Materials Research Proceedings 41 (2024) 670-677 https://doi.org/10.21741/9781644903131-74

Layer adhesion and critical strain of HFCVD diamond coatings on WC-Co substrate

LECHNER Stefan[1,a *], BARON Sarah[2,b], HÖFER Markus[2,c], STEIN Christian[2,d], MÜLLER Sören[1,e]

[1]Extrusion Research & Development Center, Technische Universität Berlin, Gustav-Meyer-Allee 25, 13355 Berlin, Germany

[2]Fraunhofer Institute for Surface Engineering and Thin Films IST, Riedenkamp 2, 38108 Braunschweig, Germany

[a]s.lechner@tu-berlin.de, [b]sarah.baron@ist.fraunhofer.de, [c]markus.hoefer@ist.fraunhofer.de, [d]christian.stein@ist.fraunhofer.de, [e]soeren.mueller@tu-berlin.de

Keywords: Compression Tests, Cobalt Content, Mechanical Properties, Interface Stability

Abstract. The extrusion of products with high demands on dimensional accuracy and surface quality, such as aluminum power bonding wires or bioabsorbable stents made of magnesium, renders high requirements on the extrusion die. With the application of HFCVD (Hot Filament Chemical Vapor Deposition) diamond coatings on cobalt-based tungsten carbide alloys, a die material with great hot strength, high surface hardness and low chemical adhesion could be provided. To identify WC-Co alloys with suitable cobalt content both for use as extrusion die and for coating with CVD diamond, investigations on ductility and hot strength as well as layer adhesion and interface stability were carried out. The mechanical properties of four WC-Co alloys containing 6 %, 9 %, 10 % and 12 % cobalt were determined by means of hot compression tests. Layer adhesion was evaluated by a standardized sandblasting test. Subsequently, hot compression tests were carried out with coated specimens to determine the critical deformation of the applied CVD diamond coatings.

Introduction

In aluminum extrusion, the production of delicate profiles such as micro-multiport profiles (MMP) for heat exchangers is a well-established process. In the case of products with similar dimensions but high dimensional accuracy requirements, such as aluminum power bonding wires or bio-absorbable stents made of magnesium, only semi-finished products have been produced by extrusion up to now. The reason for this is the high demands placed on the mechanical and tribological properties of the extrusion dies. High extrusion ratios and resulting high extrusion pressures require elevated hot strength of the die materials. Furthermore, very low dimensional tolerances (<10 µm) and optimum surface quality of the profiles necessitate considerable reduction of die wear.

The billet temperature in the extrusion of aluminum and magnesium is usually between 300-500 °C and is therefore within the optimum application range of conventional tool steels [1]. However, the high specific extrusion pressures of over 1200 MPa when extruding profiles with dimensions in the micrometer range clearly exceed their high-temperature strength. Elastic and plastic deformations are induced in the tools, which have a negative effect on the dimensional accuracy of the extruded products. Even high-performance materials such as nickel- and cobalt-based alloys, which have excellent high-temperature strength, only achieve strengths of up to 1100 MPa in this temperature range and therefore do not meet these extreme requirements [2]. Hard metals, on the other hand, exhibit compressive strengths of up to 8000 MPa. They consist of a hard material, usually carbide-based, which is embedded in a metal matrix. The metal matrix significantly increases the toughness of the composite material but reduces the hardness [3]. For extrusion dies, primarily inserts made of cobalt-based tungsten carbide hard meals (WC-Co) are used. Hard metals also have the advantage of being very wear-resistant [4], which makes them meet both requirements for the planned application [5].

The wear occurring on the tool surfaces is composed of abrasive and adhesive wear. Abrasive wear primarily influences the shape and dimensional accuracy of the profile cross-section, while adhesive wear in the extrusion channel of the die reduces the surface quality of the profile [1]. In the case of iron-based tool materials, the high adhesion tendency of aluminum and magnesium to iron causes local welds to form between billet and die material during extrusion. In the bearing channel, these cause scoring ("die line defect") on the profile produced [6]. The adhesion tendency between the material pairings is therefore a decisive factor for the surface quality of the extruded profile.

In addition to the application of wear-resistant materials, surface treatment of extrusion dies offers an effective way of keeping product quality constant over many extrusion cycles. Conventional surface modifications such as nitriding or CVD coating with TiC, TiN or Al2O3 delay the formation of adhesion, but do not completely prevent them [1,7]. Diamond coatings are unique in terms of their combination of extreme hardness, wear resistance and chemical inertness. Especially in contact with aluminum, diamond behaves largely inert and shows the lowest wetting compared to other CVD coatings such as TiN or Al2O3 [8].

In this study, the suitability of WC-Co with HFCVD (Hot Filament CVD) diamond coating for use as extrusion dies was investigated. Ductility and hot strength of four different WC-Co alloys were characterized by means of hot compression tests. To evaluate layer adhesion and interface stability of the diamond coatings on those alloys, a standardized sandblasting test was carried out. A further set of hot compression tests was performed to determine the critical strain of different diamond coatings as a function of coating morphology and thickness, as well as substrate pretreatment.

Experimental Procedure

The suitability of WC-Co for coating with CVD diamond and for use as an extrusion die poses opposing requirements for the cobalt content. Higher cobalt content favors ductility [3] and therefore the use as die but impairs application of CVD diamond [9]. To identify WC-Co alloys with suitable cobalt content both for use as extrusion die and for coating with CVD diamond, investigations on ductility and hot strength as well as layer adhesion and interface stability were carried out (see Figure 1).

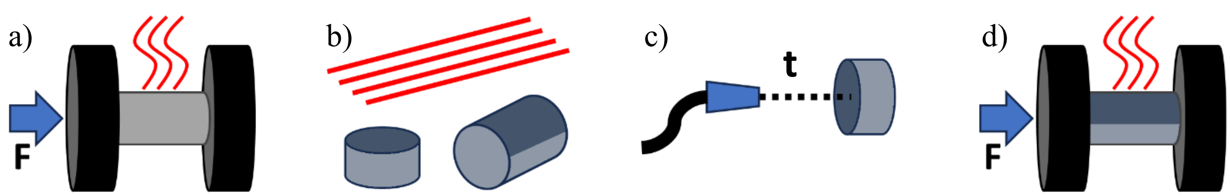

Figure 1: Schematic illustration of the experimental procedure: a) hot compression tests of WC-Co alloys, b) HFCVD coating of specimen, c) sandblasting test and d) hot compression tests of coated WC-Co specimen.

Hot compression tests on WC-Co alloys. Concerning the mechanical properties, hot compression tests were performed on four different alloys containing 6 %, 9 %, 10 % and 12 % cobalt (EMT100, EMT609, EMT210, EMT612). The average grain size for the WC-particles was 0.8 µm (EMT100, EMT210) and 0.5 µm (EMT609, EMT612). Cylinders with a diameter of Ø5 mm and a length of 7.5 mm were tested in a thermal-mechanical physical simulation system

Materials Research Proceedings 41 (2024) 670-677 https://doi.org/10.21741/9781644903131-74

Gleeble 3800. Temperatures of 300 °C, 400 °C and 500 °C were applied to the specimens by means of resistance heating. Compression was performed at a strain rate of 0.0001 s^{-1} until the specimens fractured. For each temperature and WC-Co alloy 3-5 repetitions were carried out.

CVD diamond coating of test specimen. The CVD diamond coating was carried out in a laboratory scale Hot Filament Chemical Vapor Deposition (HFCVD) system at Fraunhofer IST. The coating system enables diamond coatings on areas up to 200 mm x 240 mm. In advance to diamond deposition the cemented carbide samples were cleaned. The various WC-Co alloys were then chemically etched in order to remove the cobalt binder at a depth of a few micrometers in the surface peripheral zone, which interferes with the adhesion of the diamond coating. After ultrasonic treatment in a nano-diamond suspension for enabling diamond seeding of the surfaces, the test specimens (cylinders and flat test bodies) were put into the deposition reactor and placed on a flat substrate holder. The deposition was carried out at filament temperatures of 2150°C in a gas atmosphere consisting of hydrogen and different amounts of methane. For the deposition of microcrystalline diamond films, a pressure of 20 mbar and a CH_4 concentration of 1.6 % was used. In contrast, the nanocrystalline diamond films were deposited at 5 mbar and a CH_4 concentration of 4.0 %. During the deposition process diamond growth took place at substrate temperatures of approx. 800°C, and closed and adhering diamond films were formed. Film thickness was controlled by adjustment of the deposition time. The flat samples used for the evaluation of the adhesion by applying a standardized sandblasting test were coated with nanocrystalline diamond with a film thickness of d_{film} = 11 µm. The cylindrical specimens for the hot compression tests were coated with nano- and microcrystalline diamond films, each with thickness values of d_{film} = 6 µm and 12 µm, respectively. Since the cylinders were placed with the cylinder surface on the sample holder during diamond deposition, they were only coated on approximately one half, which was directly exposed to the process atmosphere, while the rear segments of the cylinder surfaces remained uncoated.

To be able to distinguish the differently coated samples, they were laser-engraved with individual sample numbers. The planar samples were labelled on the uncoated back sides. For the cylindrical samples, the laser engravement was applied to the front faces.

Evaluation of the adhesion strength and interface stability of deposited CVD diamond films on cemented carbides. The adhesion strength of the deposited diamond films was evaluated on flat test specimens (Ø = 18 mm, h = 5 mm) by applying a standardized sandblasting test. In this test, the diamond-coated surface is bombarded with a very intense beam of SiC particles (grit size F180). The test conditions (pressure, working distance, etc.) are selected in such a way that a good differentiation of diamond coatings with different levels of adhesion can be achieved with test times of maximum 1 to 3 minutes. The time until the first damage to the diamond coating appears is measured and provides a qualitative measure of the coating adhesion and interface stability. Since the test duration is also influenced by the coating thickness, all samples must be coated to the same thickness.

Hot compression tests on CVD-diamond coated WC-Co. A second set of hot compression tests was then carried out with diamond coated cylinders containing 6 % (EMT100) and 9 % (EMT609) cobalt to determine the critical strain, before spalling of the coating occurs. In addition, different modifications of the diamond coating were applied. Morphology (nano/micro-crystalline), coating thickness (6 µm/12 µm) and substrate pretreatment (ground/sandblasted) were varied. The strain rate was again 0.0001 s^{-1} and temperature was kept constant at 300 °C for all trials. For each combination of substrate material and coating variation, the applied strain was increased iteratively. In the first stage, a specimen was compressed to 50 % of the fracture strain of the substrate material. If there was no visible degradation of the coating or fracture of the specimen, a strain 75 % of the fracture strain was applied to a new specimen with identical coating type and thickness in a second iteration stage. Analogously, the strain was increased to 87.5 % of the fracture strain in a third iteration stage. In each iteration stage, the specimens were analyzed by means of optical light microscopy to evaluate the state of the CVD diamond coating.

Results and Discussion

Ductility and hot strength of WC-Co alloys. The mechanical behavior of WC-Co alloys is highly influenced by cobalt content and grain size [10]. To find a balance of a favorable binder content for both the coating (rigidity) and for use as an extrusion die (elasticity), hot compression tests were carried out on WC-Co alloys with different cobalt contents. The compressive yield strain (true strain) of the tested alloys is shown in Figure 2a as a function of the test temperature. Due to the brittle material behavior of the cemented carbides, the measured values scatter widely [11]. In general, an inverse dependence of the compressive yield strain on temperature can be seen for all materials. The determined strain is reduced with increasing test temperature. The only exception to this is the alloy EMT100, where a lessened strain was measured at 300 °C. On average, all four materials exhibit a similar compressive yield strain of 0.026. A slightly reduced average value was determined for EMT210 (0.023) and a moderately increased average value was found for EMT609 (0.0295). As shown in Figure 2b, the effect of temperature on the compressive yield strength is also inverse. Analogous to the compressive yield strain, an unexpectedly low compressive yield strength was measured for EMT100 at 300 °C. On average, the lowest compressive yield strength was determined for EMT210 (ca. 2780 MPa) and EMT612 (ca. 2890 MPa), which is due to their high binder contents. For EMT100 a slightly elevated average of ca. 3530 MPa was measured and EMT609 revealed the highest compressive yield strength with an average of ca. 4690 MPa. Considering the ultrafine grain of EMT 609 and EMT612, the increased strength of those alloys in comparison with their counterparts with similar cobalt content can be explained [12].

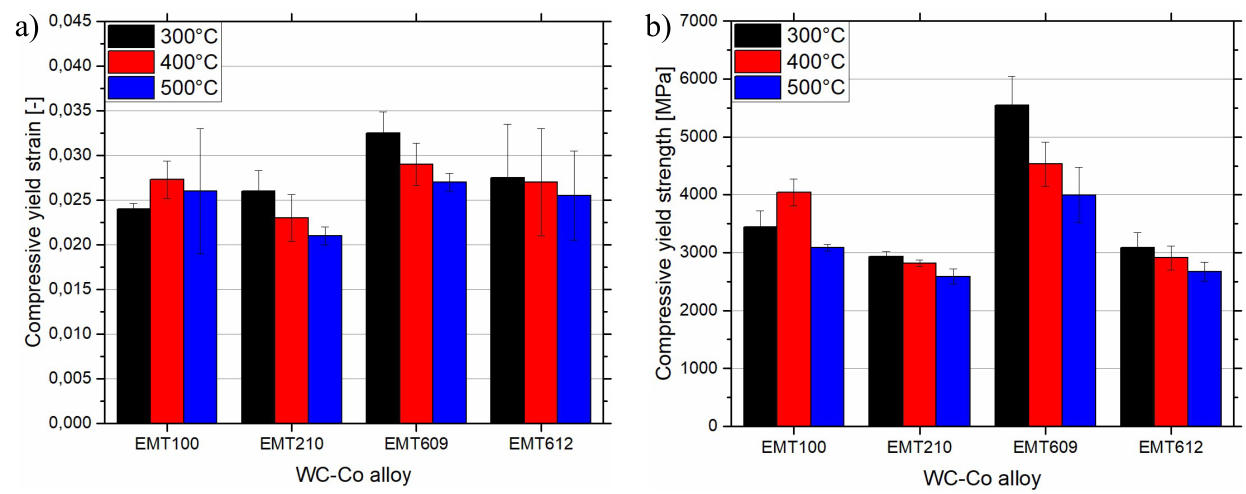

Figure 2: a) Compressive yield strain and b) compressive yield strength of the investigated WC-Co alloys.

These results are also in good agreement with the room temperature hardness of the WC-Co alloys [13]. In addition to EMT 100, the alloy EMT609 was selected for further investigations concerning the critical strain of CVD diamond coatings on WC-Co substrate due to its increased compressive yield strain and compressive yield strength in the temperature range of 300-500°C.

Adhesion strength of the deposited CVD diamond films on flat WC-Co samples. A total of 22 hard metal disks with 18 mm diameter were coated with a nanocrystalline diamond layer with thickness of 11 µm. The coated samples were tested by applying the sandblasting test under identical conditions. Figure 2 shows the times to the appearance of the first damage of the diamond coating as a function of the specified Co content of the WC grades EMT100, EMT609, EMT210, and EMT612. If no flaking occurred, the test was terminated after 300 s at the latest. The selected test conditions were extremely abrasive. With any other hard coating such as diamond like carbon

(DLC), TiC, TiN, or TiAlN, coating failure occurs within fractions of a second. If the particle beam is directed at uncoated hard metal surfaces, a hole several 100 micrometers in depth is created in just a few seconds. Figure 2 shows that the achievable test times decrease almost exponentially with the cobalt content. Our experiences with sandblasting tests of diamond-coated cutting tools show, that test times of one minute and longer indicate very good to excellent adhesion values. Such performance values were obtained for EMT100 and EMT609 samples with Co contents of 6 % and 9 %. Both WC-alloys with cobalt contents of 10 % and 12 % perform significantly worse. Nevertheless, EMT210 with 10 % cobalt still mostly reaches durability values of more than 30 seconds, which is sufficient for applications with medium requirements. Even on the EMT612 samples with 12 % Co, an adhesive diamond coating was deposited in all cases. The test times achieved are between 6 s and 22 s, which is probably only sufficient for applications with low coating adhesion requirements. Based on the sandblasting test results, we decided to evaluate only EMT100 and EMT609 as substrate materials for extrusion dies and for the hot compression tests shown in the next section.

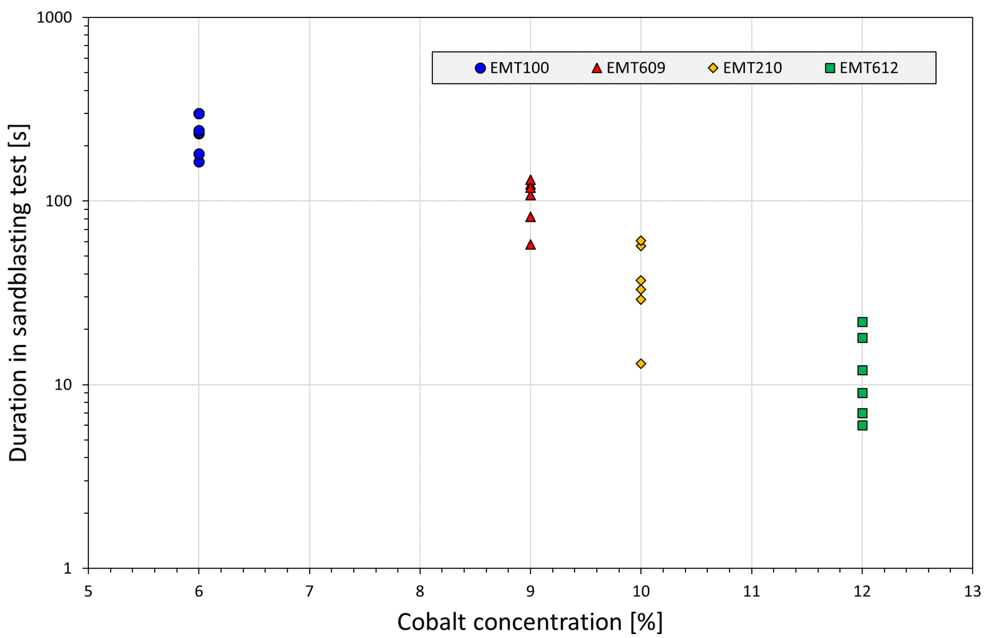

Figure 3: Results of sandblasting tests for nanocrystalline diamond coatings deposited by HFCVD on cemented carbide grades with different cobalt contents. The test duration was limited to a maximum of 300 s.

Critical strain of CVD-diamond-coatings. In order to determine the limiting deformation of the CVD coatings, hot compression tests were carried out using the WC-Co alloys EMT100 and EMT609 as substrate materials. The applied strain was derived from the previous hot compression tests of uncoated samples. Here, an average fracture strain of 0.0333 and 0.0325 was measured for EMT100 and EMT609, respectively. Therefore, the targeted strain values for the three iterations were set to 0.017 (50 % fracture strain), 0.025 (75 % fracture strain) and 0.029 (87,5 % fracture strain) for the three iteration stages. The first substrate material to be tested was EMT100. In the first iteration stage, no defects of the CVD coating were observed. Regardless of the coating configuration (morphology/thickness) or substrate pre-treatment, no visually recognizable damage to the coating occurred. Figure 4a illustrates a specimen, which was tested in the first iteration stage. In the second iteration stage, repeated failure of the substrate material occurred even though the applied strain was below the determined fracture strain. An example is shown in Figure 4b, where the specimen is split in half. Due to the early fracture of the WC-Co substrate, the designated strain could not be applied in all trials of the second iteration stage. However, no damage to the coatings caused by the compression was detected either. The microscopic examination of the fracture surface did reveal no damage to the interface between diamond coating and substrate (see Figure 5a). An exception is the microcrystalline, 12 µm thick diamond coating on ground substrate material. Here, a large area of spalling of the coating could be seen after the specimen failed (Figure 4c). In Figure 5b the delamination of the coating is visible. The gap between substrate (left) and diamond film (center) clearly indicates the separation of the interface. Furthermore, at the top of the picture a piece of the coating is missing. In the third iteration stage, the desired strain was achieved in only a few trials. In most cases, the WC-Co failed at strains close to 0.025. The frequent fracture in form of longitudinal splitting through the center of the specimens suggests the laser engraving on the cylinder front face acts as a crack initiation point. Unstable crack growth is known to be preceded by crack initiation and to be characteristic for brittle materials under mechanical load [3]. Examination of the broken specimens showed that the fracture always extends through digits of the laser engraving. Multiple additional tests with reference specimens (same batch of substrate material, different coating systems, without engraving) confirmed laser engraving as the cause of premature failure of the specimens. In the tests in which the specified strain of 0.029 was achieved, layer failure occurred in the form of large-area ablation (see Figure 4d). This suggests the critical strain for coating failure is in the range 0.025-0.029, which is above the compressive yield strain of the substrate material. This is not critical for the intended application of CVD diamond coating on dies for aluminum or magnesium extrusion, as plastic deformation of the die must be avoided.

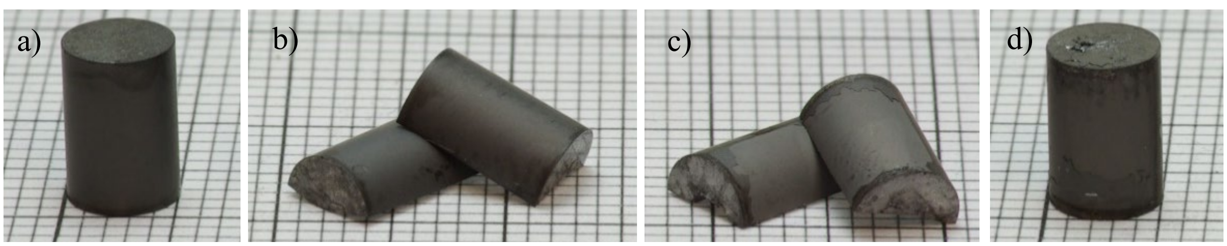

Figure 4: Observed failure modes: a) no failure, b) ablation without substrate failure, c) substrate failure without ablation and d) ablation with substrate failure.

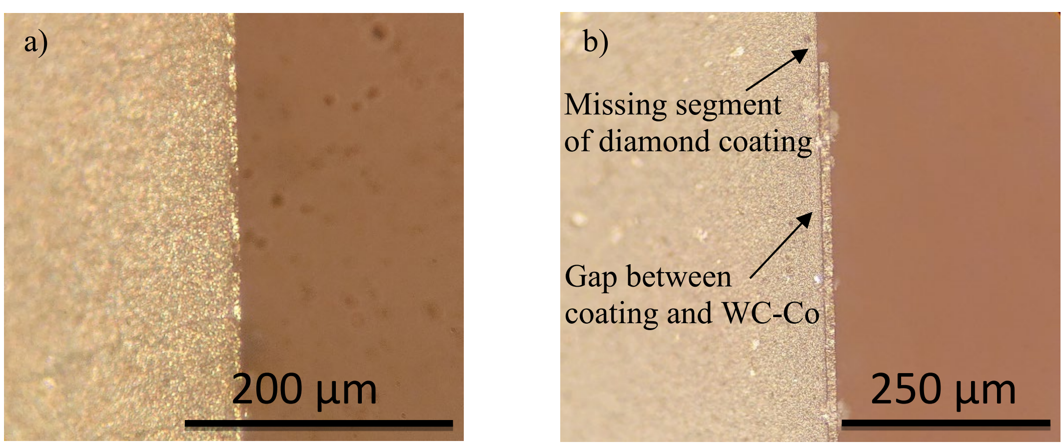

Figure 5: Interface of substrate and diamond coating after specimen fracture with microcrystalline coating on ground substrate. a) fully intact interface for the 6 µm thick coating, b) delamination of the 12 µm thick coating.

The second substrate material on which the CVD-diamond coating was applied is EMT609. With this WC-Co alloy, fractures of specimens were already observed during the first iteration stage. As described above, this is most likely due to the laser engraving and its action as a crack initiation point. The reason why material failure occurs at lower strains than with EMT100 is due to the increased strength of EMT609 [13]. With the same strain, higher stresses are present in the higher-strength material. Conversely, the strain of the higher strength-material is lower for the same load. Accordingly, EMT609 in combination with the weakening caused by the laser engraving fails at lower strains compared EMT100. Regardless of this, no damage to the CVD coating was visible after the tests on the first iteration stage. In the second iteration stage, frequent specimen failure was observed and only very occasionally the targeted 75% of fracture strain was achieved. In most cases, the samples failed at strains of 0.018-0.020. Nevertheless, the CVD coatings remained intact. Only the microcrystalline, 12µm thick diamond coating on ground substrate showed distinct layer failure in form of large area spalling. Due to the increased layer thickness, the coating exhibits reduced flexibility and can therefore tolerate less deformation. The tests of the third iteration were carried out as planned, but as in the second iteration stage no strains above 0.020 were achieved.

Summary

In this study, the suitability of diamond films deposited by HFCVD on different types of WC-Co substrates was investigated regarding its application on extrusion dies. The mechanical material properties of four WC-Co alloys (6-12 % cobalt, fine and ultrafine grain) were determined at elevated temperatures (300-500 °C) and two WC-Co materials were selected for further investigations. The alloys EMT100 and EMT609 were used to investigate the adhesion and critical strain of the diamond coating. The knowledge gained can be summarized as follows:

- Compressive yield strain and compressive yield strength at elevated temperatures of the investigated WC-Co alloys are directly proportional to their room temperature hardness.
- The combination of moderate cobalt content and ultrafine grain of the EMT609 alloy offers a good balance of toughness and strength.
- For coatings on EMT100, a compressive strain of 0.025-0.029 was identified as critical for coating failure.
- Due to premature specimen failure, coatings on EMT609 could only be subjected to a strain of up to 0.020. The coatings remained undamaged proving excellent adhesion levels of the deposited diamond films.
- The nanocrystalline diamond films shows excellent stability in hot compression tests for both film thicknesses (6 and 12 µm) independent on the type of surface finishing (ground or roughened by sandblasting). The parameter combination of microcrystalline, 12 µm thick coating on ground substrate seems to be unfavorable for the critical strain of the diamond coating, as cumulative ablation was observed.

References

[1] M. Bauser, G. Sauer, K. Siegert, Strangpressen: Aluminium Fachbuchreihe, Aluminium-Verlag, Düsseldorf, 2001. ISBN 3410221816

[2] H.J. Weintraud, Neue Werkstoffe für Strangpressmatrizen, in: J. Baumgarten (Ed.), Strangpressen, DGM-Informationsgesellschaft m.b.H., Oberursel, 1989. ISBN 3-88355-160-0

[3] Upadhyaya, G.S., Cemented Tungsten Carbides – Production, Properties, and Testing, William Andrew, Norwich, 1998. ISBN 978-0-8155-1417-6. https://doi.org/10.1016/B978-081551417-6.50002-2

[4] A.G. Guy, G. Petzow, Metallkunde für Ingenieure, in R. Sewig, D. Roess (Eds.), Technisch-Physikalische Sammlung Band 7, Akademische Verlagsgesellschaft, Frankfurt am Main, 1970.

[5] P. Kazanowski, A Study of Multi-material Die Insert Failure Mechanism in Aluminum Extrusion, Conf. 10th International Aluminium Extrusion Technology Seminar ET (2012), Miami.

[6] M.P. Clode, T. Sheppard, Formation of die lines during extrusion of AA6063, Mater. Sci. Technol., 6(8) (1990), 755–763. https://doi.org/10.1179/mst.1990.6.8.755

[7] K. Müller, Grundlagen des Strangpressens: Verfahren, Anlagen, Werkstoffe, Werkzeuge, expert verlag, Renningen, 2003. ISBN 3-81692-018-7

[8] A.K. Chattopadhyay, P. Roy, A. Gosch, S.K. Sarangi, Wettability and machinability study of pure aluminium towards uncoated and coated carbide cutting tool inserts, Surf. Coat. Technol. 203 (2009), 954-951. https://doi.org/10.1016/j.surfcoat.2008.08.047

[9] S. A. Linnik, A. V. Gaidaichuk, and V. V. Okhotnikov, Influence of Cobalt on the Adhesion Strength of Polycrystalline Diamond Coatings on WC–Co Hard Alloys, Technical Physics, 63(2) (2018), 206–210, https://doi.org/10.1134/S1063784218020226

[10] H.E. Exner, J. Gurland, A review of parameters influencing some mechanical properties of tungsten carbide–cobalt alloys, Powder Metall., 13:25 (1970), 13-31. https://doi.org/10.1179/pom.1970.13.25.002

[11] A.V. Shatov, S.S. Ponomarev, S.A. Firstov, Fracture and Strength of Hard metals at Room Temperature, in: V.K. Sarin (Ed.), Comprehensive Hard Metals, Elsevier, 2014, pp. 301-343. https://doi.org/10.1016/B978-0-08-096527-7.00010-6

[12] P. Ettmayer, Hardmetals and Cermets, Annu. Rev. Mater. Sci. 19:1 (1989), 145-164. https://doi.org/10.1146/annurev.ms.19.080189.001045

[13] EXTRAMET AG, Delivery Program 09/2022, Plaffeien, 2022. https://www.extramet.ch/wp-content/uploads/2022/08/EXTRAMET_Lieferprogramm-2022_www_202208.pdf