APPLICATION AND INVESTIGATION OF NiCrBSi ALLOY COATINGS

SPECIFIČNOSTI, PRIMJENA I ISTRAŽIVANJE SLOJEVA OD NiCrBSi LEGURA

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Ključne riječi: *slojevi, NiCrBSi legure, trošenje, korozija*

Key words: *NiCrBSi alloy coatings, wear, corrosion*

Sažetak:

U ovom radu su prikazane specifičnosti, primjena i pregled različitih vrsta istraživanja NiCrBSi slojeva. Ovi slojevi se, zahvaljujući sadržaju kroma, bora i silicija u žilavoj nikl matrici, ubrajaju u tvrde legure otporne na trošenje, koroziju i toplinu. Nanose se najčešće naštrcavanjem pomoću plinskog plamena, plazmom, HVOF i laserskim postupkom, ali se pronalaze i primjeri korištenja električnog luka, detonacijskog pištolja i nekih drugih postupaka. Najbrojnija su istraživanja otpornosti ove vrste slojeva na trošenje i koroziju, kao i istraživanja mikrostrukture, ali se često istražuju i zaostala naprezanja i čvrstoća veze između sloja i podloge.

Abstract:

In this work, the specificities, application and review of different kinds of investigations for NiCrBSi alloy coatings have been presented. Due to the amount of chromium, boron and silicon and developed hard phases in tough nickel matrix, NiCrBSi alloy coatings belong to the wear, corrosion and heat resistant coatings. These coatings are commonly deposited by flame, plasma (non-transferred and transferred arc) and HVOF spraying as well as laser cladding, but arc and detonation gun spraying and some other processes have also been found. Wear and corrosion as well as microstructural investigations are the most frequent, but the residual stresses and bonding strength investigations, are present too.

1. INTRODUCTION

At the present, there are so many coating materials as well as deposition technologies available, and therefore very wide application of surface engineering is achieved in many industrial areas. It should be mentioned that there is an increase of the application of deposition technologies for biomedical purposes. Nowadays, an attempt is made to apply materials not only to deposit coatings but to manufacture complex three-dimensional parts as well.

Polymer, metal, ceramic and composite coatings can be obtained by different deposition technologies. Among them, Ni-based self-fluxing alloy coatings are widely applied in cases where the resistance to wear, corrosion and heat is required. The presence of chromium, boron, silicon and carbon (therefore the term „NiCrBSi coatings“ also appears), contributes to the generation of hard phases dispersed in tough nickel matrix, thus achieving good wear resistance. Apart from that, B and Si, affect the reduction of melting temperature and improve the self fluxing properties. Because of Cr and Ni amount, these alloys have good corrosion properties. Therefore, they are high hardness alloys, applicable in corrosion conditions, as well as at elevated temperatures, and can be classified as hard heat-resistant alloys.

While it is most common that Ni-based self-fluxing alloys contain chromium, it is possible that chromium sometimes does not appear as alloying element (NiBSi self-fluxing alloys). In some studies it was found that Ni-based self-fluxing alloys do not contain boron, but they are also fusible according to the information from the manufacturer.

In addition to coatings based on nickel, Fe- and Co-based self-fluxing alloys can be classified as self-fluxing alloys, which will not be covered in this paper. The studying of literature on Ni-based self-fluxing alloy coatings, led the authors of this paper to the following findings: The wear resistance investigations of coatings have been implemented in numerous studies [1-6, 9-12, 14-18, 20, 22, 24, 25, 27-34, 40, 41, 43-53]. The corrosion investigations are also numerous [8, 19, 21, 23, 26, 36-38]. The autors of surveyed literature studied the erosion corrosion, too [7, 13, 35].

The behavior of coatings during the action of external mechanical loads (adhesion strength, fatigue) is investigated too. Residual stresses in coatings are also studied. In some studies, only microstructure is taken into consideration. Some of the researchers investigated the spray stream, i.e. flight, flattening, cooling and solidification of molten or semi molten particles during spraying and impacting the substrate surface. Magnetism was also the subject of the study of some scientists. In some investigations, the application of Ni-based self-fluxing coatings is only described. Sometimes, these coatings are used as a comparison (reference material), that is, they have not primarily been the subject of research. In some researches, these alloys are used as the addition to achieve composite coating.

Finally, concerning the investigations of Ni-based self-fluxing alloy coatings, wear and corrosion investigations, as well as the combination of these processes are the most frequent. Nearly all of the mentioned investigations are accompanied by the characterization of the coating/substrate interface and coating microstructure (including porosity and oxide inclusions) and by the measurement of hardness and microhardness.

2. DEPOSITION TECHNOLOGIES

Ni-based self-fluxing alloy coatings are commonly deposited by flame, plasma (non-transferred and transferred arc) and high velocity oxy/air fuel spraying (HVOF, HVAF) as well as laser cladding, but electric arc and detonation gun spraying (D-gun) and some other technologies have also been found. For the plasma transferred arc welding, abbreviations PTA or PTAW can appear. Apart from the deposition technologies covered in this paper, it is found that Ni-based self-fluxing alloy coatings can be deposited even by the following techniques: pack cementation, liquid phase sintering, vacuum infiltration casting, brazing, metal active gas welding (MAG), short-circuit metal inert gas welding (CSC-MIG), gas tungsten arc welding (GTAW), vacuum induction melting, electron beam cladding process, self-propagating high-temperature synthesis.

Five most frequently applied deposition technologies for these coatings (flame, HVOF, plasma, plasma transferred arc and laser cladding) are schematically presented in Figures 1, 2, 3, 4 and 5 [39].

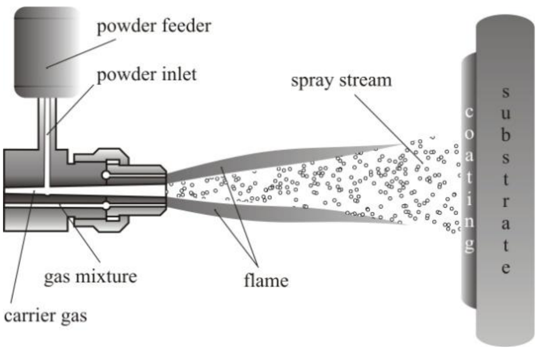

Figure 1. *Scheme of powder flame spraying*

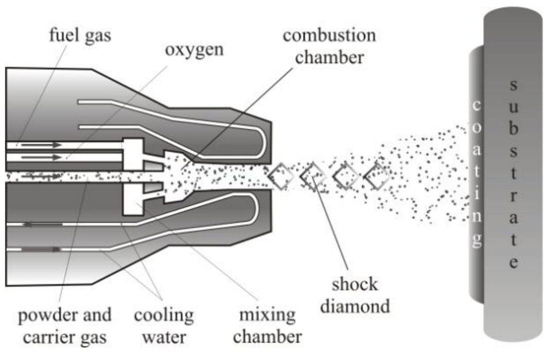

Figure 2. *Scheme of high velocity oxy fuel spraying*

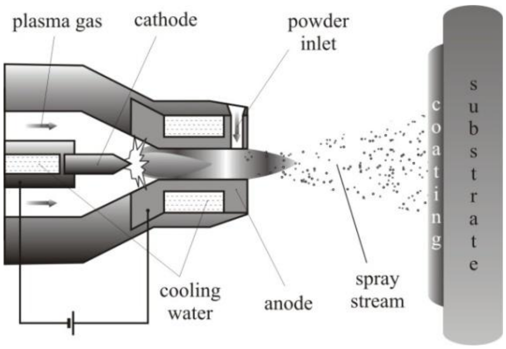

Figure 3. *Scheme of plasma non-transferred arc spraying*

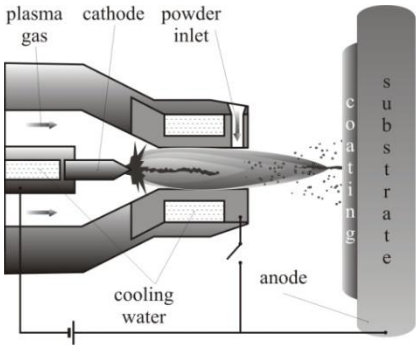

Figure 4. *Scheme of plasma transferred arc process*

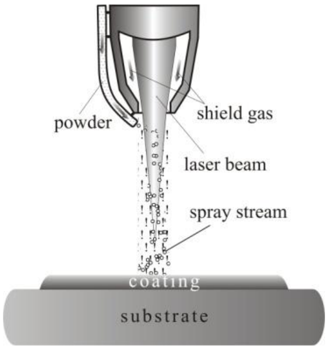

Figure 5. *Scheme of laser cladding*

The specificity of Ni-based self-fluxing alloy thermally sprayed coatings is the use of subsequent or simultaneous remelting or fusing at elevated temperatures to achieve metallurgical bond between the coating and the substrate. Consequently, the coatings have lower porosity and higher density.

When applying remelting technique, the coating is heated to a temperature between the solidus and liquidus (about 1000 to 1150 ^{o}C). However, due to high remelting temperature, there is an impact on the structure and properties of the substrate and coating, i.e. the carbide degradation, dilution (mixture of the deposited coating and the substrate) and cracking are so common.

Very common ways of remelting are flame and laser remelting as well as heat treamtment in furnace. The researchers, but rarely, have been applied TIG (tunsten inert gas) remelting and hot isostatic pressing [43, 44], hot isostatic pressing and rolling of coated material at high temperature, laser texturing [11] and vacuum sealing with polymer impregnation [35] as subsequent treatments. An impact of the remelting technique on the substrate and the formation of metallurgical bond is shown in Figures 6 and 7 [42]. In Figure 6, the interface of NiCrBSi+WC coating/42CrMo4 steel substrate is shown. High fusing temperature does not influence so significantly the microstructure of hardened and tempered 42CrMo4 steel. But there is a significant influence on the coating/substrate interface. There are two interface zones: the diffusion zone of 550 HV0,1 microhardness and dendritic zone with the smaller microhardness (400 HV0,1). This is due to carbon diffusion out of this zone down to the substrate (it results with the higher microhardness of 700 HV0,1). Martensitic structure (Figure 7) of previously hardened and tempered C45 steel after the spraying, fusing (1000^{o}C) and slow cooling, transforms to the pearlite ferrite structure. In the heat affected zone under the coating, there are coarse pearlite ferrite grains, but remote from the coating they are finer.

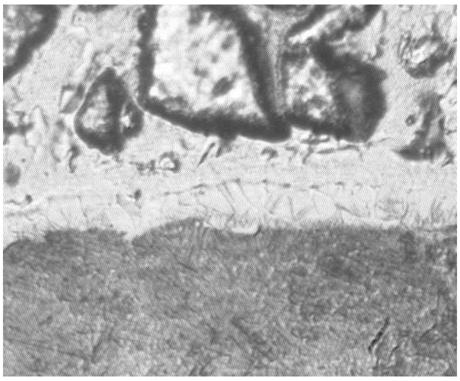

Figure 6. *Microstructure of NiCrBSi+WC coating - 42CrMo4 steel substrate, 450:1, etching: nital, light microscope [42]*

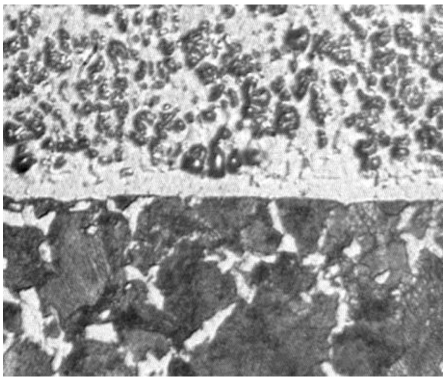

Figure 7. *Microstructure of NiCrBSi coating - C45 steel substrate, 450:1, etching: nital, light microscope [42]*

Regarding the laser cladding, it is important to note that it can be used as one stage process (for the deposition of coating), but also in combination with other methods. In such case, the laser is used for remelting or fusing of coating previously preplaced by plasma, flame or HVOF spraying or coating previously preplaced on the surface of the substrate using an organic chemical binder for binding powder. Appart from powder, the plates and chips can be preplaced in two stage laser process. When the laser is used in the two stage process, a lot of authors use the term laser heat treatment, re(melting), irradiation, radiation, surface modification or alloying.

However, many authors use the general term laser cladding even for cases when the coating is preplaced by plasma, flame or HVOF spraying process and then remelted by laser, although it is actually a laser remelting.

It should be noted that the laser heat treatment can be applied simultaneously with the thermal spraying process (then it can be called in situ laser treatment). When the laser procedure is used, an overlaping is common, but there are examples where the laser treatment is not applied onto the entire surface, but only partially [5] (because of the large heat input and opportunities for cracks). Consequently, there are scanned separated parallel lines along the coating or it can be called laser meshing.

Although it is not common to apply a subsequent heat treatment after laser cladding, there are also examples of the application of laser texturing [11], here applied in order to modify the surface and improve the friction behavior.

Apart from the above mentioned deposition technologies, there are also newer (even patented) procedures for specific purposes: a new procedure for flame spraying - DuraShell Steel Hardfacing DSH and a new laser cladding process – LDSH [45], then AC-HVAF technique - activated combustion-high velocity air fuel, as well as various hybrid techniques (HVOF process using a liquid state suspension/slurry containing small alloy powders abbreviated as LS HVOF [19] and plasma spraying process plus vacuum arc deposition of Ti-N-Cr coating to NiCrBSi coating).

3. APPLICATION

As previously stated, the Ni-based self-fluxing alloy coatings are used in terms of wear, corrosion and high temperatures. These coatings can be applied to new or worn out parts thereby prolonging service life and reducing the direct and indirect costs. Reviewing the articles, applications in almost all areas of human activity have been found, such as:

Energy production - Ni-based self-fluxing alloy coatings are often applied in all kinds of plants, and in almost all phases of the production of electricity - pumps, heat exchangers, boilers, turbines (blades). The application is found in erosion-corrosion protection of steel tubes in boilers, but also to protect the components of turbines and pumps (for example, shaft sleeves). An example of application is found in nuclear power plant (nuclear reactor components such as feed water control valves and control rod actuator in nuclear industry).

- Engines (cylinders, pistons and rings, internal combustion valve seat faces and valves and valve inserts in internal combustion engines)

Extreme wear conditions (cement production - mud purging elements; ore mining - digging picks in the surface mining of mineral ore; slurry lines in the oilsands industry; slurry pumps, sand dealing)

Tools (glass, polymer and ceramics mold industry - punches, dies, extruders; steel making industry - hot rolling mills; drilling application - drill bits and drilling tools in petroleum and gas drilling; drawing tools - wire drawing rolls, continuous casting molds; hot working punches, agricultural tools and equipment for soil treatment)

Machine parts (gears, screws, chain components, shaft sleeves …), as well as pipeline fittings, housings, mixers, rollers, blades of fans transporting gases containing solid particles

Spacecraft and aircraft industry (Ni-based self-fluxing alloy added to Ti alloy or sloj Ni-based self-fluxing alloy coating on Ti alloy, application in aerospace engines).

Ni-based self-fluxing alloy coatings can be applied in waste incineration plants, and some authors have considered the replacement of environmentally unfriendly process - hard chromium electroplating. Due to the corrosion resistance characteristic, these coatings are applied in chemical industry, food industry, oil processing industry ... It is interesting to note that these alloys can be used not only for coatings, but also for rapid prototyping.

4. WEAR AND CORROSION INVESTIGATIONS

In numerous investigations of the Ni-based self-fluxing alloy coatings referring to tribology, various tests were applied to simulate:

sliding [2, 5, 6, 9-12, 24, 25, 28, 29, 46, 48, 51, 53]
abrasion [4, 16, 18, 22, 32, 33, 41, 45]
erosion [3, 14, 15, 17, 27, 34, 40]
fretting [1, 31]
rolling [43, 44, 50]
impact [30, 52]
cavitation [20, 47, 49]

aimed at determining the mechanisms of wear, rate of wear and very often of the coefficient of friction. Corrosion, defined as undesirable material failure by chemical action of environment have been studied by many researchers. Basically all of the researches can be divided into the following three groups:

Electrochemical corrosion in the electrolyte (water, aqueous solutions of acids, alkalis, salts, moist soil, atmosphere), is investigated by the following authors [8, 21, 23], sometimes taking into account the load and corrosion F. Oliveira.

In addition to behavior of Ni-based self-fluxing alloy coatings in electrolytes, so called hot corrosion is investigated by [19, 36-38]. A review of research of hot corrosion as well as the definition of hot corrosion is given in article [36]. The articles related to hot corossion dealt with the behavior of coatings mainly in molten (or fused) salts formed due to the presence of impurities in the increasingly applied residual fuel oils (for example, molten salt sulfate-vanadate Na_2SO_4-60% V_2O_5 resulting from the condensation of combustion products of petroleum fuels; then Na_2SO_4 + 20wt % NaCl and Na_2SO_4 +25% NaCl salt mixture).

The chemical corrosion in nonelectrolytes [19, 20, 26] caused by hot gases (air, combustion gases, furnaces, internal combustion engines) and organic liquids (oil and products, lubricants, solvents) is investigated too. Corrosion products are mainly oxides and sulfides (SiO_2, Cr_2O_3, NiO, Fe_2O_3, spinels of $NiCr_2O_4$, $Ni(VO_3)_2$, CaO, FeS, Fe_7S_8).

5. CONCLUSION

Finally, regarding the sliding behavior, some conclusions can be drawn: Researchers have often dealt with the influence of adding the reinforcement particles and/or rare earth elements on the sliding properties. Many authors have used WC. Based on the surveyed literature it can be concluded that it is not generally possible to claim that the addition of hard particles increases resistance to sliding wear. Many authors have mentioned the formatin of the oxide layer and its generally protective role, but they also point to the risk of damage of oxide layer.

The researches were carried out with the aim of comparing the different deposition techniques and varying the deposition parameters. The dissolution and its impact on the sliding properties are studied too. Apart from varying the parameters of deposition technique, the testing parameters were varied very often.

When considering the abrasive wear, the following is taken into account: abrasive (type and hardness, size, shape) interface between the hard phase and the matrix, as well as the distance between the reinforcement particles changing the contents of some elements in the coating material chemical composition of the substrate.

In studies of erosive wear, porosity, ductility, fracture toughness and the angle of impact of particles as a new parameter are significant.

Considering the corrosion investigations, many authors concluded that porosity may affect the corrosion process since the corrosion medium can enter through the pore and cause local corrosion and significant corrosion of the substrate which is completely corrosion unresistant. Also, many researchers claim that besides porosity, cracks, unmelted particles and splat boundaries may significantly jeopardize the corrosion resistance of the coatings and the substrate as well. Some researchers have concluded that the corrosion products on NiCrBSi coating are more homogeneous with better adhesion to the substrate, thus providing better protection against corrosion. Most authors concluded that the remelting process increases corrosion resistance (less porosity), but some authors claim that remelting can cause cracks (thermal stress) thus affecting the reduction of corrosion resistance.

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