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Characterisation of the laser-clad stellite layers for protective coatings

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Abstract

Stellite layers produced for protective coatings in a direct process by laser remelting of the powder SF6 on plates of a high-temperature resistive alloy in Ar environment are investigated experimentally. Microphotographs and EDS analysis reveal a metallurgical bond between the substrate and coating as well as the structural homogeneity along the depth of the layer which is characterised by a chemical composition close to that of the powder. The laser-clad layers show a dendritic and fine-grained structure with a minor presence of impurities. For the coatings an improvement of mechanical properties in comparison to the base material such as the behaviour in wear resistance comparable to that of TiN and values of microhardness up to approximately 1000 HV are observed. On the other hand, corrosion properties depended on the defects and appeared on the surface as a result of the laser process parameters.

Keywords: Stellite; Laser melting; Properties

1. Introduction

The laser remelting of metal powders applied for protective coatings and also for reparation of machine parts was extensively studied in the last decade. High quality surfaces of controllable geometry can be obtained by this method while achieving the required mechanical properties and microstructure of the layers due to the effective combination of CAD/CAM design techniques with CNC controlled laser workstations [1–3]. The cw and pulsed laser sources allow for an optimised choice of the interaction parameters for a given material (base + powder) in several iterative steps. The optimisation can be supported by calculations of these parameters based on semi-empirical models where physical constants of materials and data characterising the laser interaction process are applied [4,5]. A growing interest in applications of these techniques is observed in areas where the economic impact due to material loss and degradation can be markedly improved by the cost-effective surface coatings. In particular, layers prepared by laser cladding are useful for reparation of local defects as well as for protection of the substrate material against, e.g. damages which are due to the severe working conditions and represent a serious problem of the steam turbine industry [6].

In this work the properties of the protective coatings of Stellite made by laser cladding are reported. Coatings are produced by means of an experimental device for laser remelting of metal powders. A martensitic stainless steel is utilised as a substrate. Results of sample examination obtained by optical and scanning microscopy and also by the EDS chemical analysis are presented. Moreover, the data characterising both the

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corrosion and wear resistance and also the micro-hardness are discussed.

2. Experimental

Coatings were produced by means of the 1.5-kW cw CO_2 laser stand equipped with the numerically controlled XYZ manipulator. The laser beam of 18-mm diameter was focused by the lens optics (ZnSe, $f = 127$ mm) integrated into the processing head (see Fig. 1). The beam spot of diameter 1 mm measured on the processed surface was kept constant. The applied beam intensities were equal to approximately 10^5 W/cm^2 and the laser output was controlled with an accuracy of $\pm 2\%$.

For the powder injection into the processing zone, a multi-stream, water-cooled nozzle mounted co-axially with the focussing optics and supplied by an injector-type powder feeder was applied. Ar flow was used to force the powder transport. The powder feed rate was controlled in the range of 0.05–0.33 g/s. Two additional Ar streams were used for shielding of the focussing optics and also of the interaction zone in order to prevent the production of oxides and avoid clad contamination due to the contact with surrounding. Details of the arrangement were discussed elsewhere [5]. The powder material Stellite SF6 (Deloro) of the original composition given in Table 1, and characterised by the spherical grain shape of size up to 60 μm was applied. Plates of martensitic stainless steel of a composition designed for the steam turbine blades (12% Cr, 1% Mo, 0.6% Ni, max 0.6% Mn, max 0.6% Si, 0.2% C, balance Fe) were used as substrate material. The laser scan rate applied during experiments did not exceed 25 mm/s. Tracks of the remelted powder material of dimensions of 1 mm $\times$ 0.3 mm (width $\times$ height) were applied for the surface coating. For layers of higher thickness the vertical sample feeding was controlled stepwise and steps equal to the layer height were applied. Samples of the laser-cladded surfaces of overall dimensions of 20×20 mm^2 (see Fig. 2a), were completed by overlapping of consecutive tracks at approximately 30% track intervals. All samples obtained from experiment were characterised by the same, regular, multi-strip-like structure of the top surface.

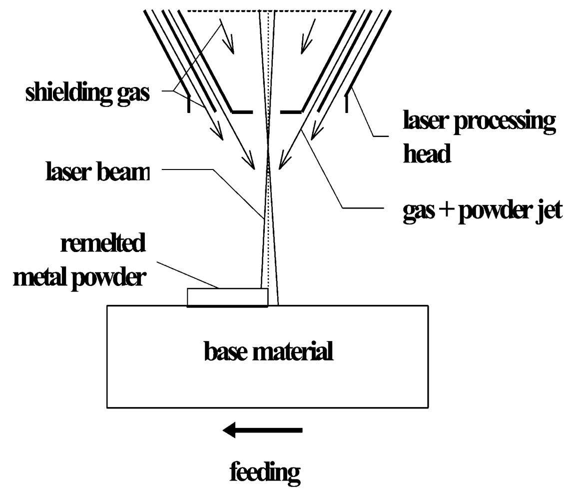

Fig. 1. The axially-symmetric experimental setup applied for the laser cladding of stellite powder.

The stellite coated samples were examined by means of optical, chemical, and metallographic methods. After cutting, polishing and etching of the samples an inspection of the microstructure was performed by means of optical and scanning electron microscopes of the types PME-3 (Optimus) and JXA-840 (JEOL), respectively. For chemical analysis of the local sample constituents energy dissipative X-ray spectrometer-EDS (Roentec) was applied. Measurements of the Vickers microhardness were made using a load of 300 g in the sample cross-sections vertical to the clad-track directions at different distances from the coating–substrate interface. The wear resistance was determined by the weight loss due to friction controlled by means of a spinning disc apparatus (Dow Corning). The disc of SAE steel, conforming to ASTM standards and of a hardness of 58–63 HRC together with a block of tested material at a load of 1 kg and at 100 rev./min were used for the test.

Electrochemical tests with a conventional three-electrode corrosion cell were carried out at room tempera-

Table 1
Comparison of the chemical composition (wt.%) of the original stellite powder and the semi-quantitative EDS data obtained for the laser-clad coating

	Co	Cr	Ni	W	Fe	Si	Mn
Original powder composition	bal.	19	13.5	7.5	3 (max.)	2.3	1 (max.)
EDS data this experiment	43.88	18.79	13.91	9.94	5.09	1.83	0.74

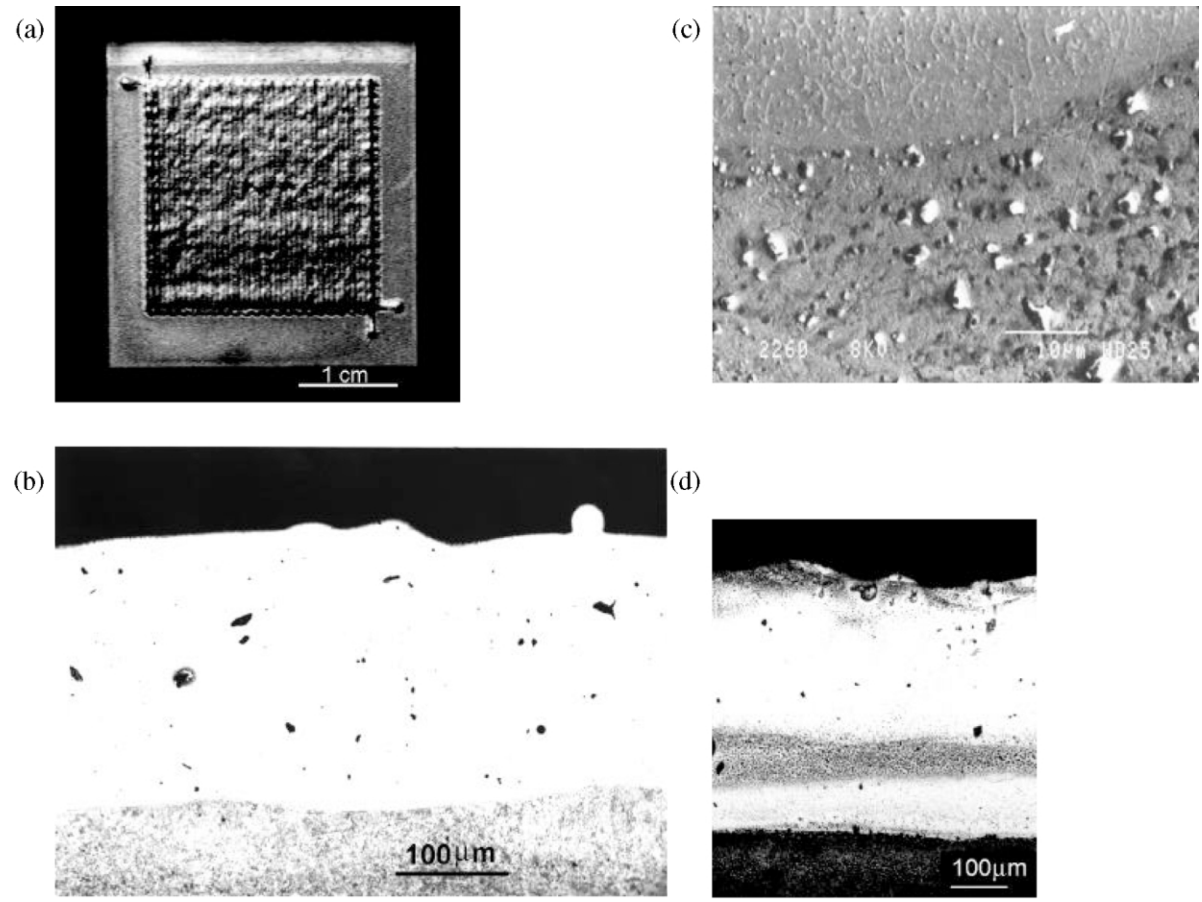

Fig. 2. (a–d) Photographs of the sample structure: a general view of the stellite coating of dimensions $20\times20\times0.7$ mm^3 (a); cross-section of a single-layer coating (b); SEM micrograph of the dendritic structure of the stellite (upper zone) and the structure of the substrate; the interface and also white precipitates are clearly observed (c); and a cross-section of a stellite clad, total height of two layers = 0.7 mm, magnification (d).

ture, using a Gamry CMS 105 DC corrosion test system. Polarisation curves were performed in a standard solution of 3.56% NaCl. The sample surface of 1 cm^2 served as working electrode. A rolled platinum wire was used as counter electrode to ensure a homogeneous distribution of the current. Finally, the potentials were referred to a standard saturated calomel electrode (SCE). Once the samples were immersed in the solution, and after stabilisation of the corrosion potential a cathodic step was applied to obtain the voltage of −1000 mV/SCE. Then a potential sweep was applied from −1000 mV/SCE at a scan rate of 1 mV/s till a current density of 1 mA/cm^2 was achieved.

3. Results and discussion

For the laser cladded stellite coatings shown in Fig. 2a, a uniform microstructure is observed by means of an optical microscope showing a clear boundary at the interface between the substrate and coating (see the upper and lower part in Fig. 2b, respectively). The entire thickness of the coating results from the double-layer procedure applied. The slight modulation of the substrate-clad boundary position has a periodicity determined by the positions of consecutive tracks due to 30% overlap. A smooth, homogeneous region of the boundary corresponds to the fusion zone and indicates on a good adherence of the clad. In the coating-upper region in Fig. 2b, local inhomogeneities can be observed. The small, dark areas of irregular shape represent the gas cavities and impurities. Due to their minor content they do not influence the mechanical properties and bond quality of the coating.

The higher magnification of the SEM micrograph in Fig. 2c makes possible to distinguish more clearly the existence of a metallurgical bond rather than an interface between the clad and the substrate. This supports the conclusion on the bond quality and is in agreement with the result of Fig. 2b also. The SEM data reveal different structures of both materials. A smooth zone due to epitaxial growth on the substrate proceeds vertically and transforms into a quite narrow, cellular region due to drastic changes in cooling rates and thermal gradients with height. The directional, dendritic growth is representative for the upper part of the melt pool. Dendrites are formed directly from the liquid phase during rapid solidification, and this characteristic structure does not change significantly with depth which is in agreement with observations of other authors [3]. A minor number of structure defects (micro-cracks) evidenced at some locations in the coating and not shown in the photographs result most probably from the residual, thermal tensions induced in the sample by the high thermal gradients and cooling rates due to short-term, intense laser radiation. In the substrate region close to the fusion zone an array of white precipitates is observed (lower part, Fig. 2c). The precipitates are ascribed to chromium carbides and this will be discussed later.

Changes in the chemical composition due to laser cladding were investigated on the basis of semi-quantitative EDS results regarding the major chemical constituents of both substrate and coating. The composition representative for the bulk of the laser-clad obtained from experiment and that corresponding to the original stellite powder given by the supplier are summarised in Table 1. It follows from comparison of the data that in the remelted stellite powder the relative quantities of the original components are reproduced. This also indicates that during deposition and remelting no changes are induced in the chemical composition. Effects of de-alloying or oxidation were not evidenced. Data for species B and C are not reliable given the low signal to noise ratio of the EDS apparatus at low energies.

A set of the depth-dependent EDS data were collected in the vicinity of the coating–substrate interface. They are shown in Fig. 3a as the comparison of relative intensities of spectral lines recorded for two different locations in respect to the interface. The slight differences in chemical composition of the laser clad compared to that of the bulk stellite can be observed exclusively in the stellite zone close to the substrate. In this region the higher intensity of the Fe line at approximately 6.4 kV represents a higher content of Fe, and indicates an efficient dissolution of this substrate constituent. It is due to interaction of both the high temperature and surface tension in the melt which leads to intense mixing and convective migration within the bath.

Dependences of the contents of Fe, Co, Cr, and Ni on the vertical co-ordinate along the clad cross-section are extracted from the EDS data and gathered in Fig. 3b. These plots contain, in a discrete form, information similar to the known EDS line-scans. A substantial decrease of the iron content along the depth of the processed zone can be observed. Its falls from the original value specified of 83% for the substrate at a distance of approximately -25 μm from the interface which agrees well with data of Table 1 to approximately 50% at the interface (0 μm), and to 28% observed for

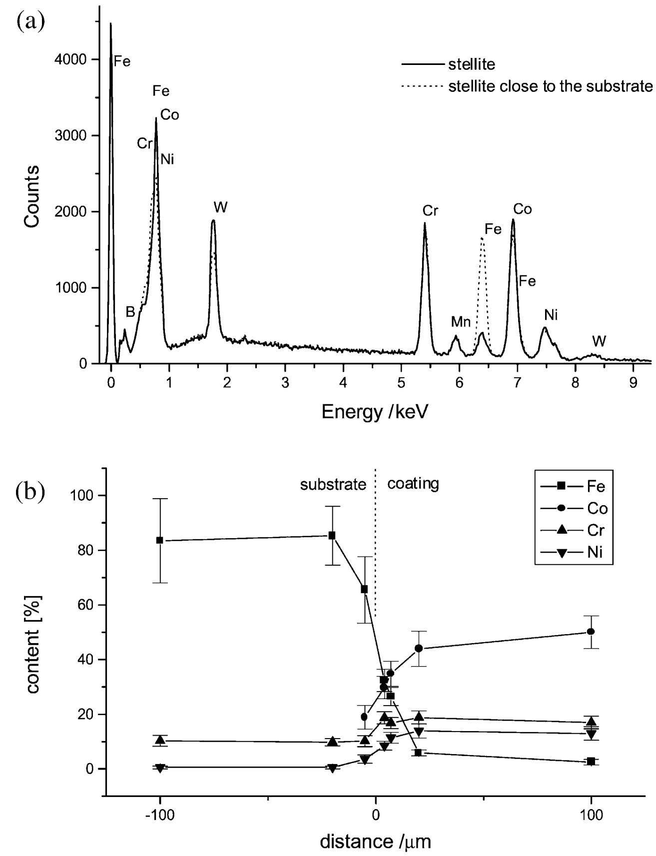

Fig. 3. (a,b) Semi-quantitative EDS data on the dominant chemical components of the bulk stellite-full line, and of its region close to the base material-dashed line (a); dependence of the relative content (%wt.) of constituents Fe, Co, Cr, and Ni on the distance from the substrate–clad interface (b).

the stellite coating close to the interface (+10 μm) reproduces the changes obtained from another EDS measurement (see Fig. 3a) done for the coating alone. On the other hand, the change of the constituent Fe related to its original content in the stellite powder represents an increase, thus indicating agreement of the results in Fig. 3a,b. For Co, and less markedly for Cr and Ni even absolute content growths with the distance coordinate are observed.

Results of the EDS analysis of the white precipitates observed in Fig. 2c reveal a prevailing content of Cr and C. This support a preliminary conclusion from microscopic observation on the chromium carbides Cr_mC_n which result from an enrichment of the local carbon sites promoted by melting of the carbon steel used as substrate.

The dependence of the Vickers hardness on the distance from clad surface measured for the case of a double layer clad (see photograph in Fig. 2d) in the cross-section perpendicular to the clad direction is presented in Fig. 4. Results indicate that the outer part of the laser-remelted track of a thickness not exceeding 150 μm reveals values close to 1000 HV which are

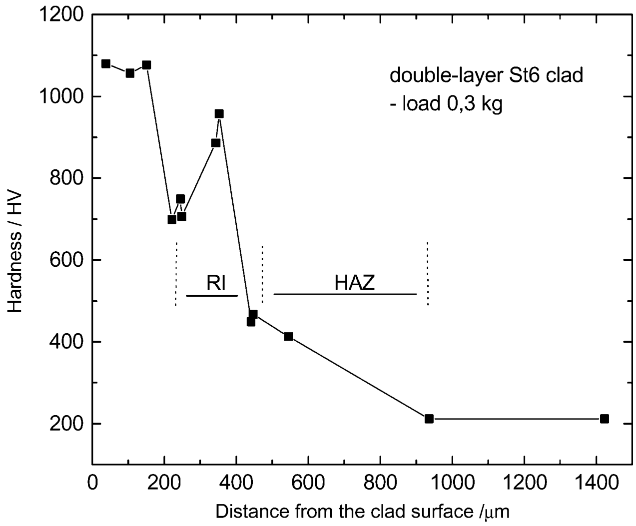

Fig. 4. The dependence of the Vickers microhardness on the distance from the top surface of the coating; marked are the remelted interlayer (RI) and heat affected (HAZ) zones, data correspond to the sample shown in Fig. 2d.

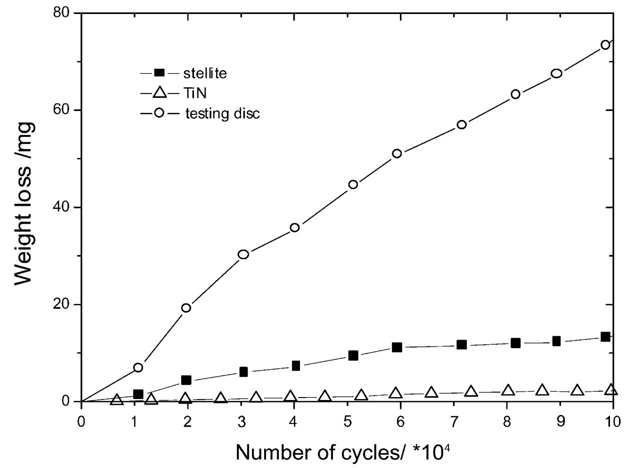

Fig. 5. The wear resistance as a dependence of the weight loss due to friction on the test duration; experimental data refer to the stellite (squares), and to the testing disc (circles); the data of TiN (triangles), are given for reference only.

considerably high compared to that of approximately 200 HV measured for the substrate. However, at a distance of approximately 150–250 μm from the surface the hardness decreases up to approximately 700 HV, to recover values higher than 900 HV at deeper distances of approximately 360 μm again. This agrees with the literature and supports the general conclusion that for laser-clads the microhardness values higher by approximately 180–380 HV than those of plasma sprayed layers can be measured [7]. The observed, sharp decrease in microhardness corresponds to the laser-remelted interlayer zone and appears between scanned tracks [see (RI) in Fig. 4]. Also, a characteristic fall of the hardness is observed for a depth decreasing from 400 to approximately 900 μm. This effect refers to the heat affected zone of the base material (HAZ in Fig. 4), i.e. of the first deposited stellite layer in this case, and leads to a local dissolution or redistribution of the inclusions and precipitates, thus promoting a finer structure with improved mechanical properties in comparison to the bulk of the substrate. At deeper sample areas the values of approximately 200 HV corresponding to the substrate steel are measured.

For the coatings a test aimed on estimation of the wear resistance has been carried out, and also data of other materials were collected for comparison under the same testing conditions as well. Dependence of the weight loss due to friction on the test duration for both the block of clad material to be tested and the testing ring. A comparison with previous results obtained for TiN of similar hardness was used for reference (Fig. 5) [8]. It follows from comparison of the data that the disc of carburised carbon steel reveals a weight loss faster than the stellite sample. This indicates that laser cladding of stellite improves resistance to wear and is in agreement with literature values [6,8]. Moreover, the weight loss of stellite and of TiN which is known as extraordinarily wear resistive are both represented by a similar slope of the time dependence and the values measured for both materials are comparable, too.

For investigation of the corrosion behaviour the electrochemical studies of samples immersed in a 3.5% NaCl solution were carried out. From a corrosion point of view even singular structure defects such as microcracks observed locally in the coating on microphotographs at higher magnifications should result in a decreased protection capability. Results of the corrosion tests in the form of potentiodynamic curves of the laser-clad stellite coating (dots) and the substrate mate-

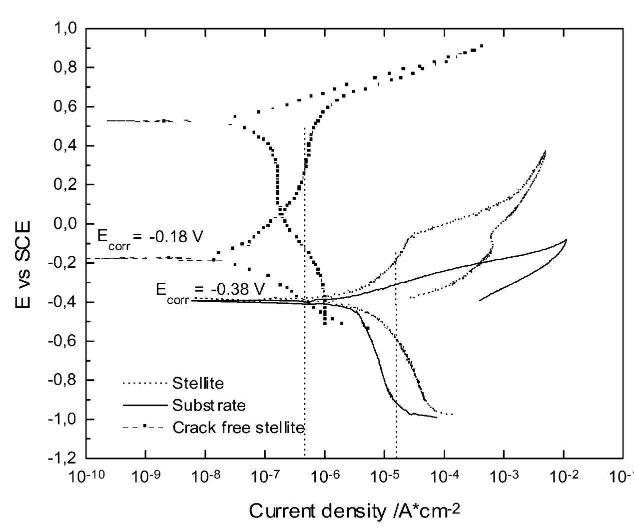

Fig. 6. Dependencies of the electrochemical corrosion potential with respect to the saturated calomel electrode (SCE) on the current density for the substrate (solid line), the laser-clad stellite layer (dots), and for the defect-free reference layer (squares).

rial (full line) both of the investigated samples, and also the reference layer of a crack-free stellite obtained elsewhere are presented in Fig. 6. The value of the corrosion potential of -0.38 V observed for the coating under investigation is almost the same as that of the uncoated substrate. For the coated sample the presence of a nearly vertical stage typical for a passive material can be distinguished, however, the height of this stage is quite small. The current density of the range of mA/cm^2 corresponding to passivity is similar to that of the corrosion current density. This behaviour is in agreement with the previously mentioned observation of a minor number of micro-cracks in the coating. They expose the base material locally to an aggressive environment leading to the observed effect. As a consequence, the corrosive agents may reach the substrate through these defects launching a corrosion attack which can extend in to the substrate in subsequent steps.

The occurrence of micro-cracks due to thermal tensions induced in the sample is observed by other authors and discussed in the literature [9]. An improvement of the final effect can be obtained under conditions of a careful selection of the clad composition and preheating of the base material to a given temperature, and also controlled cooling rate. However, the temperature-dependent properties of materials under investigation indicate that the process can be influenced by other contributions. For example, it follows from the thermophysical data and from our calculations made for stellite coating [10] that its thermal conductivity κ at high temperatures of approximately 1300 K is similar to that of the substrate but falls with the temperature decrease and approaches a value of 1.4×10^{-2} W/(mm K) at 300 K which is several times lower than that corresponding to the substrate.

4. Conclusions

Multilayers of controllable geometry were produced for protective coatings in a direct process by means of laser cladding of the SF6 powder on plates of a martensitic stainless steel. For the powder remelting a cw CO_2 laser beam at intensities of approximately 10^5 W/cm^2 together with an experimental multi-stream nozzle characterised by a powder feeding coaxial with the laser beam was applied. Results of the optical, chemical, and metallographic examinations obtained for the SF6 layers revealed the fine-grained and chemically homogeneous structures of an excellent adhesion to the base material, and with only a minor presence of local impurities and structure defects. The underperformance of the corrosion behaviour was ascribed to the presence of singular micro-cracks, and the high values of microhardness close to 960 HV measured in the coating surface region were confirmed by a high wear resistance comparable with that of TiN.

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References

[1] Levis GK, Schlienger E. Practical considerations and capabilities for laser assisted direct metal deposition. Mater. Design 2000;21(4):417–423.
[2] Yellup JM. Laser cladding using the powder blowing technique. Surf. Coat. Technol. 1995;71(2):121–128.
[3] Jendrzejewski R, Klimczuk T, Sadowski W, Sliwinski G. Multilayer laser cladding of metal powders for fast prototyping. Proc. SPIE 1998;3571:383–387.
[4] Vilar R. Laser alloying and laser cladding. Mater. Sci. Forum 1999;301:229–252.
[5] Jendrzejewski R, Conde A, de Damborenea J, Sliwinski G. Experimental study of a laser processing head with integrated jet of metal powder for rapid prototyping and production of protective coatings. Proc. SPIE 2000;4184:603–606.
[6] Ritter U. Laser coating proven in practice. Sulzer Tech. Rev. 1991;3:18–20.
[7] Shepeleva L. Laser cladding of turbine blades. Surf. Coat. Technol. 2000;125:45–48.
[8] King E, Fernándes BJ, de Damborenea J, Ruiz J. High temperature gas nitriding of Ti_6Al_4V to improve wear surface properties. Rev. Metal. Madrid 2000;36:403–409.
[9] Wulin S et al. Cracking susceptibility of a laser-clad layer as related to the melting properties of the cladding alloy. Surf. Coat. Technol. 1999;115:270–272.
[10] Jendrzejewski R. Thesis, PASci IF-FM, Gdansk; 2000.