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Effect of plasma sprayed and laser re-melted Al_2O_3 coatings on hardness and wear properties of stainless steel

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Abstract

Commercially available austenic stainless steel substrate was coated with commercially available, raw Al_2O_3 powder applied by means of plasma spraying method and then re-melted with CO_2 laser beam of various parameters. Tribological and mechanical properties of the 120J/mm and 160J/mm laser re-melted coatings were compared with the tribological and mechanical properties of the "as-sprayed" coating. The influence of the laser beam of various parameters on the microstructure, phase constituents, and mechanical and tribological properties of the ceramic coating was investigated by means of scanning electron microscopy, light microscopy, computer tomography , X-ray diffraction technique and nanoindentation tests. The micro sliding wear performance of the coatings was tested using a nanoindenter. The study showed an improvement of the mechanical and tribological properties caused by the laser treatment. The best results were achieved for coating re-melted with 120 J/mm laser beam.

Keywords: Laser treatment; Mechanical properties; Al2O3; Wear parts

1. Introduction

Nowadays, the austenitic stainless steels have been applied extensively due to their high corrosion resistance and machining ability. However, their further applications are greatly restricted by the poor tribological properties. Various methods, such as covering the steels and nonferrous alloys with ceramic coatings and films are employed to protect them against the abrasion and surface wear [1-6]. Ceramic coatings are widely applied for improving the resistance to corrosion, erosion, cavitation erosion and wear of different grades of steel and nonferrous alloys [6-16]. Currently, air plasma spray (APS) is one of the methods of manufacturing the Al_2O_3 coatings. However, these coatings are formed by successive impingement and interbonding of multiple splats. Their lamellar structure is heterogeneous with voids, intersplats and intrasplats cracks [17]. Such strongly heterogeneous structures resulting from the spraying process substantially influence the mechanical properties and must be taken into account when utilized. For example, fracture toughness and abrasive resistance or high temperature corrosion resistance may be reduced due to relatively high degree of porosity. In many circumstances, the products of the wear process are not allowed to penetrate the surrounding environment - for example, the hip implant's wear products must not be released into the patient's organism. Laser surface treatment is a promising method that can be employed to produce homogenous surface layer and to eliminate porosity. Laser re-melting of existing Al_2O_3 coating allows obtaining more homogenous surface layers which are less prone to spalling. Unfortunately, very limited research has been conducted to identify the influence of laser surface re-melting of air plasma sprayed Al_2O_3 coatings on their microstructural and tribological properties. Ibrahim et al. [18] reported that laser treatment plays a major role in modifying the surface morphology of the coating, followed by the pulse repetition rate. Their metallographic observations demonstrated that the microstructure of the laser treated surface is composed mainly of nanometre – sized γ - Al_2O_3. In turn Iwaszko et al. [19] concluded that such treatment causes growth of the share, or the appearance of the most metastable and hard α - Al_2O_3 phase without negative effects such as cracks or reduction of the adhesion to substrate. Another advantage is the possibility of obtaining a very thick layer (several hundred micrometres) as compared to PVD and CVD layers containing a hard phase of aluminium oxide. Li et al. [20] also reached similar conclusions. Wang et al. [21] reported that the lamellar defect of the as-sprayed coating was erased, and the compactness of the coating was improved significantly after laser re-melting. According to them, there are still some nanoparticles remaining after laser re-melting of Al_2O_3 – 13% wt. TiO_2 coating because of an insufficient time for the growth of grains. In turn, the investigations undertaken by Li et al. [22] revealed that laser re-melted Al_2O_3 – 13% wt. TiO_2 coatings exhibit more compact and homogenous structure as well as strong metallurgical bonding to the substrates. The results they obtained indicate that the dominating metastable γ-Al_2O_3 phase in the as-sprayed coatings transforms into stable α-Al_2O_3 after laser re-melting. The transition of the γ form into the α-Al_2O_3 leads to the occurrence of approximately 10% contraction as a result of density differences between both α and γ forms. This phenomenon can lead to the decrease of durability and protective properties of laser re-melted coatings [23]. Laser re-melting of plasma sprayed Al_2O_3 – 13% wt. TiO_2 also increases the hardness from 700–1000 HV0.3 to 1100–1800 HV0.3 [22]. With the decrease of the laser scanning velocity, the micro hardness is increased. Also Wang et al. [24] reported that laser re-melting of plasma sprayed nano-structured Al_2O_3–TiO_2 coatings causes an increase of hardness;

the increase of the laser power translated into the increase of hardness. In another work, Wang et al. [25] concluded that after laser re-melting of the same kind of coatings, the average porosity was reduced to 0.9%, compared with the average porosity of 6.2% in the case of the as-sprayed coatings. Furthermore, significant decrease in surface roughness was also found in the laser re-melted coatings. In turn, Sure et al. [26] reported that the surface morphology of a laser melted coating showed that inhomogeneities are reduced, however, a network of cracks was formed regardless of the power density. Iwaszko in [23] showed that weight loss in abrasive wear test of laser re-melted Al_2O_3 – 13% wt. TiO_2 coatings is six times lower than in the case of the non-remelted coatings.

In the process discussed in this paper, commercial Al_2O_3 ceramic coatings applied onto the stainless steel by means of plasma spraying were re-melted by CO_2 laser. Laser re-melting was used to improve the bonding strength, fracture toughness and compactness as well as fretting resistance of the plasma sprayed Al_2O_3 coatings. The purpose of this work is to investigate the effects of re-melting the as-sprayed coatings with various parameter laser beam on the tribological and mechanical properties of the coatings.

2. Experimental procedure

2.1. Substrate material

A X5CrNi18-10 austenitic stainless steel was chosen as the substrate material. The chemical composition (wt%) of the substrate material is as follows: 0.031 C, 18.49 Cr, 8.01 Ni, 0.372 Mo, 1.98 Mn, 0.67 Si, 0.030 P, 0.020 S, while Fe constitutes the remaining balance. The specimens with a diameter of 32 mm and thickness of 12 mm (see Fig. 1) were made using a lathe.

2.2. Plasma spraying and subsequent laser re-melting

Air plasma spraying was used to apply the commercially available pure Al_2O_3 ceramic coatings on the X5CrNi18-10 austenitic stainless steel substrates. The samples were grit blasted, using 250 μm Al_2O_3 grit (EB-12 corundum) at a pressure of 0.5 MPa in order to improve the adhesion of the sprayed coating to the substrate. The plasma spraying was performed using a PS50M installation which included PLA5000 gun, 2007MF-PF powder feeder and PS50M DIPS power supply. The commercially available 80/20 NiAl powder was plasma sprayed on the treated substrate. The NiAl coating was used as a bonding coat to provide a rough surface for mechanical bonding of the top coat. A mixture of Ar and H_2 was used as the plasma gas and the air was used as the particle carrying gas. The parameters of plasma spraying were as follows: current – 500 A, voltage – 80 V, primary Ar gas pressure – 0.4 MPa, secondary H_2 gas pressure – 0.4 MPa, Ar gas flow rate 0.83 dm^3/s, H_2 gas flow rate – 0.17 dm^3/s, powder feed rate – 0.33 g/s, spray distance – 110 mm. The particle size of the Al_2O_3 powder was in the range of 20 to 40 μm. The total thickness of the both of the as-sprayed coatings was approximately 300 μm, with the thickness of the Al_2O_3 layer was approximately 150-170 μm. Next, the as-sprayed flat coatings were re-melted by means of pulse wave CO_2 laser with the maximum output power of 1750 W. During the laser re-melting, a continuous flow of Ar was supplied to the melted zone to prevent the oxidation. Laser re-melting consisted in making a single path (see Fig. 1). A constant laser spot diameter D = 3 mm at the surface of the treated coatings was adopted during laser re-melting.

Focal length of focusing lens was L = 200 mm. Laser beam pulse duration was 2 ms and pause between the pulses was 1 ms. Different sets of parameters of the laser beam were employed during laser re-melting. The power of the laser beam was in the range of 610 W to 800 W and the velocity of the laser beam was in the range of 4 mm/s to 8 mm mm/s. Two samples were selected to examine the tribological properties. One sample, designated as HP, was re-melted with the power of 800 W and a scanning velocity of the laser beam of 5 mm/s, while the second sample, designated as LP, was re-melted with the power of 600 W and laser velocity of 5 mm/s. Tribological properties of the laser re-melted coatings were compared with the tribological properties of the as-sprayed coating. The sample with the as-sprayed coating was designated as the R (reference) sample.

2.3. Characterization

The microstructure of the coatings before and after laser re-melting was examined with the aid of X-ray diffractometer (XRD, with Cu Kα radiation λ=0.15418 nm), scanning electron microscope (SEM, JOEL JSM-7800F) equipped with X-ray energy-dispersive spectroscopy (EDS), CT-scanner (phoenix v/tome/x s 240 kV) and light microscope (LM, Leica) respectively. Computer Tomography (CT) parameters were as follows: voxel size 4,99 µm, voltage 110 kV, current 100 µA, detector type dxr-250 rt. Microhardness of the as-sprayed and re-melted coatings was measured with NanoTest Vantage nanoindenter . Hardness test was performed to determine the qualitative residual stresses in the melted paths and in the as-sprayed coating. Qualitatively residual stresses were identified by the work of elastic deformation to be established in the hardness test. Hardness tests were performed for the loads in the range of 1 N to 15 N. Berkovitch indenter was used in the hardness investigations. Loading and unloading rates were 50 mN/s. Indentation involving one cycle with 5 s dwell at maximum load Nanoindenter was also used for fretting and scratch tests. Fretting tests were performed for the load equal to 250 mN, at frequency of 1 Hz, and the duration of 240 min. The vibration amplitude of the conical diamond tip with 5 μm diamond tip radius was 1000 nm. The same diamond tip was used for the scratch test. The parameters of scratch tests were as follows: scratch load – 0 - 6000 mN, loading rate - 40 mN/s, scan velocity - 3 μm/s, scan length - 500 μm.

3. Results and discussion

3.1. Microstructure and phase composition of the as-sprayed and laser re-melted coatings

Table 1 presents the results of the measurements of the thickness of the re-melted coatings depending on the parameters of the laser beam applied.. The thickness of the re-melted coatings was measured in the cross sections of the metallographic specimens. It clearly seems that the thickness of the re-melted coatings becomes larger when the laser power increases and the velocity of the laser beam decreases. . The best quality of the surface of the re-melted coatings was obtained using a laser beam velocity of 5 mm/s. Therefore, samples number 5 and 7 were selected for further tests. Sample No. 5 was designated as HP and sample No. 7 was designated as LP. Comparative coating was the as-sprayed coating and it was designated as R sample. The depth of re-melting both HP and LP samples was lower than the thickness of the as-sprayed Al_2O_3 coating. Fig. 2 shows the digital micro-photograph of the cross section of the HP sample. Columnar crystals zone is visible in the re-melted surface layer. The non-re-melted Al_2O_3 coating is under this layer and NiAl coating at farther distance from the surface is visible. The microstructure of the LP sample was similar; the difference consisted in the re-melting depth. Fig. 3. presents the light microscope (LM) image of the microstructure of the surface of the HP sample. Microstructure of the laser treated samples consisted of fully melted regions and non-completely re-melted areas. As is apparent from Fig. 3, fine, nearly equiaxial and polygonal type grains are formed during the re-melting process. The range of the grain size is 3.0–14 μm. Laser treatment leads to high speed heating and melting, followed by a rapid solidification process. Non-melted particles of Al_2O_3 acted as nucleation sites during rapid solidification process that resulted in non-directional growth of crystals. The laser melting of Al_2O_3 process resulted in obtaining fine equiaxial grains distributed homogeneously. In order to determine the compactness of the coating structure, CT scans were performed before and after laser re-melting. Fig. 4. presents the examples of CT scans of the surface layers after spraying (Fig. 4a) and after spraying and laser re-melting (Fig. 4b,c). Then, defect detection was made on an area of approximately 2.5 mm^2 using the Volume Graphic Studio software. The results of the detection are shown in Fig. 5. As is apparent from the histograms shown in Fig. 5, both the number of defects and their volume have been significantly reduced as a result of laser re-melting, but only in case of the LP sample. 2430 defects were found in the as-sprayed coating and their total volume was 47276,58 x 10^{-6} mm^3. The average volume defect calculated for this sample is 19.46 x 10^{-6} mm^3 per a defect. By comparison, the number of defects in a LP sample was only 605 and in HP sample - 2141. The average volume per defect was 4.08 x 10^{-6} mm^3 in LP sample and 22.21 x 10^{-6} mm^3 in HP sample. According to the results of CT tests, laser treatment of Al_2O_3 coatings enabled the erasing of the lamellar defects of the plasma-sprayed coating but only in case of the LP sample (120 J/mm). The increase of the heat input to 160 J/mm (sample HP) causes the formation of pores and it does not contribute to an increase in the density of the structure. Fig. 6 shows the X-ray diffraction patterns of the as-sprayed coating and laser-treated coatings . In the as-sprayed coating, the peaks of α-Al_2O_3 and γ-Al_2O_3 are indexed. Additionally, the presence of θ-Al_2O_3 is demonstrated in coatings after laser re-melting. The XRD analysis has shown that the as-sprayed coating contains α-Al_2O_3 as major phase and γ-Al_2O_3 as minor phase. The intensity of α-Al_2O_3 (113) peak, which is the main peak of α-Al_2O_3, decreases by about 10% as a result of laser re-melting, and the intensity of other peaks of alpha phase increases at the same time. On the other hand, the intensity of the main γ-Al_2O_3 peak (400) decreases, and intensity of other peaks of gamma phase decreases or remains unchanged at the same time. This is attributable to the fact that the metastable γ-Al_2O_3 phase in the re-melted region was partially transferred into stable phase of α-Al_2O_3. Wu et al. [27] and Ramachandran et al. [28] also reported that the volume fraction of fully melted regions which composed mainly of metastable γ-Al_2O_3, does not increase due to the laser re-melting. Laser re-melting also causes changes in the proportion of crystallographic directions of the alpha phase. Half-width of the peaks in the diffraction pattern of the as-sprayed coating is almost the same as in the case of the two laser re-melted coatings. This means that the grain size has not changed in the result of laser re-melting process.

3.2. Hardness measurements

Hardness measurements were made applying different loads, in order to determine the local and global properties. Fig. 7 presents the changes in hardness as a function of load. As can be seen from Fig. 7, hardness decreases with the increasing load. The maximum depth of indenter penetration, for the load of 15 N, did not exceed 30 µm in case of the as sprayed coating, while the maximum penetration depth for the re-melted LP and HP coatings was less than 13 and 8.5 µm respectively. The influence of the substrate on the results of the hardness test is negligible since the thickness of the re-melted coatings was greater than 90 µm. Three main types of hardness can be identified in the Fig. 7. Local properties can be observed for low depth of the indentation and load of 1 N. The HP re-melted coating exhibited the highest local hardness of 39.27 GPa. Local hardness of the re-melted LP coating was 24.03 GPa and the hardness of the as sprayed coating at the same load was only 5.49 GPa.

There is an increase of the global hardness for both types of the re-melted coatings. This phenomenon is caused by the increase of the compactness and the decrease of the number of defects after the laser treatment. In order to explain the increase of the local hardness of the re-melted coatings, the graph analysis of the load vs. intender displacement was performed. These graphs were registered during the hardness tests. In the course of the hardness measurement, the indenter performs the work needed for elastic and plastic deformation of the tested material. The work of the elastic deformation (W_{el}) is defined as the area under the unload curve as shown in Fig. 8. W_{el} can reflect the residual stresses in the investigated material. Such a relationship is of qualitative nature, rather than quantitative. Fig. 8 shows the load curve vs. the depth of the intender for the laser treated and the as sprayed coatings. The hardness measurements were performed for the maximum load of 1 N. W_{el} for the as sprayed coating was 38.8% of the total work performed by the indenter, whereas the W_{el} for the re-melted coatings was 43.6% and 42.9% for the LP and HP sample respectively.

This means that laser processing introduces significant residual stress to the treated surface layer which leads to the increased local hardness after the laser treatment.

3.2.1. Fracture toughness

The indentation fracture (IF) method was used to calculate the fracture toughness of the re-melted coatings. The IF method derives from the experimental procedure that is commonly followed in hardness tests. This method consists in relating the toughness of the material to the lengths of the cracks growing in the corners of the Berkovich indentation when a load (P) is applied. The test was performed on the laser treated surfaces and did not require large scale specimen preparation and precracks to be introduced. The method relies upon an optical measurement of the crack size. Cracks usually appear at the corners of the residual impression in brittle materials. Fig. 9 shows radial crack pattern from Berkovich indenter. There are a number of equations that can be applied to calculate K_{Ic} by IF method. The equations applied to calculate K_{Ic} can be divided into two groups: empirical and experimental. One of the most popular equations among the experimental group is the equation proposed by Dukino and Swain [29].

Knowing the Young's modulus and hardness, the fracture toughness K_{Ic} can be calculated using the formula [29]:

$$K_{Ic} = 1.073(0.015)\left({}^{a}/{}_{l}\right)^{1/2}\left({}^{E}/{}_{H}\right)^{2/3}\frac{P}{c^{3/2}} \qquad (1)$$

where:

E – Young modulus,

H – Hardness,

P – Maximum load during indentation

a, c, l – geometrical sizes presented in Fig. 9

Figs. 10-11 present micro-photographs of the re-melted surface coatings after indentation test and Table 2 shows the sizes required for the fracture toughness calculation and the results of the calculations. The Young's modulus was calculated from the load–depth plot. The indentation test did not allow the designation of fracture toughness for the as-sprayed coating, because there were no visible radial cracks. The indentation test was performed for the load equal to 20 N to determine the global fracture toughness of the tested coatings. Berkovich indentations presented in Figs. 10 and 11 show that the cracks are emanating from the corners of the indentation in Al_2O_3 coatings re-melted by laser beam. The zigzag of the crack path as can be seen in Figures 10b and 11b indicates the crack propagation with associated crack deflection. Cracks presented in these figures reveal the mode of crack propagation. As can be seen in Fig. 10b, the crack propagation for the LP sample is intergranular in nature, indicating that the crack deflection is the predominant mechanism for the higher toughness (7.04 MPa · $m^{1/2}$) resulted in this sample. This fracture toughness is about 40% higher than the fracture toughness of Al_2O_3 ceramics prepared by solid state sintering [30] and it reaches the value as for the Al_2O_3–30 vol % $TiN_{0.3}$ composite [31]. In turn, the mixed nature of crack propagation is detected in the HP sample (see Fig. 11b). It is mainly intergranular but also transgranular mode can be seen. The lower fracture toughness of this sample (0.95 MPa · $m^{1/2}$) is also due to the increased number of pores present in the microstructure of the sample. Fig. 11b presents a crack that connects the surface pores. The increase in porosities could possibly worsen the interfacial load transferring capacity of the system, hence, deteriorate the fracture toughness of the HP sample coating. Additionally, the residual stress in the laser treated samples that develops in the course of the cooling process after the laser re-melting, generates small cracks affecting the fracture toughness of the materials [32].

3.3. Micro scratch testing of the coatings

During micro scratch testing (MST) a conical diamond tip was drawn across the coated surface with an increasing load, resulting in various types of failure at specific critical loads. MST identifies critical loads optically using a microscope. These critical loads were used to quantify the adhesive and cohesive properties of the re-melted coatings. In addition, failure points were determined using frictional force and depth measurements.

Figs. 12-15 show the scratch test results of the Al_2O_3 coatings. Each coating was tested under the progressive load of 0 mN to 6000 mN . The depth of the indenter vs. normal load for all the investigated coatings is plotted in the Fig. 12. The results are the arithmetic mean of three measurements. The results reveal that with the increase of the load, the indenter penetration of the surface of the coatings is greater. The greatest depth of the indenter penetration was shown in the R coating and the smallest in HP coating. LP coating shows minor depth of the path with the increment of load. These results seem to be obvious from the point of view of the hardness of the coatings. The higher is the global and local hardness of the coating, the value of the indenter penetration is lower. Additionally, the lamellar structure of the “as sprayed” coating easily collapses under the normal load due to subsurface pores, increasing the penetration depth. In turn, the friction force changes plotted as a function of path distance for the investigated coatings are presented in Figs. 13-15. As clearly results from Figs 13-15, the friction force increases with the distance made by indenter, that is, with the increase of the load on the intender. Evolution of the friction coefficient for Al_2O_3 ceramic under increasing normal loads is also reported in [33]. It was found that friction forces varied over a considerable range during the scratch test for all tested samples. The friction force tended to follow a complex series of changes before reaching a steady-state condition. This steady-state condition was not reached in scratch test. Variations of frictional force were due to the plastic yielding occurred on top of the asperities of coating. Fluctuations in friction force are also observed because of the composition and microstructure of the coatings varied through the coating depth. The friction force across different normal loads for all coatings was within the same range. The greatest changes of the local value of friction force have been exposed for the "as sprayed" coating. This is due to high porosities and low hardness of this coating. The increase of the frictional forces during the scratch test due to the increase of porosity of Al_2O_3–TiC nano-composite sintering by spark plasma was also reported by Kumar et al. [33]. Scratching behavior of the coatings was identified using a scanning microscope. SEM investigation revealed the interaction between the scratch load and damage observations. Critical normal loads that occurred during the scratch test are presented in Table 3. Damage mechanisms are different for all the investigated coatings. Material of the coatings undergoes degradation under the moving tip. Angular cracks and delaminations are observed at the scratch groove edge. These defects are the result of the occurring stress. The resultant stresses around the moving tip are superposition of the internal residual stress due to coating process, compressive stresses due to the friction in front side of the sliding tip and tensional stresses in the trail of the sliding tip [34]. Scratch profile observations revealed that scratch width was consistent along its entire length for all the investigated coatings. Such a relationship indicates the overall deformation in the bulk of the scratch groove. For the “as sprayed” coating, the track shows ductile behavior of the coating. First delamination was observed at low load equal to 1119 mN due to the presence of surface open porosities and low hardness. This delamination occurred along the whole scratch path made at higher loads. First cracks appear simultaneously with the occurrence of the delamination. Sudden changes in the groove width, probably due to collapsing of subsurface pores along the scratch path, were observed for the load equal to 2113 mN. The hardness of the laser treated coatings is significantly higher indicating that the phenomena occurring during the travel of indenter on these coatings are different than in the case of the “as sprayed” coating. Greater hardness of these coatings results in the higher resistance to the indenter. This in turn causes the changes in the mode of deformation from ductile to brittle. Contrary to the “as sprayed” coating, another mechanism of degradation during the scratch test was observed for the HP coating. The first angular edge cracks appeared at low normal load equal to 350 mN. The cracks were caused by low fracture toughness of this coating. Delaminations appeared at higher loadings. First delamination was observed at 2794 mN. Only the part of the groove showed delamination at larger loads. The high resistance to delamination of the HP coating was related to the high hardness and a smaller number of pores per 1 square unit as compared to the “as sprayed” coating. Laser processing could have also introduced beneficial compressive stresses which contributed to the higher delamination resistance. There were no visible changes in the groove width due to collapsing of subsurface pores along the scratch path for both the HP and LP coatings. This may indicate that the laser processing increased the compactness of the coating and reduced the degree of porosity of the structure. In turn, for the LP coating, delamination occurred for the first time at lower loads and the angular crack appeared only at higher normal loadings. Critical load for delamination was 1491 mN and for the angular crack it was 2548 mN respectively. In the case of laser-treated coatings, the value of the load at which the first angular crack occurs is higher for the LP coating. This is due to the fact that LP coating has greater fracture toughness than HP coating. Also, the smallest degree of porosity of the structure of the LP coating contributed to the greatest critical load at which angular cracks appeared. Larger residual stresses due to the LP coating processing could also contribute to this, if their nature was compressive.

3.4. Micro-fretting behavior of coatings

The nano-fretting mode allows investigation of fretting and reciprocating wear at the micro/nano-scale. The micro fretting tests were performed for 14,400 cycles. The vibration amplitude of the conical diamond tip was 1000 nm and the normal load was 250 mN. The course of micro fretting wear as a function of number of cycles for all tested coatings is presented in Fig. 15a. As shown in Fig. 15a, the greatest wear was shown by the “as sprayed” coating. Wear expressed by the average depth groove of the coating amounted to 12.5 µm. After the same time, the worn track section of the LP and HP coatings was similar and amounted only to 3.5 µm. Also, the length of the worn track sections for these coatings was less than that of the “as sprayed” coating. The length of the worn track sections for the “as sprayed”, LP and HP coatings was 1153 nm, 231 nm and 401 nm respectively. Taking into account the length and depth of the worn section, the LP coating suffered the smallest volume loss . The product of the length and depth of the groove for the “as sprayed”, LP and HP coatings was 14.4 μm^2, 0,81 μm^2 and 1,40 μm^2 respectively. Coatings wear mechanisms can be traced in double logarithmic scale graphs (see Fig. 15 b,c,d). Two different mechanisms of micro fretting wear occurred for each of the coatings. Low cycle and high cycle micro wear mechanisms can be defined. There is a linear relationship between the depth wear and the number of cycles in a log*(d)*-log*(N)* scale for both mechanisms of destruction. The following equation can be used for the both mechanisms of destruction: $d = C \cdot N^a$, where d is the depth of wear, N is the number of cycle, and C and a are the constants. Constant a also expresses the wear rate of coatings. All values of the micro fretting wear parameters are presented in Table 4. The “as sprayed” coating has the longest period of the low cycle destruction (N = <1, 358> cycles) and the highest wear rate in the initial period of degradation (a = 0.489). This is due to the lowest local hardness of the coating. Probably, the abrasive wear dominates the fretting wear mechanism in the initial period of degradation for all the investigated coatings. The mechanism of destruction becomes different over 358 cycles. Sliding wear begins to dominate in the second period of the wear. The wear rate is much lower (a = 0.177) and it is even lower than the wear rate of the LP coating during its high cycle degradation (a = 0.206). The HP coating exhibits almost the same high wear rate in the early stage of destruction as the “as sprayed” coating (a = 0.459), despite having the largest local hardness. This fact indicates the presence of another mechanism of destruction for this coating. Probably the abrasive wear mechanism is associated with low fracture toughness of the HP coating. In turn, the LP coating with relatively high local hardness and the best fracture toughness practically shows no wear to 100 cycles (a = 0.009). However, the wear rate is higher than for the HP coating (a = 0.206) after this incubation period. Further studies are needed to provide the detailed understanding of the micro fretting wear mechanisms of the investigated coatings.

4. Conclusion

The commercially available austenitic steel substrate was coated with the raw, commercially available Al_2O_3 powder and was subsequently re-melted with CO_2 laser beam of various parameters. The following conclusions were reached after conducting the research:

1. The microstructure of the coatings varied with parameters of each laser treatment and in relation to the ”as sprayed” coating. Laser treatment enabled the erasing of the lamellar defect of the processed coating. The best results were obtained for the LP coating (120 J/mm). The increase of the heat input to 160 J/mm (HP sample) causes the formation of pores and it does not contribute to the significant increase of the density of the structure. At the same time, the contribution of metastable γ-Al_2O_3, did not increase due to the laser re-melting.
2. The global hardness increases for the both of the re-melted coatings. This was caused by the increase of the compactness and the decrease of the number of defects after laser treatment. Laser re-melting also caused the increase of the residual stresses. The LP coating revealed the highest residual stresses as a result of its processing.
3. Higher fracture toughness (7.04 MPa · $m^{1/2}$) was observed for the LP coating. Intergranular crack propagation is the predominant mechanism for higher toughness resulted in this sample.

4. The values of the critical normal loads measured during the scratch test were much higher for the laser treated coatings as opposed to the “as sprayed” coating.
5. Low and high cycle mechanism of micro fretting occurred for each of the coatings. There is a linear relationship between the depth wear (*d*) and the number of cycles (*N*) in a *log(d)-log(N)* scale for both mechanisms of destruction. During fretting tests, the LP coatings suffered the smallest volume loss.

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Figure caption:

Fig. 1. Scheme of the sample used in investigations

Fig. 2. Cross-section of the HP sample surface layer. SEM. 1 – re-melted columnar crystals zone, 2 – not re-melted Al_2O_3 zone, 3 - NiAl coating

Fig. 3. Microstructure of the HP sample. Fully melted region contains fine equiaxed grains of Al_2O_3. Not completely re-melted areas, depicted by arrow, are also visible. LM

Fig. 4. CT scan of the surface layer of the as sprayed sample – (a), of the LP sample – (b) and of the HP sample – (c)

Fig. 5. Histograms of the defects detected in surface layer of the as sprayed sample – Fig. a, for LP sample – Fig. b and for HP sample – Fig. c

Fig. 6. XRD diffraction patterns: (a) the as-sprayed coating; (b) the laser re-melted LP coating; (c) the laser re-melted HP coating

Fig. 7. Hardness changes of the Al_2O_3 coatings as a function of the load

Fig. 8. Load vs. depth of indenter for laser re-melted Al_2O_3 coatings and as sprayed coating

Fig. 9. A schematic indentation pattern from Berkovich indenter with radial cracks

Fig. 10. Indentation after hardness testing for LP sample (a) and an enlarged view of one crack path depicted by black arrow (b). SEM

Fig. 11. Indentation after hardness testing for HP sample (a) and an enlarged view of one crack path (b). SEM

Fig. 12. The depth of the indenter vs. normal load for all investigated coatings

Fig. 13. Friction force as a function of distance traveled by the indenter and appearance of the groove for “as sprayed” coating

Fig. 14. Friction force as a function of the distance travelled by the indenter and groove outlook for LP coating. Angular crack with delamination is depicted by the arrow

Fig. 15. Friction force as a function of the distance travelled by the indenter and groove outlook for LP coating. Delamination is depicted by the arrow

Fig. 15. Fretting wear as a function of the number of cycles for all investigated coatings – (a) and the same relationship in double logarithmic scale for the “as sprayed” coating – (b), for the LP coating – (c) and for the HP coating – (d)

Table 1. Effect of laser treatment on the thickness of the re-melted coatings

No.	Power P [W]	Velocity v [mm/s]	Thickness of the re-melted layer t [µm]
1	790	6,7	90
2	610	6,7	70
3	790	5,3	115
4	610	5,3	86
5	800	5	120
6	700	8	60
7	600	5	90
8	700	4	110
9	700	5	100
10	700	5	100
11	700	5	100

Table 2. Fracture toughness of the re-melted Al_2O_3 coatings and data for their calculation

Coating code	Radius indentation a [µm]	Crack length l [µm]	Load P [N]	Hardness H [GPa]	Young's modulus E [GPa]	Fracture toughness K_{Ic} [MPa·m$^{1/2}$]
LP sample	48.55	8.81	20	2.33	18.89	7.04
HP sample	32.80	61.00	20	3.84	26.64	0.95

Table 3. Critical normal loads measured during scratch test

Coating code	Critical normal load [N]					
	Angular crack		Delamination		Collapse	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
R	966	303	1119	256	2113	438
LP	2548	183	1491	80	-	-
HP	350	67	2794	364	-	-

Table. 4. Values of the micro fretting wear parameters

Coating code	Number of cycles [N]	Constant [a]	Constant [C]
R	<1, 358>	0.489	356.5
	(358, 14400>	0.177	2235.5
LP	<1, 100>	0.009	608.4
	(100, 14400>	0.206	493.4
HP	<1, 100>	0.459	202.5
	(100, 14400>	0.126	941