallic binder, but rather detached to a certain degree as a result of the graphite layer.

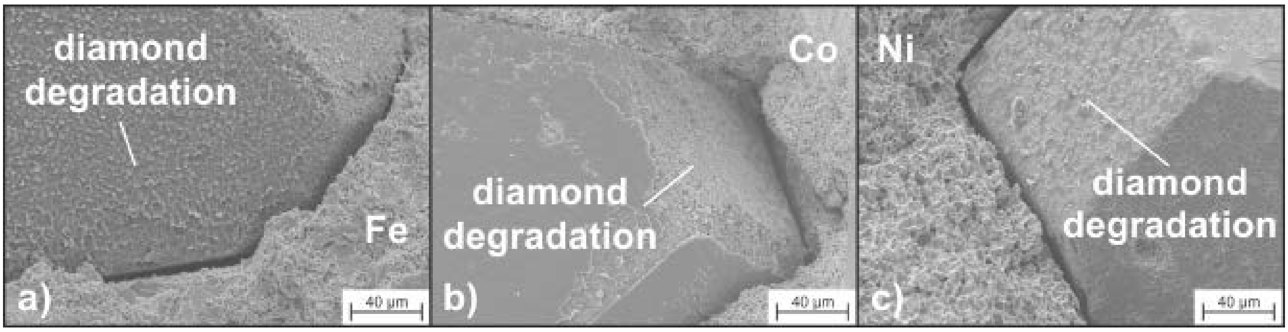

Fig. 4: Close-up of the diamond-metal-interface of hot pressed (a) Fe-based diamond segments, (b) Co-based diamond segments, and (c) Ni-based diamond segments

However, the diamond retention is strengthened by the addition of Cr to the Fe- and Co-based matrix as shown in Fig. 5 and Fig. 6, respectively. Although the diamond segments were broken, the diamonds remain embedded in their position and fractured across the fracture area. The remaining diamond fragment is also fixed tightly in the counterpart of the segment. Still, a few diamond particles of the Fe samples are not fractured but rather surrounded with a layer and bonded to the metallic matrix of the fractured surface, as visible in Fig. 5. A close-up of the diamond-metal-interface of FeCr- and CoCr-based samples reveals that the diamonds are completely surrounded by the binder, as shown in Fig. 7 (a) and (b). This bonding behavior indicates an improved embedding. This is due to the reduction of graphitization and an intensification of the carbide formation induced by the addition of Cr [9].

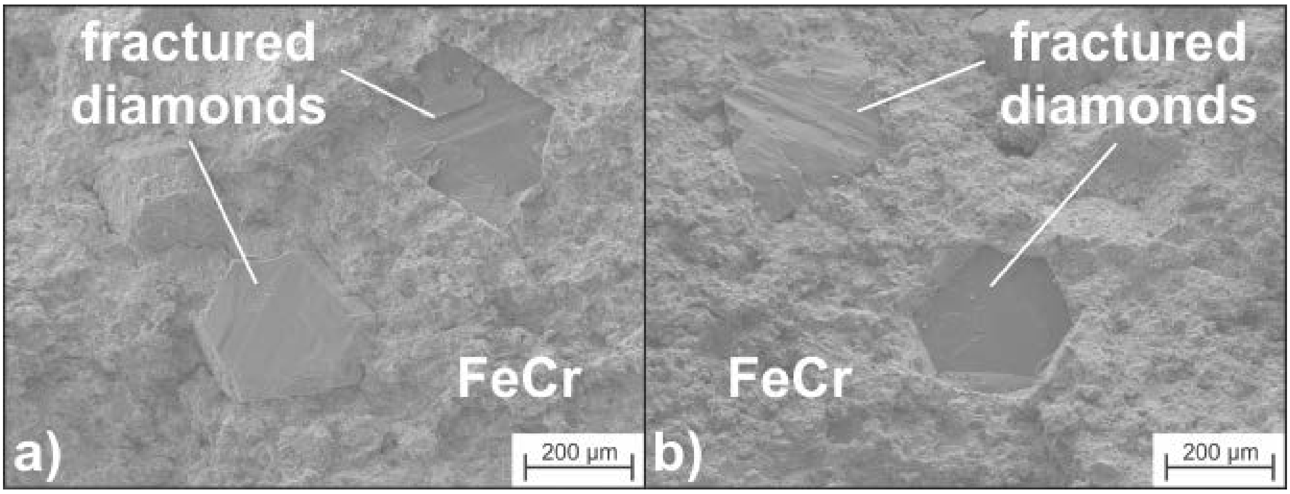

Fig. 5: Fractured surfaces of hot pressed FeCr-based diamond segments

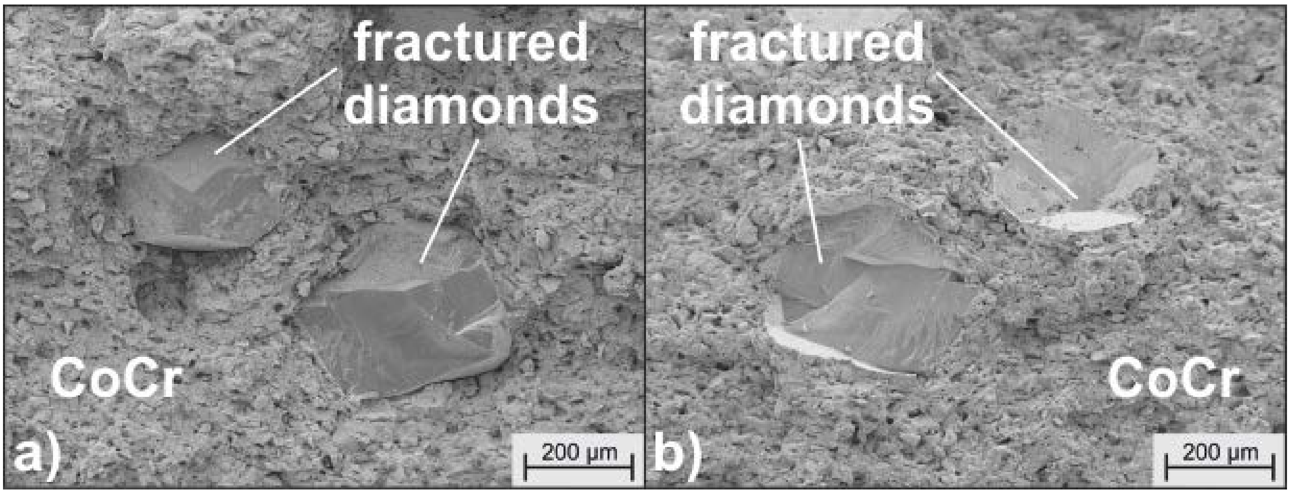

Fig. 6: Fractured surfaces of hot pressed CoCr-based diamond segments

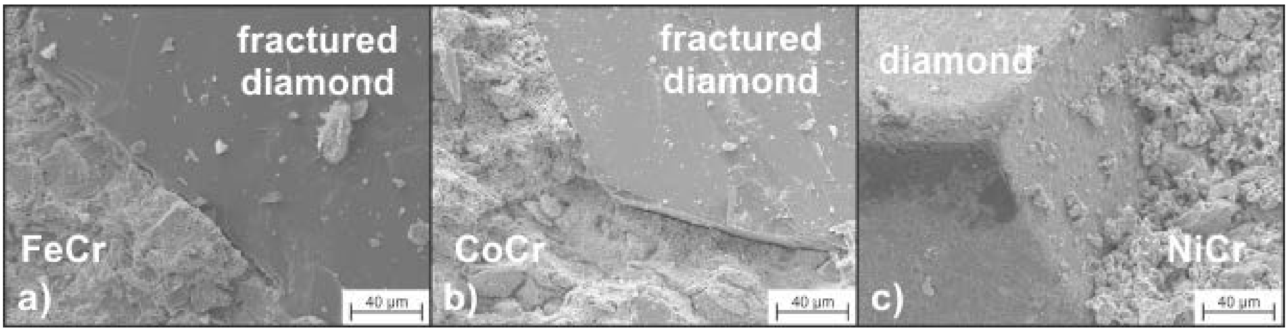

Fig. 7: Close-up of the diamond-metal-interface of hot pressed (a) FeCr-based diamond segments, (b) CoCr-based diamond segments, and (c) NiCr-based diamond segments

Such a strong bonding as presented with FeCr- and CoCr-based matrices is not observed with NiCr samples. After the mechanical fracture, the diamonds remain unbroken on one side of the fragment while its vacancies are marked on the counterpart, similar to the single metallic components, yet with the difference that the diamond particles are fully bonded to the metallic binder without any gap. Fig. 7 (c) shows the diamond-metal-interface of NiCr-based diamond segments. In comparison to the FeCr- and CoCr-based diamond segments, the diamond retention was weaker. This behavior can be explained with a previous work, which observed a reduction of graphitization by adding 15% Cr to Ni-based matrices although a formation of a carbide structure was not observed [10]. Therefore, no carbide formation occurred but rather a mechanical bonding of the diamonds.

3.2 Thermally post-treated diamond segments

The fractured surfaces of post-treated Fe- and Co-based samples are shown in Fig. 8 and Fig. 9. The diamond particles remain in one part of the fractured surface, while the vacancy of the diamond particles are marked on the counterpart of the diamond segment. The surface of the diamond shows a strong diamond degradation, whereas a reaction product, most probably graphite [9], remains in the vacancies after breaking the segment, as visible in Fig. 9. Furthermore, the gaps between the diamond and metallic binder are larger compared to the hot pressed Fe- as well as Co-based samples. These features indicate a stronger graphitization during the thermal post-treatment which can be explained due to the high temperatures as well as the strong catalytic effect of Fe and Co. The catalytic effect causes an allotropic transformation of the diamond into graphite and is observed as black dots on the diamond surface as seen in Fig. 9.

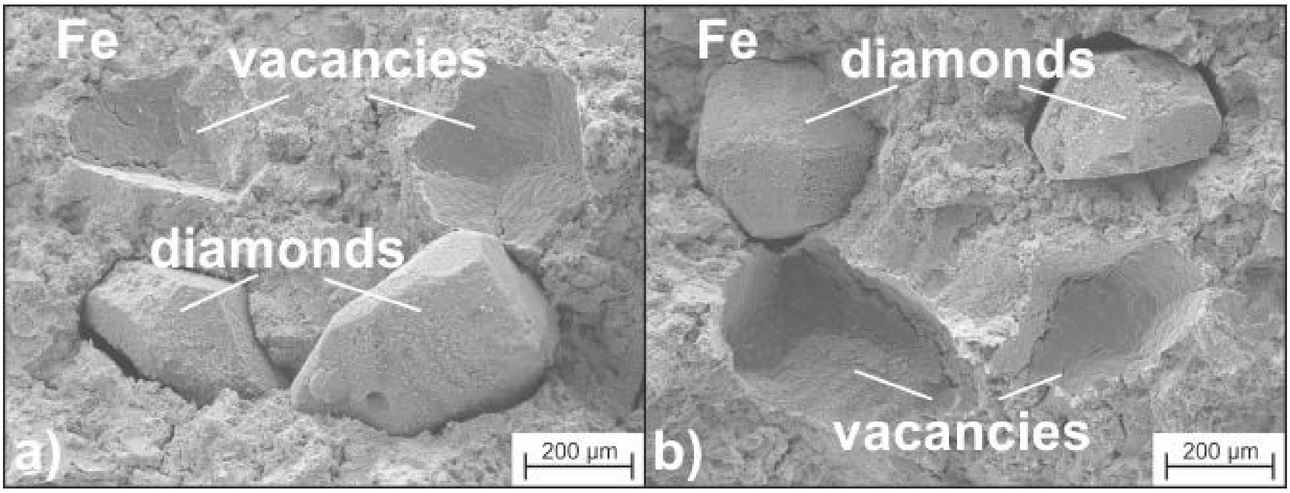

Fig. 8: Fractured surfaces of thermally post-treated Fe-based diamond segments

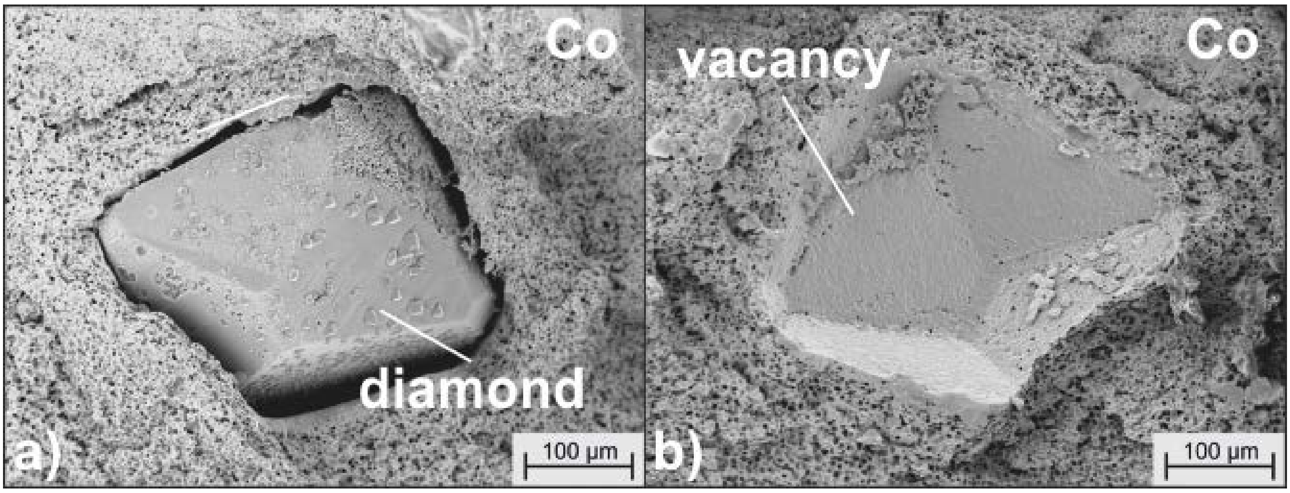

Fig. 9: Fractured surfaces of thermally post-treated Co-based diamond segments

The post-treated Ni-based samples do not show such a strong graphitization of diamond grains as Fe and Co. However, the diamonds are slightly degraded as they present a rough surface which indicates a graphitization. In addition, a large gap between the diamond and matrix is also visible, as shown in Fig. 10. The diamonds of Ni-based samples are not as strongly degraded as the diamonds of Fe- and Co-based samples, which can be explained due to the stronger catalytic effect of Fe and Co.

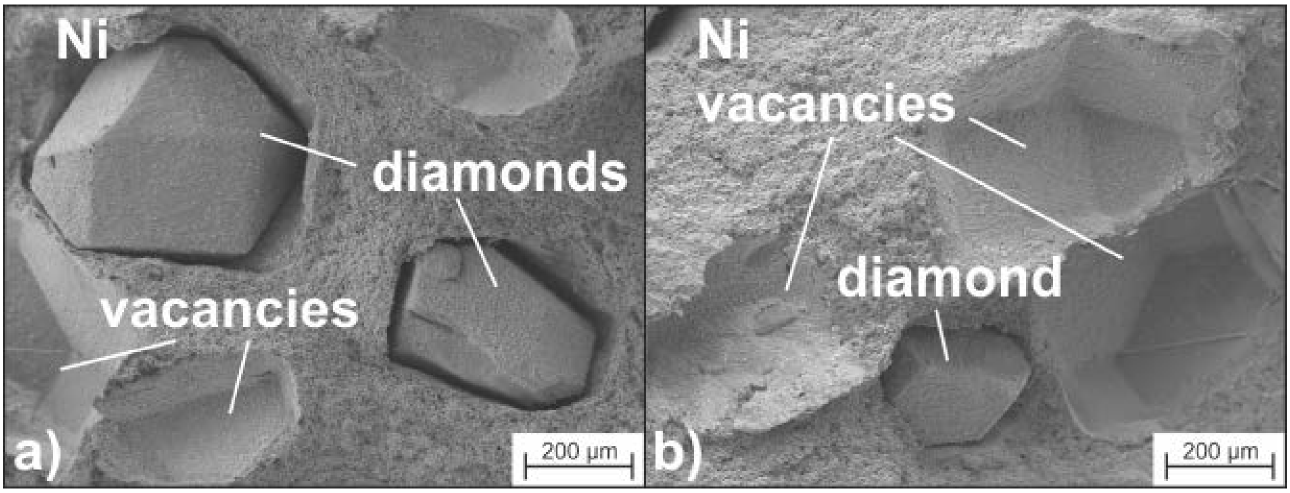

Fig. 10: Fractured surfaces of thermally post-treated Ni-based diamond segments

Fig. 11 and Fig. 12 show the fractured surfaces of thermally post-treated FeCr- and CoCr-based samples. The diamond particles are surrounded by a shell-like structure which is cracked and partially torn off. This shell-like structure indicates the carbide formation that occurred during hot pressing and remained after the thermal post-treatment. However, the diamond retention of post-treated FeCr- and CoCr-based samples is not as strong as after hot-pressing. The post-treatment might have caused the diamond degradation due to the high temperatures, releasing the strong diamond-carbide-bonding. However, the shell-like carbide layer protects the diamond from a stronger degradation as there is no graphitization visible.

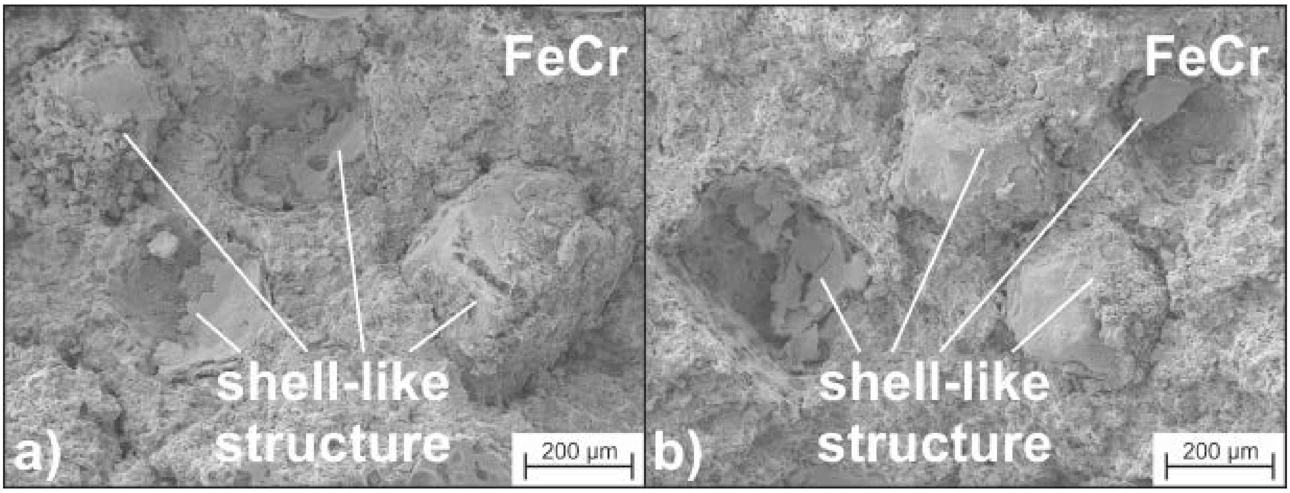

Fig. 11: Fractured surfaces of thermally post-treated FeCr-based diamond segments

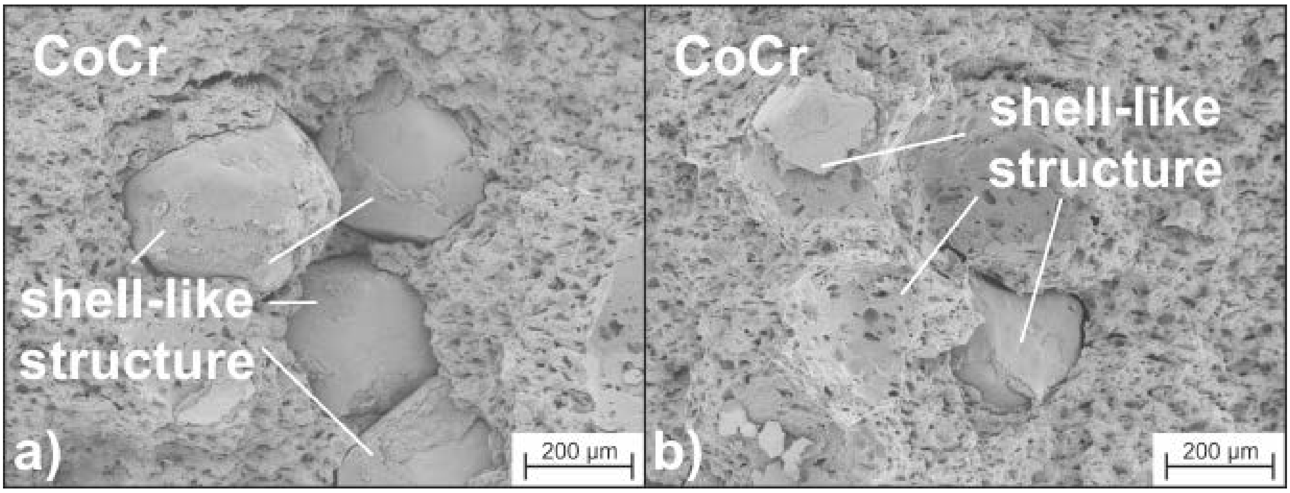

Fig. 12: Fractured surfaces of thermally post-treated CoCr-based diamond segments

A shell-like carbide formation surrounding the diamond particles is not observed with NiCr-based diamond segments. This confirms the results on hot-pressing as there was no indication for the formation of carbide structure as well. However, the diamond bonding is stronger than with single Ni-based diamond segments as the diamonds are tightly embedded into the matrix. Apparently, 15% of Cr content inhibits also the graphitization process and maintains the mechanical bonding of the diamond particles during the thermal post-treatment.

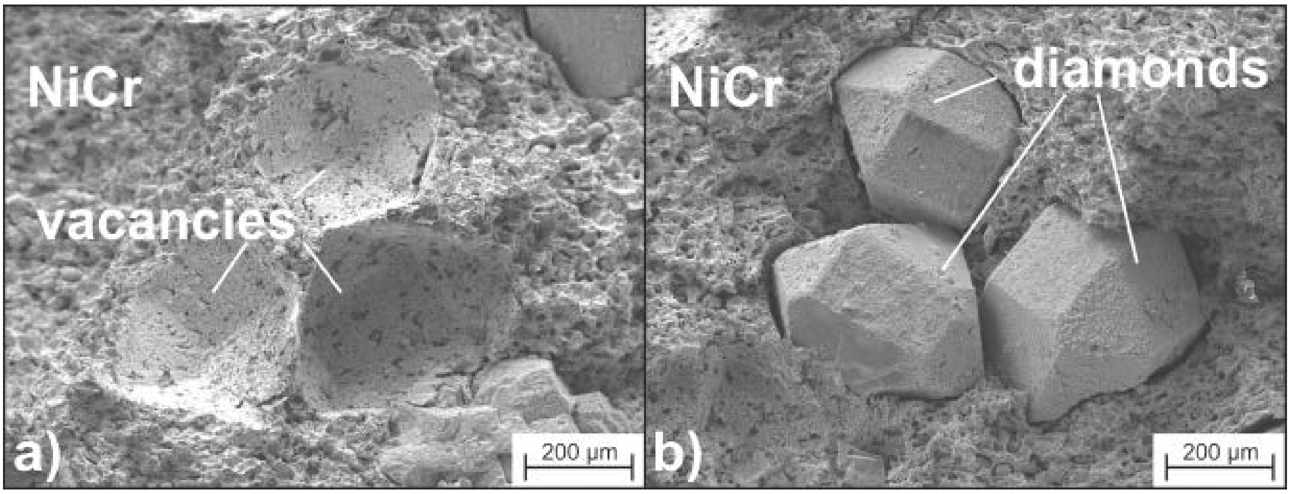

Fig. 13: Fractured surfaces of thermally post-treated NiCr-based diamond segments

4. CONCLUSION

Even though the process time of hot pressing is short, single component matrices with elements with a catalytic influence slightly degrade the diamond particles. By additionally doping 15% Cr to the metallic matrix, the diamond degradation is inhibited. Furthermore, an indication for the formation of a carbide structure is seen with FeCr- and CoCr-based diamond segments due to the strong diamond bonding.

A thermally post-treatment causes a strong degradation of the diamonds impregnated with Fe- and Co-based matrices. The matrices doped with the carbide former do not show any indication for a strong degradation. Furthermore, a shell-like carbide structure is visible in the case of the FeCr-and CoCr-based diamond segments. However, the diamond retention is not as strong as after hot pressing due to the thermal post-treatment.

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