Tungsten Carbide-Cobalt: with 3D metal printing to wear-resistant coatings for technical applications

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The mechanical protection of component surfaces sliding on each other against wear, as in mechanical seals, can typically be achieved by the deposition of hard coatings. Depending on the kind of application suitable material combinations and deposition techniques have to be selected. In case of cobalt-based tungsten carbide coatings usually physical vapor deposition (PVD) is used. However, a promising approach uses 3D printing to produce such coatings with enhanced adhesion and extreme wear resistivity. Characterizing those coatings in tribological tests under severe wear inducing conditions, it can be found that the coatings are extremely wear resistant. The measured coefficient of friction against tungsten carbide-cobalt highly depends on the surface topography. It is obtained that different surface properties strongly influence the tribological behaviour.

1 Introduction

Additive manufacturing (AM) is an efficient and versatile way to produce components with complex geometry. A variant of AM is the so-called laser powder bed fusion (L-PBF) process. It produces metal parts in a powder-bed-based process by selectively irradiating successive layers of powder with a laser beam, which selectively and locally melts the illuminated areas and subsequently solidifies them as a solid [1]. It has been shown that almost all materials produced by additive manufacturing exhibit anisotropy in their structure and behaviour due to the manufacturing process. Due to the intensive energy input of the laser on a very small area of the component and rapid cooling, temperature coefficients occur that cause residual stresses in the component, which can lead to deformations. To counteract this, the L-PBF process requires, among other things, thermal post-treatment [2]. In order to minimize the residual stresses already in the manufacturing process, it is possible to expose the respective powder layers in a systematic way by means of the laser during the manufacturing process. Surfaces such as mechanical seals that are exposed to mechanical forces usually require additional treatments or coatings to meet the wear resistance requirements and to achieve an adequate lifetime. State-of-the-art processes here would include plasma nitriding [3], electroplating, and vacuum coating of transition metal nitrides or carbides such as WC [4, 5]. These transition metal nitrides exhibit excellent material properties in the wear resistance point. However, the production of such coatings with good adhesion and adjustable stoichiometry usually requires highly complex vacuum coating processes, which require a very high technical effort. They are associated with low deposition rates and thus a long coating time as well as a limited maximum coating thickness of usually less than 10 µm. Achieving good adhesion involves intensive cleaning and preparation. In order to increase the lifetime of valuable components, a higher coating thickness than is possible with PVD processes is usually required.

In this work, the approach is therefore to protect high-quality mechanical seals from wear with an additively manufactured WC/Co layer with a layer thickness of 1 - 3 mm and to optimize the life time of the component. At the same time, the resulting coating effort is to be optimized compared to that of a state of the art PVD layer. Previous investigations have already shown that sinterable WC/Co can be used to a certain extent for the L-PBF process [6]. Similarly, initial results have already been published on the coating of stainless steel with carbides produced by the L-PBF process [7,8]. The analysis of the wear resistance of the prepared surfaces with and without additional surface treatment was performed by quantitative oscillation tribometry. In particular, wear tests were performed under dry conditions against WC/Co counterparts to test the prepared coatings in the extreme case of dry friction in the case of, for example, cracking of a lubricant film. Subsequently, the resulting coatings were measured and evaluated for friction.

2 Experimental

The specimens were fabricated with a selective laser melting (SLM) system, an SLM 280 HL (SLM Solution Group AG, Lübeck, Germany), using the L-PBF process. A 400-W Yb fiber laser was used as the laser source, operating with a minimum spot diameter of about 80 µm and argon as the process gas. The build space is cylindrical with a diameter of 90 mm and a height of 100 mm. Preheating an operating temperature of the build platform was T = 200 °C. A standard WC/Co powder "Amperit 526.059" was used for the L-PBF process. It is used in flame or plasma spraying and offers the properties required for the L-PBF process, such as flowability and particle size. The powder was in an agglomerated and had a Co content of 17 %. The particle size distribution was D90 of 28 µm, D50 of 18 µm, and D10 of 12 µm. The parameters for the L-PBF process were selected according to a parameter study [7]. A chromium-nickel-molybdenum austenitic stainless steel was used for the substrate plate (1.4404). The volumetric energy density (E_V (J/mm3)) is determined by the laser power P (J/s), the scanning speed v (mm/s), the line spacing d (mm) and the layer thickness h (mm), as depicted in Equation (1). A combination of good coating adhesion and a homogeneous microstructure was achieved at an E_V of 444 J/mm².

$$E_V = \frac{P}{v*d*h} \quad (1)$$

Table 1: Applied process parameters for the manufacturing of WC/Co in the L-PBF process.

Parameter	Value
Laser power (P)	*200 W*
Scan speed (v)	200 m/s
Hatch distance (h)	0.045 mm
Layer thickness (d)	0.05 mm
Volumetric energy density (E_V)	444 J/mm³

After defining the coating parameters and the exposure pattern, circular-shaped specimens are additively manufactured having a diameter of 20 mm and a height of 3 mm. These cylindrical specimens serve as test subjects for the subsequent oscillating tribometry. Three, metallurgically different zones are usually formed during the additive manufacturing process, and they were also found in the process of this work. The substrate zone is the base material, stainless steel 1.4404. In the boundary zone, mixing of the base material and the coating material was observed, which is also interspersed with pores and voids. Finally, near the surface of the materials (coating zone), a homogeneous WC/Co structure was detected [7]. A cross section through one of the samples showed the three zones as shown in the left of Figure 2. The right-hand side of Figure 2 shows a coated base body of a mechanical seal.

The seal has an outer diameter of 62 mm, an inner diameter of 56.5 mm and a layer thickness of 3 mm WC/Co was deposited on the substrate. The wear resistance of the surfaces was investigated by means of oscillation tribometry with an Optimol SRV 3 tribometer (Optimol Instruments Prüftechnik GmbH, Munich, Germany), portrayed in Figure 1.

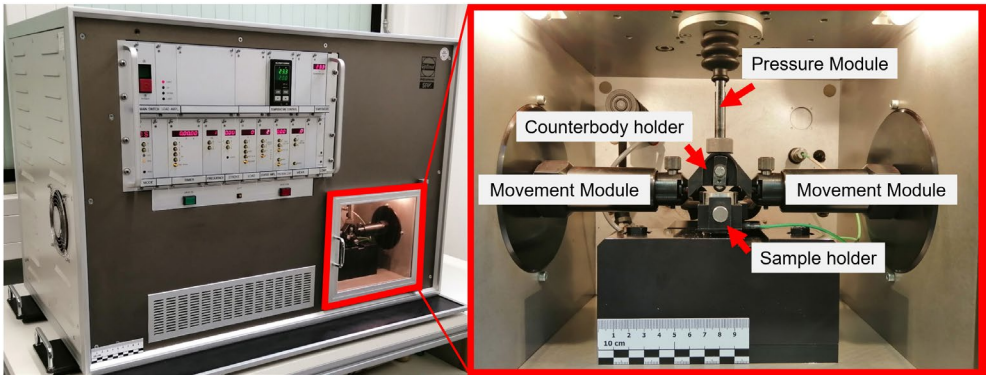

Figure 1: Optimol SRV 3 oscillating tribometer (left) with integrated sample chamber (right). The sample chamber consists of a sample holder with inserted sample, a counterbody holder with a WC/Co ball (diameter 10 mm), the movement modules on the left and right for the horizontal, oscillatory movement of the counterbody and a pressure module for the vertical application of the normal force.

Since material pairings of tungsten carbide coated surfaces are frequently used in technical applications, such as mechanical seals, all tests were carried out with WC/Co counter bodies. WC/Co balls with a diameter of 10 mm were used under an exceptionally large normal load of F_N = 50 N without lubricant. A further increase in friction and wear was realized by choosing a small vibration frequency of f = 2 Hz with a corresponding stroke of s = 1 mm (table 2).

Table 2: Applied process parameters for the oscillation tribometry of WC/Co

Parameter	Value
Normal load F_N	*50 N*
Frequency f	*2 Hz*
Stroke s	1 *mm*

The test parameters were chosen in this way and additionally lubrication was omitted in order to test the generated coatings under severe wear conditions. The topography of the generated wear scars was quantitatively analysed with high spatial resolution using white light interferometry in combination with classical light microscopy.

Coefficients of friction (COFs) were extracted from these experiments and correlated with the microstructure of the wear scar.

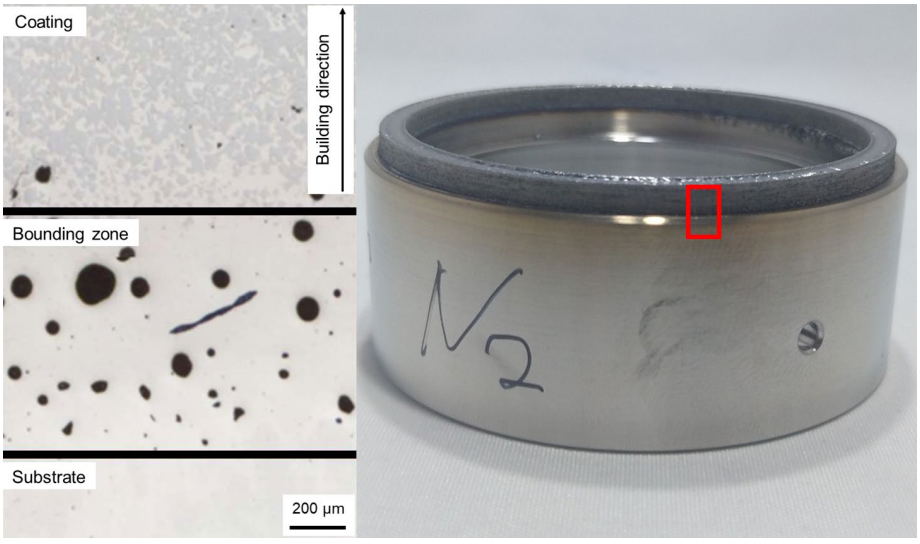

Figure 2: A 3 mm WC/Co-coated base body of a mechanical seal (right) as well as a microscopic image of the developing microstructure in the cross-section of the coating (left). It corresponds approximately to the image section in the red rectangle.

3 Results

The cross-section of a cobalt-supported tungsten carbide layer produced by the L-PBF process is shown in the left of Figure 2. The bounding zone seen in the centre is interspersed with pores. This zone results from the very high energy input of the laser into the steel substrate during the exposure of the first powder layers. At 444 J/mm³, the energy density for exposing the tungsten carbide is about six times higher than the energy density required to illuminate the stainless steel. The bounding zone consists exclusively of stainless steel. The structure of the WC/Co can be seen in the irradiation zone. The tungsten carbide, shown in dark grey, is embedded in the light grey cobalt matrix. In this zone, it can be shown that the coating parameters used have succeeded in producing a compact microstructure of the material, which can be described as homogeneous and widely defect-free. By increasing the laser power, the substrate heating can be operated at a low temperature of 200 °C in these investigations, compared to previous results [6, 9]. This not only leads to a defect-free microstructure, but also protects the substrate from being aged at an elevated temperature for too long.

Figure 3 shows the additively manufactured tungsten carbide layers 'as manufactured' (top row) and after mechanical post-processing (bottom row). Shown are images created by optical microscopy (left) and three-dimensional models of the corresponding surfaces created by white light interferometry (right). Both surfaces were analysed by oscillation tribometry without lubricant. Under the above conditions, the maximum relative velocity is 6 mm/s. The test duration is t = 600 s in each case. The coefficients of friction (COF) determined show large differences. While an average coefficient of friction of $\mu = 0.5$ is obtained for untreated surfaces, a COF of $\mu = 0.22$ is obtained for mechanically post-processed samples.

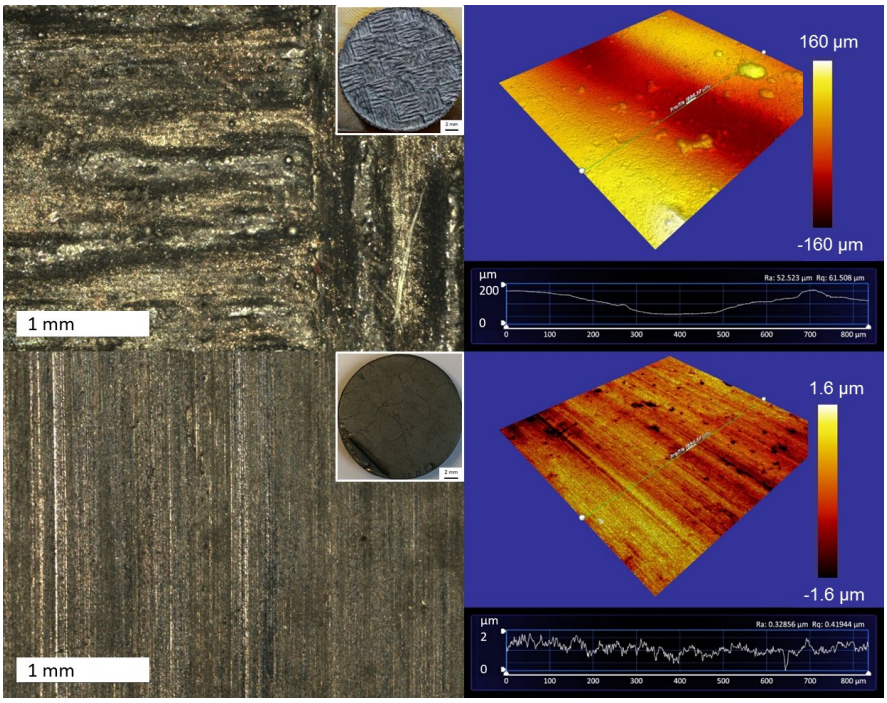

Figure 3: Characterization of 2 different WC/Co surfaces via optical microscopy (left) and interferometry (right). The top row shows the surface directly after manufacturing while the bottom row shows the same surfaces after a mechanical surface treatment. The two-dimensional profiles below were extracted from the solid lines in the interferometry pictures. It can be shown that the mechanical treatment decreased the surface roughness approximately by two orders of magnitude from Ra = 0.32 µm (left) to Ra = 0.05 µm (right). The corresponding samples are illustrated in the upper right corner of the microscopic images.

Since the wear volume in the tests is very low, it is not possible to separate surface structure and wear. For this reason, the test duration was increased from 600 s to 8000 s in an additional investigation, shown in Figure 4. Here, the profile of the COF is shown over the test duration. The range can be divided into three phases. After a short initial period, the COF plateaued at µ = 0.22 (I). At about 1200 s, a transition region begins in which the COF increases to µ = 0.38 until t = 2500 s (II). This is followed by a second plateau at a constant COF of µ = 0.38 (III).

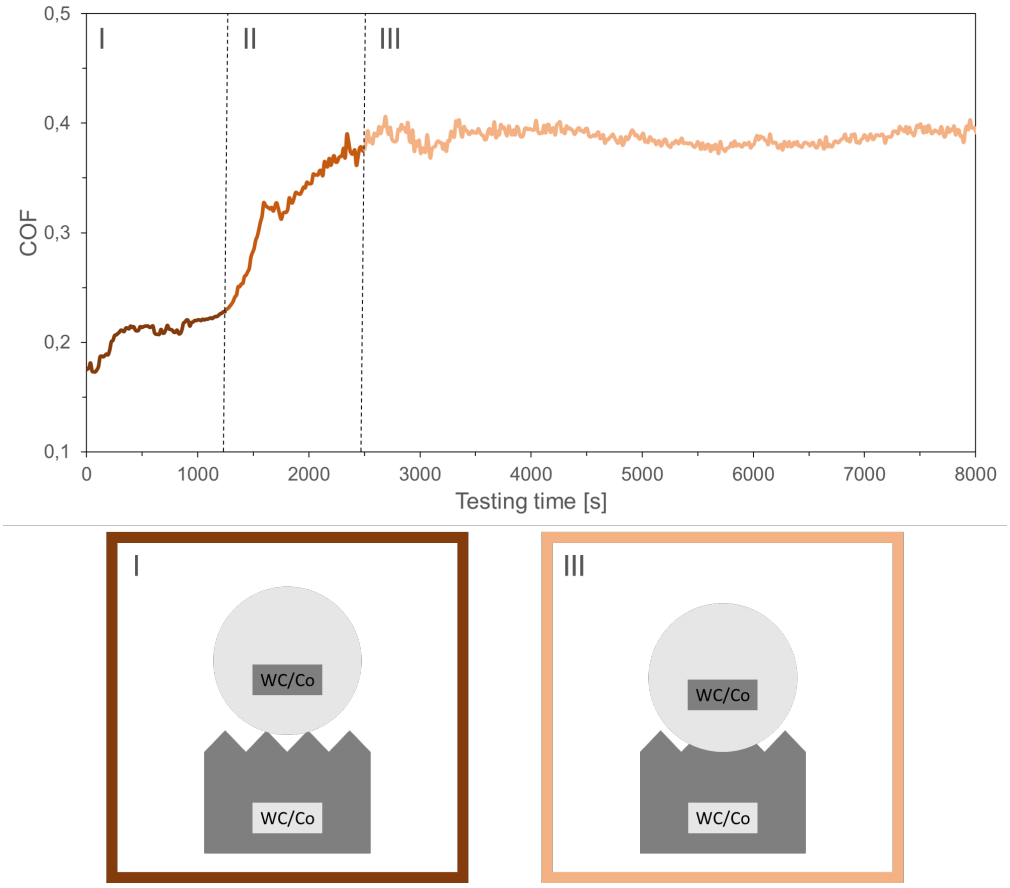

Figure 4: Top: COF of a mechanically treated surface over a long term of 8000 s. The curve can be split in three phases consisting of two plateaus where the COF can be considered stationary (I, III) and a transition region with a rising COF in phase II. Bottom: Sketch of the local friction geometry in the phases I and III.

4 Discussion

To understand the obtained results, it is important to consider the microstructure of the surfaces. The untreated surface has its origin in the selected illumination pattern during coating production. The structure of the processed surface evolves during post-processing where grinding grooves appear. It has already been shown that microstructuring of a surface leads to optimized wear behaviour of the coating [10-12]. Surface patterns can act e.g. as a reservoir for emerging wear particles. These are introduced into the microstructures by the movement of the friction bodies and remain there. Thus, they serve no longer as third bodies in the progressive friction process. The size and height-to-width ratio of the microcontainers are essential for the functionality of these microstructures.

The untreated 3D-printed surface showed an increased COF, although this sample has a prominent surface texture. However, due to the size of the structures, they could not fulfil the objective of trapping and storing the resulting particles in the long term. The coarse structuring thus merely resulted in a smaller contact area at the same test load, which causes higher Hertzian pressures in frictional contact and thus promotes the formation of abrasion particles, resulting in increased wear. Thus, for these structures, it can be assumed that as the structures are removed, the COF decreases and subsequently levels off at a lower value.

A strikingly low coefficient of friction is shown by the mechanically post-treated surface. The anisotropic grinding grooves show microstructuring that is a factor of 100 smaller than the structure of the non-treated surface. This type of structuring leads to a drastic reduction of the COF. Accordingly, the microstructures have a dimensioning that is beneficial for the sustained storage of the resulting particles. This assumption also explains the progression of the COF in Figure 4. In phase I, the influence of the structures is evident from a low coefficient of friction. The second phase shows a steadily increasing coefficient of friction. Here, the microstructures are successively worn away by abrasion, which lowers the wear-reducing effect of the structures. In the third phase, in turn, the microstructures are completely removed by abrasion, and the contact between the two friction partners is unaffected by structures. This state proves to be very stable even over long testing times.

5 Conclusions

Additive manufacturing can be used to produce wear resistant WC/Co coatings in different geometries and layer thicknesses that exhibit very good adhesion to stainless steel. Likewise, the production of a homogeneous cobalt matrix with embedded tungsten carbide is possible. Tribological tests showed very constant coefficients of friction. A post treatment process of the 3d-printed surfaces additionally allows the introduction of surface micropatterns that further optimize the friction conditions even under unlubricated and extreme mechanical loads.

6 References

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