Effect of Ti and C alloyants on the microstructure of laser cladded cobalt-chromium coatings

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Abstract. The article presents the results of Ti and C additives on the microstructure of the Metcoclad 6 coating. Effect of chemical composition with optimal laser cladding parameters has been studied in the terms of modification of the carbide morphology. The experiments were carried out on TruDisk 3302 Yb:YAG disk, equipped with a disc powder feeder. As a deposited material Metcoclad 6 powder produced in inert gas-atomization process was used. To assess the impact of alloying elements on microstructure, SEM observations and EDS analysis were carried out. Vickers microhardness tests were provided on the cross-section of coatings on Wilson Wolpert 401 MVD device. It has been stated that addition of titanium changes the morphology of carbides from lamellar eutectic carbides to isolated primary TiC while addition of Ti and graphite allowed to maintain the structure typical for pure Stellite 6 alloy, but additional formation of primary carbides were observed.

1. Introduction

The wear processes present in the industry are one of the major problems encountered when analyzing the factors influencing the failure of machines. The requirements for the currently used materials due to the long life cycle of the product are mainly focused on the maximum wear resistance in various forms: metal against metal, metal against non-metal or metals against fluid, because the movement between the surfaces of different materials causes damage by abrasion, galling, cavitation, erosion or corrosion. Cobalt alloys have found a special application in industry due to the combination of high wear resistance, corrosion resistance, high hardness and cavitation resistance. A popular group of cobalt-chromium alloys is called the Stellite and was developed in 1910 by E. Haynes [1,2].

The Stellite alloys as a wear resistant material play an important role in application on valves, turbine blades, steam valve guides or flame tubes of gas turbines due to high resistance to galling and fretting up to 300°C. The high corrosion resistance allowed to use this material in chemical industry especially where the material has contact with the corrosive environment in combination with abrasive wear. An example of such an application may be the sealing ring wear for submarine rudder, chemical scraper blade or knives for cutting fibres. Standard cutting tools were made of high speed steel but development and application of Stellite alloys allowed to increase the feed rate to be increased about three times which was very important during second world war [1-3].

Stellites owe their high performance properties to the combination of carbides with cobalt matrix. Cobalt in this alloy occurs in fcc crystal structure, because of the sluggish nature of the transformation from fcc to hcp crystal structure. The fcc structure ensure the high yield strength and...
ability to absorb stress through transformation to hcp structure. In Stellite chromium has a dual function as a main carbide former (most of carbides are Cr rich) and as a alloying element which is strengthening the matrix and improving the resistance to corrosion and oxidation by forming the oxide layer. Small additions of tungsten and molybdenum are responsible for strengthening mechanism of matrix due to their large atomic size impeding dislocation flow and improving general corrosion resistance of material. In large amounts, they are responsible for formation carbides during solidification. Small addition of nickel stabilizes the γ-Co matrix in face-centered cubic structure [3-6].

There are two basic group of Stellites: CoCrW and CoCrMo. The first group includes the Stellite 6 alloy, which is one of the most commonly used cobalt-based alloys due to its high wear resistance combined with good plastic and strength properties. The described material is characterized by high impact strength, resistance to cavitation, and a very good resistance to chemical wear in a wide temperature range while maintaining its properties up to a temperature of 500°C. Stellite 6 is suitable for hardfacing and therefore has a wide range of applications on pump shafts, valve seats, bearings, erosion shields or rolling couples [7-13].

In the conducted research, laser cladding tests were carried out with modified Metcoclad 6 powder (the chemical composition is the same as in Stellite 6) by adding titanium as well as graphite and titanium in order to obtain unique layers characterized by high performance. Based on the research carried out by Ying [14], it can be concluded that the addition of titanium will modify the type of carbides in microstructure of Stellite 6, influencing on the material properties. The second mixture of powders, containing titanium and graphite, was used in order to obtain an unchanged lamellar eutectic structure of the Stellite 6 with an increased amount of TiC carbides.

2. Materials and Methods

Non-alloy S235 steel with dimension of 100x50x10 mm was used as a substrate material in conducted research. Before cladding the samples were grinded and cleaned using acetone in order to obtain clean surface of high purity. As a laser cladding powder, Metcoclad 6 produced in inert gas atomization process with the particle size in the range from 50 – 106 μm was used. In order to obtain unique layers characterized by high hardness, new powder mixtures were created, consisting of the addition of titanium and graphite (both 99.9 wt% purity with particle size between 80 and 150 μm) in the base Metcoclad 6 powder. Chemical composition of individual powder mixtures (in weight ratio) is presented in table 1. All the powders were mixed mechanically using a planetary ball milling machine.

### Table 1. Chemical composition of original and modified powder of Metcoclad 6.

| Sample no. | Chemical composition (wt.%) |
|------------|-----------------------------|
|            | Co  | Cr  | W  | Si  | C   | Ni  | Mo  | Fe  | Mn  | Ti  |
| 1          | Bal. | 27.3| 4.4| 1.6 | 1.1 | 0.8 | 0.1 | 0.1 | <0.1| -   |
| 2          | Bal. | 26.2| 4.2| 1.5 | 1.1 | 0.8 | 0.1 | 0.1 | <0.1| 4   |
| 3          | Bal. | 25.9| 4.2| 1.5 | 2.0 | 0.8 | 0.1 | 0.1 | <0.1| 4   |

The laser deposition process was performed on TRUMF disk laser Nd:YAG TruDisk 3302 with numerically controlled positioning system of the head and the treated substrate. The laser emits a continuous beam with a wavelength of 1.03 μm at a maximum power of 3.3 kW. The transmission of the laser beam was carried out using a 20 m long optical fiber. The detailed parameters of laser are shown in table 2. Argon with purity of 99.999% was used as a powder carrier and shielding gas. The laser station was equipped with a disk feeding system for precise control of powder feeding rate in the range from 0.6 to 12 g/min.
Table 2. TRUMPF TruDisk 3302 laser parameters.

| Characteristic                  | Value   |
|--------------------------------|---------|
| Wave length [μm]               | 1.03    |
| Maximum output power [W]       | 3300    |
| Laser beam divergence [mm-rad] | <8.0    |
| Fibre core diameter [μm]       | 200     |
| Collimator focal length [mm]   | 200     |
| Focusing lens focal length [mm]| 200     |
| Beam spot diameter [μm]        | 200     |
| Fiber length [m]               | 20      |

In order to obtain high quality laser clads the preliminary tests were carried out. Conducted tests included different parameters of: powder feed rate, laser beam power, focal length, shielding gas flow in order to obtain cladding layers fully adhered to substrate with low dilution and high powder melting rate. Quality of obtained layers was evaluated using the visual testing method. During the surfacing tests it was found that changing parameter of focal point to 30 mm above the material surface gives the best result for laser cladding ensuring the low mixing degree of clad with base material. Selected parameters used in laser cladding process are presented in table 3. Every coating consisted of 5 single beads with constant control of the interpass temperature, which not exceeded 50 °C. During laser cladding, argon shielding gas was used at a flow rate of 10l/min blown through a cylindrical nozzle aligned with powder nozzle.

Table 3. Technological parameters of the laser cladding process.

| Shielding gas flow rate – argon [l/min] | Carrier gas flow – argon [l/min] | Inclination angle of the nozzle relative to the laser head [°] | Powder feeding nozzle diameter [mm] |
|-----------------------------------------|----------------------------------|---------------------------------------------------------------|------------------------------------|
| 10                                      | 3                                | 30                                                            | 2                                  |
| Step-over width [mm]                     | Laser power [W]                  | Cladding speed [mm/min]                                       | Powder flow rate [g/min]           |
| 2.6                                     | 1000                             | 75                                                            | 0.035                              |

The microstructures of obtained laser clads were examined by using scanning electron microscope Phenom World PRO equipped with energy dispersive spectroscopy (EDS). The samples were cut in the middle of clad length where the parameters were stable. For macro and microstructural analysis, the specimen surface was grinded with sandpapers and polished with 1 μm alumina powder. The polished surfaces were etched with aqua regia for 10 seconds at temperature 20°C. In order to assess the quality of obtained layers, parameter of percentage dilution on cross section was calculated by following equation:

\[ U_p = \frac{F_W}{(F_N + F_W)} \times 100\% \]  

(1)

where: \( U_p \) - dilution of base material with the coating, \( F_W \) – penetration surface, \( F_N \) – coating surface.

In order to assess the impact of chemical composition on properties of different chemical composition of laser clads the Vickers microhardness tests were provided. The measurements were carried out on cross-section from surface to the substrate at an interval of 0.2 mm on Wilson Wolpert 401 MVD with load of 500 g for the time duration of 10 seconds.

3. Results and discussion

The macrostructures images of obtained coatings are presented in figure 1. On prepared coatings no imperfections in a form of porosity or cracks were found. The coatings were characterized by very low dilution level which is the result of combining the correct parameters of laser cladding with optimum...
powder feed rate based on the preliminary tests. Microstructure analysis confirmed that coatings have an excellent metallurgical bond with the substrate free from any defects.

Sample 1 (Metcoclad 6)
Dilution – 4%

Sample 2 (Metcoclad 6 + 4% Ti)
Dilution – 4%

Sample 3 (Metcoclad 6 + 4% Ti + 1% C)
Dilution – 6%

Figure 1. Macrostructure images of obtained coatings.

In order to determine the chemical composition of obtained coatings with different chemical compositions, the EDS analysis has been performed. The SEM examinations were performed on transversal cuts of coatings to characterize the microstructure of obtained laser clads in which presence of different phases can be observed.

The microstructure of pure Metcoclad 6 laser clads consist of dendritic, cobalt rich matrix which is formed as a primary phase during solidification. In the next stage, the eutectic structure containing cobalt phase and carbides solidifies in the interdendritic regions. A significant change can be observed when the chemical composition of Metcoclad 6 was changed by addition of titanium. Titanium content of 4% wt. caused the replace of eutectics by formation of isolated particles. Those precipitates contain a high content of Ti, C, in their composition. In coatings made of pure Metcoclad 6 powder the eutectic structure is rich in chromium while addition of titanium changes significantly elemental segregation where chromium is segregated to the matrix. This is a result of enrichment of titanium and carbon in the carbide particles.

In the case of third chemical composition of Metcoclad 6 with titanium and graphite the microstructure changes dramatically. The structure consisting of cobalt matrix and eutectic lamellar phase is retained, however there are many precipitates in a form of primary carbides. The precipitates are characterized by very high dispersion in structure and consist high concentrations of Ti, W, Si and C.

Titanium is known as a strong carbide forming element [14]. During laser welding in the melted pool atoms of carbon first interact with Ti forming carbides and then react with tungsten or chromium because of the chemical affinity [12]. As shown in figures 2, 3, 4 powder mixture consisting titanium
addition revealed structure with primary carbides which replaced the formation of eutectic carbide. Coatings with addition of titanium and graphite made it possible to maintain the structure typical for Stellite 6 with eutectic carbide formation and additional primary carbides (MC type) which will influence on performance properties. Analyzing the EDS maps it has been stated that for sample no 2 chromium is mainly distributed in cobalt matrix which is in the opposite to pure Metcoclad 6 coating, where chromium is a main eutectic carbide former.

Figure 2. SEM image of sample 1 (Metcoclad 6) and corresponding EDS elemental maps (according to table 1).

Figure 3. SEM image of sample 2 (Metcoclad 6 + 4% Ti) and corresponding EDS elemental maps (according to table 1).
Figure 4. SEM image of sample 3 (Metoclad 6 + 4% Ti + 1% C) and corresponding EDS elemental maps (according to table 1).

The results of coatings Vickers microhardness are presented in figure 5. It can be observed that hardness of coatings is much higher than the substrate for all samples. The use of optimal cladding parameters allowed to obtain coatings characterized by low dilution which can be observed by sharp decline of hardness between coating and substrate.

Figure 5. Microhardness profile of coatings with different chemical compositions.
4. Conclusions
The conducted laser surfacing research of commercially available Metcoclad 6 powder and modified layers with titanium and graphite allowed to obtain high-quality coatings with low dilution level without imperfections. It has been stated that addition of titanium changes the morphology of carbides from lamellar eutectic carbides to isolated primary TiC carbides of average size 1.5 μm. It can be observed that reaction between carbon and titanium caused segregation of chromium in the cobalt matrix. Addition of titanium and graphite allowed to maintain the microstructure typical for Stellite 6 alloy, but additional formation of primary carbides were observed. The difference in hardness between samples 1 and 2 is not significant, but in the case of sample 3 there was a major change in hardness caused by formation of primary carbides precipitates while maintaining the lamellar phases of the eutectics.

5. References
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