

Short-Pulse Laser Sintering of Multilayer Hard Metal Coatings: Structure and Wear Behavior

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Abstract This paper reports on the phase composition and properties of multilayer hard metal coatings deposited on steel by a process variant of Selective laser melting (SLM). The process is based on layer-wise short-pulse laser sintering of high-dispersive WC-Co powder on a steel substrate. High temperature in the molten zone and chemical interaction with the substrate explain high level of adhesion strength between the coating and the substrate. The technique allows obtaining both high quality hard-metal multilayer gradient coatings with thickness up to 200 μm , density near to the theoretical density (TD), hardness up to 21 GPa and complex 3D objects by layer-wise powder based process such as SLM.

Keywords Selective laser melting · Gradient coatings · Hard metal · Hardness · Abrasive wear resistance

Introduction

Protective coatings based on hard metal powders meet increasing requirements for commercial applications. This explains considerable interest in scientific researches on the formation of hard coatings on the surface of steels. Coatings properties should be carefully gauged in terms of its specific working conditions. Lakhothin et al. (2009) [1] have shown that choice of a technique for coating deposition should be based on required thickness, hardness, adhesive strength and microroughness. Modern physical vapor deposition (PVD) techniques provide thin (a few microns) coating layers with high hardness. They are mostly used to improve performance of cutting tools. Savarimuthu et al. (2001) [2] described that unlike PVD methods, gas-thermal techniques allow deposition of thick layers (over 100 μm), where hard particles of tungsten carbide are binded by low-melting particles (usually Co and Ni). Chemical vapor deposition (CVD) methods are based on chemical reactions or decompositions of

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components directly on the deposited surface and used for the rapid production of coatings on parts with complex geometry. CVD methods allow producing high quality coatings which do not require finishing. Among significant problems of described methods are low adhesive strength and high operating temperature up to 600 °C.

A problem of the low adhesion strength between the coating and substrate may be solved by applying a concept of gradient coatings, wherein there is a gradual change of properties over the thickness of the coating. Softer inner layers may provide better adhesion strength, whereas harder outer layers ensure high durability. A technology which has the possibility for creating such gradient coatings might be based on Selective Laser Melting (SLM) or laser cladding of metal matrix composites (MMC). SLM as one of rapid prototyping technologies is suitable for making 3D parts layer-wise directly from metal powders and potentially can be used to produce 3D hard metal functional parts from commercially available powders. The main disadvantage of SLM related to hard-metal parts is high level of porosity [3]. Porosity can be reduced by impregnation of the sintered hard metal parts by a bronze alloy, but according to investigations in this area performed by Maeda and Childs [4] impregnation does not lead to satisfactory abrasive wear resistance in compare to full density hard metal parts produced by powder metallurgy.

Laser sintering of preplaced powders has a lot in common with laser cladding of MMC. In a study, performed by Dubourg and St-Georges [5], coatings were made from a nickel-base matrix and WC with a volume fraction of 50 %. Authors of the study investigated the influence of the laser cladding parameters in CW mode on the geometry and composition of MMC coatings. In laser cladding of MMC the fraction of hard metal phase dispersed in metal matrix usually does not exceed 50 vol. %. Techel et al. [6] studied coatings microstructure and established the influence of partial carbide dissolution and formation of new hard phases on the hardness and wear behavior. High energy input during laser processing can lead to excessive heating of WC particles to forming brittle phase, which is drawback for MMC coating [7]. Thick WC-Co coatings can be deposited by thermal spraying as High Velocity Oxygen Fuel (HVOF), detonation spraying and also using direct metal deposition [8].

Comparing to powder metallurgy, laser sintering has much lower exposure time of local volumes at high temperatures, so the high density of hard metal parts might be achieved by steep increase in the temperature only. Unlike CW mode, lasers operating in short pulse mode can generate much higher peak power density of the order of GWcm^{-2} because the energy of a pulse is emitted over a short duration. The resulting effect on the material is instantaneous melting, vaporization and ionization of the expanded gas. The short pulse time and plasma generation lead to appearance of a heat-sustained shock wave that moves radially outwards from the interaction cite. The high pressure behind the shock wave exerts a comprehensive force on the material, known as evaporation recoil force. This compressive force has been shown by Morgan et al. [9] to result in modification of the melt pool shape, resulting in increasing of the material density. The authors also studied the effects of Q-Switch pulsing frequency, scanning speed and scan spacing on density of 316 L stainless steel cubic primitives. So the use of a short pulse laser in SLM of hard metal alloys can potentially increase the density and functional properties of sintered layers.

This paper reports on the phase composition, density, hardness and abrasive wear resistance of thin multilayer hard metal coatings deposited on steel by a short pulse laser sintering. The coatings were characterized with the use of optical, XRD and SEM

methods, measurements of the density, hardness and abrasive wear resistance tests at different conditions.

Experimental

Experimental Set-up

The experimental facility consists of an ytterbium fiber laser and a process chamber with controlled atmosphere. The chamber is initially evacuated by a backing pump and then filled with high purity argon at the pressure of 1.05 bar. The laser has maximum power of 50 W operating in a short pulse mode with the wavelength of 1.065 μm and the pulse repetition frequency in the range from 20 to 100 kHz. The powder feeding system allows building multi-layer coatings, but the microstructure and properties analysis was performed after deposition of each layer of the multilayer coating. A commercially available WC–20 wt.% Co mixture with an average grain size of 1 μm and an apparent density of 3.4 g/cm^3 was used as powder. The thickness of powder beds was set to 60 μm .

Energy Characteristics and the Scanning Strategy of the Laser Sintering Process

The laser chosen for laser sintering process has a pulse time of about several tens of nanoseconds which is much longer than the relaxation time for energy transfer from gas of valence electrons (which absorbs laser energy) to lattice of metal parts. So the action of laser energy on powders can be described mainly by thermal mechanism, but the pulse time is short enough to ensure the high rate of heating (about 10^7 K/s) and high temperature gradient (10^7 – 10^8 K/m) in the treated zone. These parameters were established by Kharanzhevskiy and Krivilyov [10]. The variation in process parameters had a significant effect on the material density. The influence of the pulse repetition frequency, scan speed, scan spacing and scan strategies on the density of multilayer coatings was investigated to obtain the optimal process parameters of laser sintering. Results of that preliminary study are summarized in paper [11]. It is shown that density and roughness of sintered layers can be improved by an appropriate choice of the processing parameters, which minimizes ‘balling effect’ and distortions due to thermocapillary forces which is good for post-processing. This work aims to study the phase composition and functional properties throughout a coating, composed of multiple layers with a number from 1 to 10.

The coatings were produced with the parameters listed in Table 1. The power was kept at the maximum value of 50 W at the pulse repetition frequency of 100 kHz. The laser beam was focused in a spot with the diameter of 30 μm . By the computer simulation of heat transport in porous media [12] it was established that such energy characteristics lead to local overheating of the powder bed up to the melting point of tungsten carbide (2870 °C). Due to the high temperature gradient in the irradiated area, a thin layer of the steel substrate with a thickness 10–30 μm has been melted. That makes the conditions of active mixing in the molten zone which lead to chemical interaction between tungsten carbide and iron and provides better adhesion strength between the coating and substrate.

Kruth et al. [13] found that both the appropriate process parameter adjustment and the application of special scanning strategy influence on resulting roughness, microstructure, density and mechanical properties. Our preliminary study [11] has shown that the best result in those terms was observed when an O-type scanning strategy which is shown in Fig. 1 was applied. The scanning speed of the laser beam V_b is in the fact the velocity of the beam motion along the circle of O-type track in Fig. 1. When the resulting scan speed V_S over the y-axis was 20 mm/s a laser-spot overlapping was characterized by the value of 70 % in x-direction and 53 % in y-direction. The scan spacing value Z is defined here as the distance between consecutive O-type tracks scanned by the laser. The scan spacing Z was chosen as a fraction of the width of the track. The width of the track was fixed in this study at the value of 200 μm . The complex motion of the laser beam with the beam speed of 0.9 m s^{-1} was performed by a scanning head with the use of integrated scanning mirrors. The scan speed V_S was set by the definite shift between consecutive rings of O-type track.

Wear Tests of WC-Co Coatings

The wear resistance of the WC-Co coatings (with 4 sintered layers) has been measured using two-pin pin-on-disk tribometer at different load conditions: (A) – in case of insufficient lubrication. The lubrication was filled with 50 vol% of alumina with the average grain size 5 μm ; (B) – in case of dry abrasive wear with silica sand abrasive which particles have the average size of 150 μm . The total load was 10 kg, giving a nominal contact pressure of 0.8 MPa. Number of loading cycles was $1 \cdot 10^5$ at the friction speed of 35 m/min.

Results

Microstructure Analysis

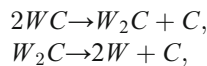
The results of X-ray diffraction study of coatings with different number of sintered layer in range from 1 to 10 are shown in Fig. 2. The diffraction patterns of WC-Co powder and steel substrate are also included in the plot. Figure 2 clearly shows deep changes in the phase composition of sintered coatings from layer to layer. Diffraction pattern taken from the first sintered layer (curve 01 in Fig. 2) demonstrates the high amount of alpha and gamma phases of iron. Peaks of these phases are more intense in compare to the peaks of WC and W_2C phases. Quantitative phase analysis of all the diffraction patterns was performed with the use of the Rietveld refinement method. According to the results, presented in Table 2, the first sintered layer has amount of iron phases about 80 % which is higher than the value obtained from SEM investigation. X-ray energy-dispersive microanalyses (EDS) gives the following concentration of elements on surface of the first layer: Fe-66; W-25; C-7; Co-2 wt.%. The overstated value of alpha-iron, obtained by XRD study, may be caused by a relatively small thickness of layer which results in penetration of X-rays into substrate giving influence on the result of the quantitative analysis. It is also should be noticed that EDS-analysis gives a surprisingly low content of cobalt in coatings. Absence of cobalt may be explained by the steep difference in the melting point of WC in compare to Co. Actually, the melting

Table 1 Parameters examined for production of coatings

Parameter	Examined values
Power (W)	50
Beam speed V_b (mm s ⁻¹)	900
Scan speed V_s (mm s ⁻¹)	20
Scan strategy	O-type
Scan spacing Z (μm)	200
Pulse frequency (kHz)	100

point of WC (2870 °C) is comparable to the boiling point of cobalt (2927 °C) which leads cobalt to evaporate actively.

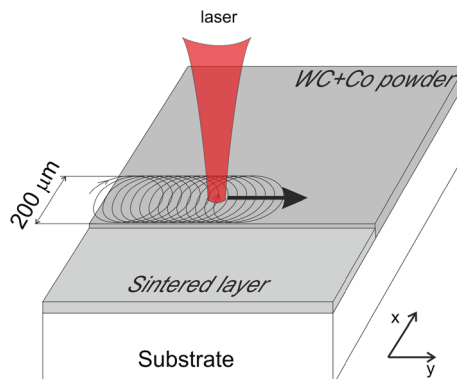
The diffraction patterns of all sintered layers have also peaks corresponded to W_2C cubic and hexagonal phases and traces of Fe_3W_3C phase. Their appearance indicates high temperature thermal decomposition of tungsten carbide corresponding to the reactions



and chemical interaction with Fe.

The increase in the number of sintered layers leads to the steep increase in quantity of tungsten carbide phases. As it shown in Fig. 2 and Table 2, after the 3rd sintered layer, α -Fe has only traces on diffraction patterns. The EDS-analysis confirms that result. The concentrations of elements on the surface of the fifth sintered layer are: Fe-5; W-75; C-13; Co-4 wt.%. After the fifth sintered layer the phase composition of coatings seems to be independent from the number of layers so after that point the coatings have stable phase content which fully consists from carbide phases.

The results of SEM-investigation of coatings lead to the following implications. Firstly, they show good quality of the coating with low amount of pores. Secondly, they enlarge the results of X-ray diffraction study that layers have a gradual changing in the phase composition from layer to layer as it was shown above. In Fig. 3a a general view

**Fig. 1** The scanning strategy

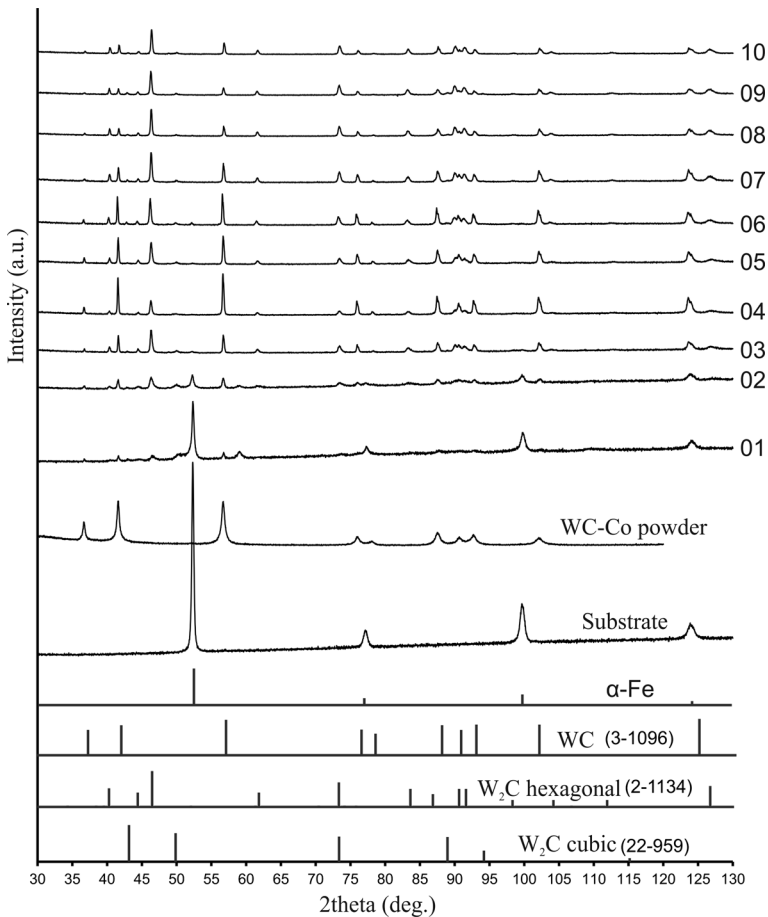


Fig. 2 Results of XRD study: the substrate, the WC-Co powder and sintered layers. Digits on the left of diffraction patterns correspond to the quantity of sintered layers of the multilayer coatings (JCPDS card numbers of phases are in brackets)

of the single layer coating is shown, wherein traces of the laser beam movement are clearly visible. Cylindrical-shape pores are rare and take not more than 1 % of the coating surface area. In Fig. 3b the surface area near a pore is shown in the phase contrast mode (by back scattering electrons). According to EDS-analysis light areas mainly consist from tungsten and carbon atoms whereas dark gray areas have about 70 wt.% of iron. The dark areas also contain large amount of needle shape microcrystallites which indicates high temperature in the irradiated area that is more than the melting point of iron during laser sintering process.

The increase in the quantity of sintered layers leads to the increase in porosity and microcracks appearance. Figure 4a shows the SEM-image of the surface after sintering of the fifth layer where several microcracks can be seen which formed due to the thermal stresses. The area of the surface near one of them is shown in Fig. 4b with higher magnification. In this area the large amount of the cubic-shaped crystallites are visible that can belong to a tungsten carbide phase only, which indicates extremely high temperature over the melting point of the tungsten carbide, formed during laser short

Table 2 Thickness, phase composition (wt. %) and theoretical density (TD) of multilayer hard metal coatings versus the number of sintered layers

Number of layers	Thickness, μm	WC	W ₂ C (hex)	W ₂ C (cub.)	Fe ₃ W ₃ C	α -Fe	γ -Fe	TD ^a , gcm^{-3}
1	21	8	9	3	1	63	16	9.6
2	39	19	24	4	4	42	7	12.1
3	54	39	48	7	2	4		16.1
4	66	67	28	3	2			16.0
5	74	53	38	5	2	2		16.1
6	91	48	39	9	2	2		16.2
7	109	41	48	11				16.6
8	137	32	57	10		1		16.7
9	167	27	56	14	3			16.6
10	195	39	50	8	3			16.4

^a by XRD phase composition

pulse processing. So the proceeding technique used in this study might be categorized as a Selective laser melting (SLM) method.

Results of density measurements are shown in Fig. 5. It is clearly seen that the increase in the coatings thickness influences the density. As it follows from the XRD phase analysis the decrease in the density of multilayer coating comes along with reducing the iron content in layers up to 4th sintered layer. After that point the phase composition became more or less stable which stabilizes the density of coatings at value of about 70 % TD. So we can conclude that gradual changes in the phase

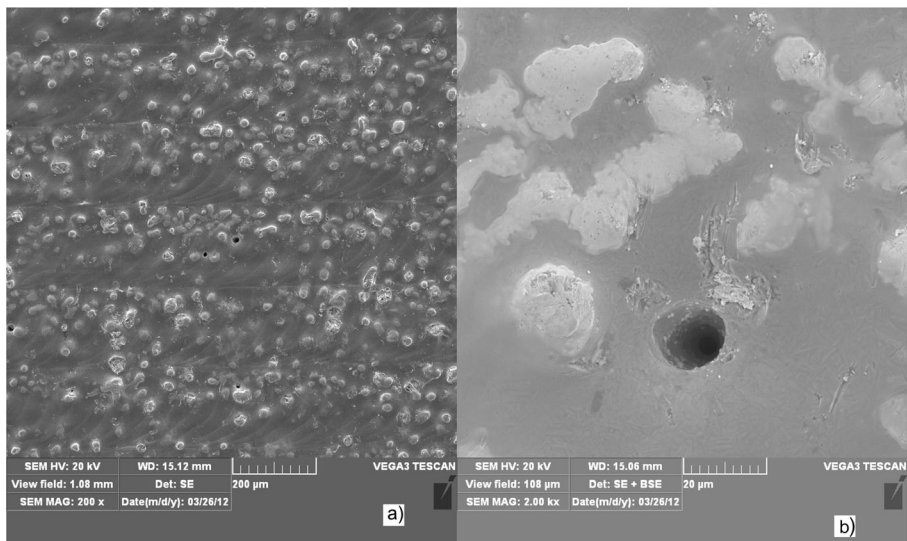


Fig. 3 SEM-micrograph images of the first sintered layer: **(a)**—the visual image of the surface in secondary electrons (SE); **(b)**—the composited image of the surface near a cylindrical pore in SE and back scattering electrons (BSE)

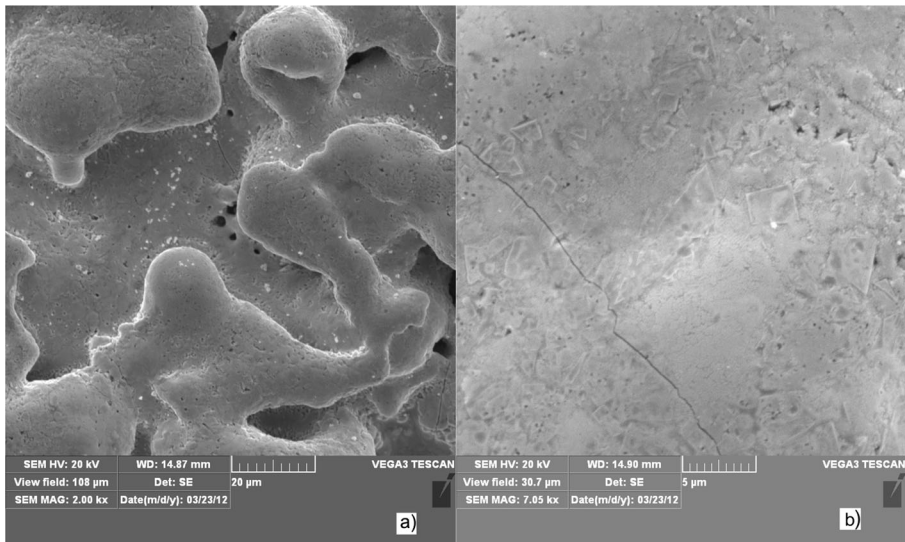


Fig. 4 SEM-micrograph images of the fifth sintered layer

composition and the porosity of layers are interrelated which influence on hardness of coatings.

Hardness of Multilayer Coatings

Results of Hardness measurements are shown in Fig. 6 in compare to the phase composition. Each point on the plot represents hardness of the surface produced with different number of sintered layers in range from 1 to 10. A step change in phase composition, as indicated by bars in Fig. 6, is responsible for steep hardness increases of first six layers with the peak value of 21 GPa. According to the investigations performed by Lakhotin et al. [1] the carbide WC and subcarbide W_2C phases have

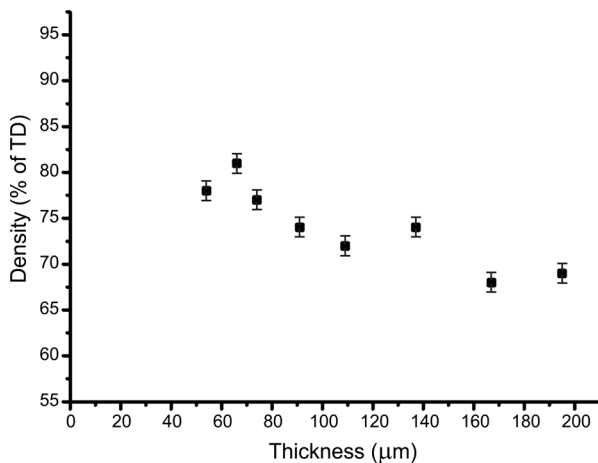


Fig. 5 Results of density measurements of hard metal multilayer coatings

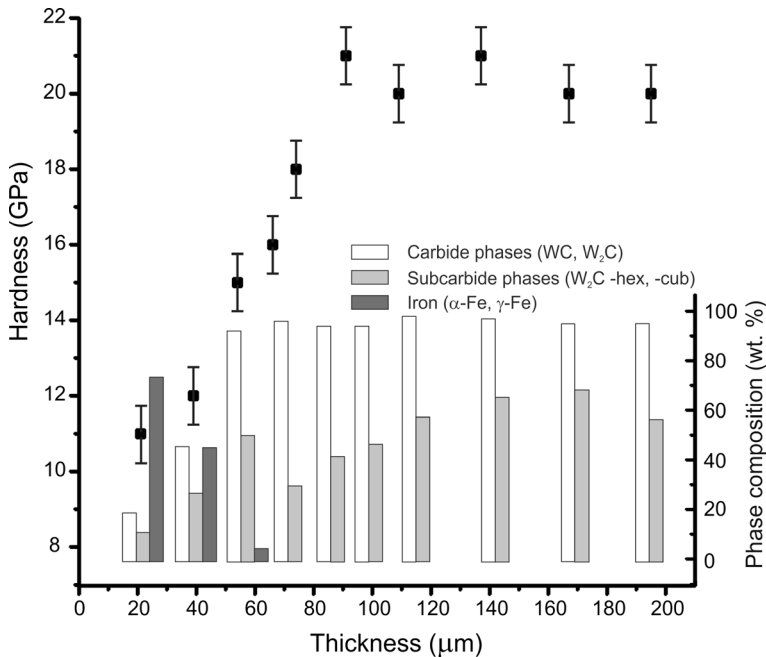


Fig. 6 Hardness of hard alloy multilayer coating. Hardness of each layer is shown by dots; bars under each dot present the phase composition of the layer

hardness of 24 and 35 GPa respectively. Comparing between the hardness and the phase composition of sintered layers from 3 to 6 leads to the reasonable conclusion that the quantity of W_2C phases (cubic and hexagonal) is responsible for layer hardness increases. And otherwise the remaining iron phases in layers from 1 to 3 are responsible for steep decrease in the hardness. Therefore, sintered in this study multilayer coatings have a gradient change in the phase composition and in the hardness.

Abrasive Wear Tests Results

Abrasive wear tests results of coatings with 4 sintered layers at loading conditions A (insufficient lubrication with alumina abrasive) and B (dry friction with silica sand abrasive) are summarized in Table 3. For comparison, Table 3 also shows the results of

Table 3 Abrasive wear resistance

N	Material	Density, % TD	Loading scheme	Deterioration, $\mu\text{m}^3/(\text{N}\cdot\text{m})$
1	Hard metal coating 4 layers	80	A	24
2	Compacted WC-10 %Co alloy	100	A	20
3	Steel Fe-0,45 %C	100	A	880
4	Hard metal coating 4 layers	80	B	55
5	Steel Fe-0,45 %C	100	B	2700
6	Compacted WC-10 %Co alloy	100	B	42

abrasive wear tests of parts made of hard metal alloy WC-10 % Co, produced by powder metallurgy, and steel Fe-0.45 %C parts, which were hardened and tempered to the hardness 45 HRC. According to the data in Table 3, properties of hard metal coatings are comparable with items made of compact hard alloy WC-10 % Co and considerably surpass wear resistance of parts, made of hardened Fe-0.45 % C steel. The main reasons for that are the high level of density, the hardness and the carbide phase content.

Discussion

It has been shown that the dense hard metal coatings can be produced by short-pulse laser sintering. The entire process may be described as a SLM technique, but the short-pulse mode gives very high power density which leads to the rapid temperature rise over the melting point of tungsten carbide. High temperatures and special scanning strategy allow to produce coatings with high quality in the terms of roughness, abrasive wear resistance, hardness and density. As hard metal powders are very expensive, their coatings should be smooth and have good properties. Roughness of sintered coatings can be reduced by an appropriate choice of the processing parameters, which minimizes ‘balling effect’ and distortions due to thermocapillary forces which is good for post-processing [11].

Thus, the short pulse laser sintering allows obtaining high-density gradient coatings with the gradual change in the phase composition and properties from layer to layer. First two sintered layers contain α - and γ -phase of iron giving good adhesion strength between the coating and the substrate, whereas the outer layers have high hardness because they are saturated by tungsten carbide and subcarbide phases. Determination of the adhesion strength between the coating and the substrate using a normal fracture method leads to the conclusion that the adhesion strength is more than the breaking strength of the coating. To demonstrate this property an image of a coating after a shock action by a sharp hard indenter with the kinetic energy of 2 J is shown in Fig. 7a. The kinetic energy is sufficient to break through the entire thickness of the coating, which was 120 μm , and cause the considerable plastic deformation of the substrate to depth of about 1 mm. As a result of the indenter penetration, there is a displacement of the considerable volume of metal towards to the edge of hole and to the surface of the

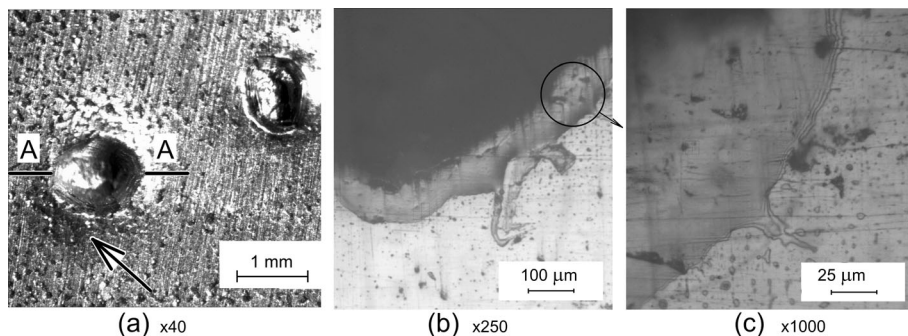


Fig. 7 Areas of plastic deformations of the coating with thickness 120 μm after indenters shock action. The *arrow* indicates the starting place of the plastic deformation in which the metal flows up from the surface

sample which may be described as a plastic flow of metal. It is clearly seen in Fig. 7a that such impact does not lead coating to have cracks or exfoliation. Contrariwise, the coating with hardness 20 GPa plastically deformed together with the substrate. The cross section, made in plane A-A of the impact zone, which is marked in Fig. 7a, clearly demonstrates this ability. Figure 7b shows, that there is no exfoliation of the coating, but microcracks in hard outer layers are registered. Such behavior might be explained by relatively softer inner layers, which gives good adhesion strength. Figure 7c shows appearance of periodic structures with a wave nature in the interface between the substrate and the coating, probably caused by severe plastic deformations during shock impact. An introduction of the indenter with the same kinetic energy into a substrate without coating gives deformation to depth of about 2 mm.

In our experiments, the laser power was set to the maximum value (50 W) but extremely high energy density was obtained due to short time of pulse (about 10 ns). Further decreasing time of a laser impulse may not lead to better density of the coating because there would be insufficient time for heat transfer from the irradiated zone which will lead to overheating of local area and sufficient evaporation of the material.

Conclusion

Our experimental results show the possibility of obtaining hard metal coatings by the process variant to Selective Laser Melting, using a laser, operated in a short pulse mode. The coatings have functional properties such as hardness and abrasive wear resistance which are comparable to the solid WC-10 % Co parts made by powder metallurgy. The hardness of the coatings achieves 21 GPa. Careful selection of processing parameters allows to form dense coatings with gradual change in phase composition. The coatings properties are characterized by the high adhesion strength to the substrate because of relatively soft inner layers, but very hard outer layers explain a high value of achieved wear-resistance. The presence of residual porosity does not allow using the coatings for cutting tools but the technique is efficient for parts which operate in abrasive wear condition with high contact pressure and shock loads. Results of investigation may be put into the commercial practice by coating of such parts as thread-rolling heads, punches, contact surfaces, rock augers, etc. After the fifth sintered layer, the phase composition and density became stable, which allows to use the processing technique for complex 3D objects manufacturing by layer-wise powder based process such as SLM.

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