

## POTENTIODYNAMIC EVALUATION OF CORROSION RESISTANT COATINGS

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### Abstract

In terms of corrosion protection, metal passivity is a very important phenomenon, as it leads to slower corrosion process in oxidative environments. This phenomenon is of particular advantage in power plants, where electrochemical corrosion, especially on surfaces of components, occurs very often. In this study, selected cermet and alloy based coatings were investigated. The selection of coatings was carried out considering their potential use in power plants. The selected coatings were Cr<sub>3</sub>C<sub>2</sub>-NiCr, Cr<sub>3</sub>C<sub>2</sub>-CoNiCrAlY, TiMoCN-Ni, Stellite 6, Hastelloy C-276 and NiCrBSi. These coatings were deposited on W.Nr. 1.0421 substrate carbon steel using HP/HVOF and were tested using potentiodynamic corrosion tests. The surface after corrosion testing was evaluated by optical microscopy. The microstructure of selected coatings after deposition was evaluated by SEM microscopy. The results show that cermet coatings exhibited the highest resistance in 5% electrolyte solution of H<sub>2</sub>(SO)<sub>4</sub> and Hastelloy C-276 reached the highest resistance out of alloy based coatings.

**Keywords:** HP/HVOF, coating, potentiodynamic corrosion test, corrosion

### 1. INTRODUCTION

Electrochemical corrosion is a heterogeneous reaction on the coating surface involving oxidation of metals. Oxidation is a condition in which the metals lose electrons. Most metals are inherently unstable and spontaneously oxidize, whereby the possibility and the extent of transition differs for each metal. The oxidation is characterized by the reduction of free enthalpy in  $\Delta G$  system. Electrochemical corrosion includes corrosion of metals in electrolytes and comprises two partial reactions - anodic and cathodic reaction. The relationship between the polarization and the real value of current density creates the polarization curve. Consequently, it can be said that the polarization curve shows the progress of corrosion, i.e. resistance of metals (passivity). Polarization curves are used to study the corrosion behavior of materials. They are also used to determine potentials, in which the selective dissolution of some phases occurs depending on the current density. The polarization curve is divided into three main areas. These areas will be further described in the discussion in connection with measured results [7].

Thermally sprayed coatings are widely used technology, particularly in areas requiring good wear and corrosion resistance. Some investigations shows that porosity, different phases content, plastic deformation and residual stress influence the electrochemical behavior of coating-substrate system. Many studies were focused on the reduction of these factors by optimization of spraying parameters, application of anticorrosive layers, adjustment of layer thickness etc. [1].

Coatings based on zinc and aluminum and on their alloys are used especially in common practice for several years. They work as sacrificial coatings which are able to protect the substrate, even if they are directly exposed to the electrolyte. However, these solutions are only temporary and cannot protect the substrate for longer time period [1].

While applying noble metals (often more noble than the substrate) to protect the substrate as a passivation barrier, a problem associated with continuity of applied layer occurs. These discontinuities enable electrolyte to reach the substrate, and thereby a galvanic cell is created and the local corrosion is considerably accelerated. Many technologies, such as diffusion deposition, sputtering, CVD, electrocladding, thermal spraying and others, are capable of noble metal and corrosion resistant layers depositing [1].

Within the thermal spraying technologies, the HVOF technology is being spread in the last years. This technology shows better results in connection with electrolytic corrosion than other technologies. This fact is mainly caused by better quality of coating, lower porosity and strong adhesion between coating and substrate material [1].

The coatings selected for this investigation are generally used as corrosion protection. The selected coatings are two cermet coatings  $\text{Cr}_3\text{C}_2\text{-NiCr}$  and  $\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$ , one experimental coating  $\text{TiMoCN-Ni}$  and three alloy based coatings  $\text{CoCrWC}$  (Stellite 6),  $\text{NiCoCrMoWFe}$  (Hastelloy C-276) and  $\text{NiCrBSi}$ .

$\text{Cr}_3\text{C}_2\text{-NiCr}$  cermet coating deposited by HP/HVOF technology is along with the WC-Co commonly used replacement of hard chromium plating. Unlike the WC-Co, this type of coating can be used even in environments up to 850 °C, and it still retains its abrasion and friction resistance. High chemical stability of this coating makes it ideal for use as an alternative to hard chromium plating in applications requiring high corrosion and wear resistance [2].

$\text{Cr}_3\text{C}_2\text{-CoNiCrAlY}$  coating provides components with excellent erosion and wear protection even at temperatures approaching 1000 °C. Furthermore, it was found out that the coating exhibits better oxidation resistance than  $\text{Cr}_3\text{C}_2\text{-NiCr}$  coating. Nowadays, it is used for furnaces and turbines components operating at high temperatures [3].

Experimental  $\text{TiMoCN-Ni}$  seems to be a promising coating for the use in certain parts of devices operating in aggressive conditions. This coating is supplied by the Japanese company Fujimi, and due to the high content of Ti, it is expected to be resistant in corrosive environment.

Stellite 6 ( $\text{CoCrWC}$ ) was chosen among alloy coatings. Stellite alloys are characterized by high hardness, toughness and typically exhibit excellent anti-corrosion properties. These alloys can also be used for devices operating at high temperatures due to the content of Co and Cr. They behave at high temperatures as diffusion barrier for degradation media. This behavior is caused by the formation of chromium oxide on the splat borders rich in Co and by the formation of surface oxides, particularly cobalt and chromium oxides, together with cobalt-chromium and nickel-chromium spinels [4].

$\text{NiCrMo}$  (Hastelloy) based coatings exhibit excellent corrosion protection. It was found out that corrosion resistance is increased with reduction of unmelted particles proportion in the coating. Especially the borders between splat creating the coating are susceptible to corrosion due to the presence of oxides [5].

Nickel alloys have generally very good corrosion resistance. However, these alloys are very expensive, and therefore they are being replaced through the use of nickel alloy based thermally sprayed coatings on steel substrates, which are thus improved through the corrosion resistance of nickel alloys [1].

Potentiodynamic corrosion tests in the environment of 5% aqueous solution of  $\text{H}_2(\text{SO})_4$  were performed for all these six above described coatings.

## 2. EXPERIMENT

### 2.1. Sample preparation and characterization

Five commercially available powders were used to prepare the samples. These powders were Amperit 588.074 ( $\text{Cr}_3\text{C}_2\text{-25%NiCr}$ ) with particle size distribution for HVOF (-45+15 mm), Amperit 594.074 ( $\text{Cr}_3\text{C}_2\text{-25%CoNiCrAlY}$ ) with particle size distribution for HVOF (-45+15 mm), M-484.33 ( $\text{CoCrWC}$ ) with particle size distribution for HVOF (-53+20 mm), M-341.33 (Alloy C-276) with particle size distribution for HVOF (-53+20 mm), M-771.33 ( $\text{NiCrBSi}$ ) with particle size distribution for HVOF (-53+20 mm) and one experimental powder labeled T10 ( $\text{TiMoCN-Ni}$ ). All coatings were deposited by HP/HVOF (High Pressure/High Velocity Oxygen Fuel) technology with JP-5000 torch from the company TAFE Incorporated. Already optimized spray parameters were used for each coating.

Structural steel W.Nr. 1.0533 (DIN 11 523) was used as the base material. The substrate surface was degreased and grit blasted before spraying. Brown corundum F22 with grain size (0.8 to 1.0)mm was used as abrasive medium.

## 2.2. Measurement conditions

The corrosion behavior of coatings was evaluated by polarization method performed using electrochemical cell. 5% solution of H<sub>2</sub>SO<sub>4</sub> was used for better comparison with our previous study based on immersion test in the same solution. A potentiostat (Gamry Reference 600) used to perform the potentiodynamic tests. Potential range was ranging from - 0.7 and 1.2 V, and a scan rate was set to 2mV/s. In order to activate the surface, before polarization, the samples were cathodically cleaned for 60 seconds at -50 mV. The microstructure evaluation was made before and after corrosion testing using Nikon Epiphot 300 microscope.

## 3. RESULTS AND DISCUSSION

### 3.1. Anodic polarization experiments

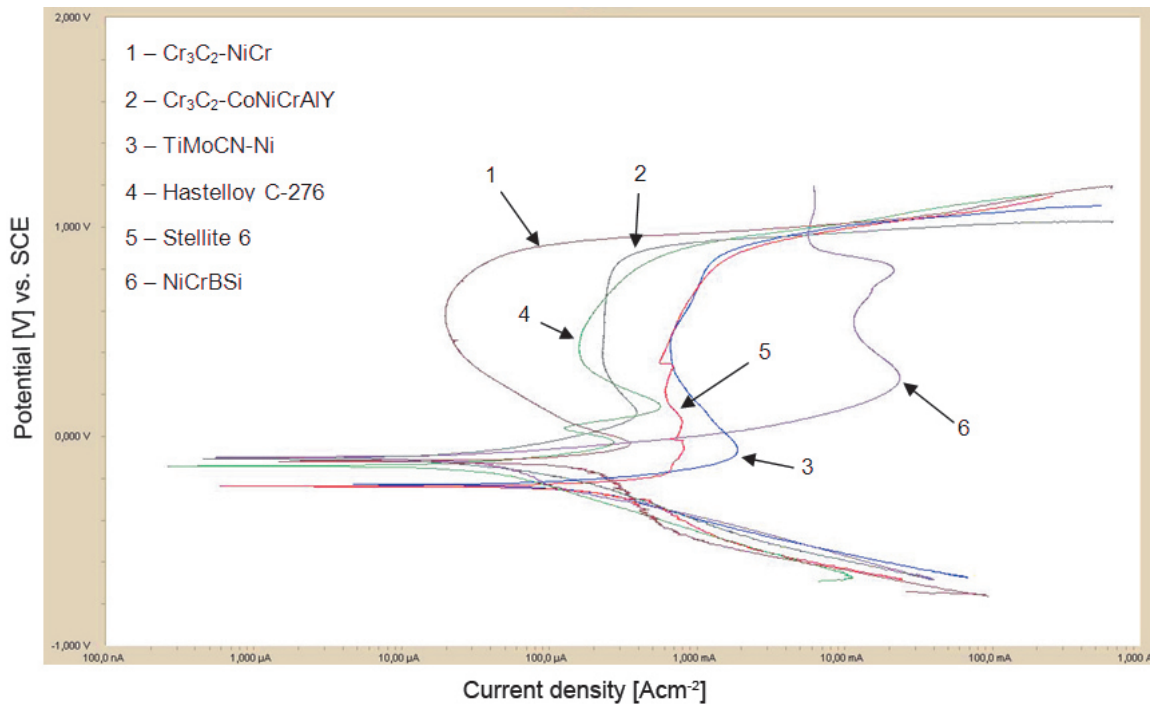
The passivation potential is an electrochemical potential during which the passivation of coating occurs. For this reason, it is evident that the lower the value of this potential is, the higher is the corrosion resistance of the coating. The passivation ability is dependent not only on the electrochemical potential, but also on the critical passivation current density. The lower the current density is, the easier the spontaneous passivation by means of oxygen occurs.  $J_{corr}$  is a place in the graph from which the coating is considered to be passive. After reaching this value, only the corrosion of oxide passive layers occurs.

While evaluating the passivation properties using this method, it is also important to evaluate the change in curve direction in passivation area of the graph. The different curve shape in the passivation region signifies various formations of various passivation films on the coating surface. Two types of protective films can be formed on the coating surface. The first one is a three-dimensional solid film and the second one is an absorbent film. If a compact film covering the entire surface and protecting the metal from corrosion is formed due to the electrochemical reaction, the passivation stable state begins. If only one dimensional absorbent film of oxygen is formed on the metal surface, it can prevent the dissolution of metal, but it cannot protect the metal completely. Positive direction in change signifies the formation of three-dimensional passive film protecting the coating. Negative change signifies the formation of one-dimensional layer which only slows further corrosion attack.

The potentiodynamic polarization technique is used to detect any tendency of the substance to passivity. Anodic polarization data for all HVOF sprayed coatings are shown on **Fig. 1**. The results of the test are shown in **Table 1**.

**Table 1** Summary of the corrosion parameters obtained from the polarization curves

Sample	$E_{corr}$ [mV]	$J_{corr}$ [ $\mu$ A.cm <sup>-2</sup> ]
Cr3C2-NiCr	82	125
Cr3C2-CoNiCrAlY	335	230
TiMoCN-Ni	340	680
Hastelloy C-276	156	550
Stellite 6	186	830
NiCrBSi	554	12150



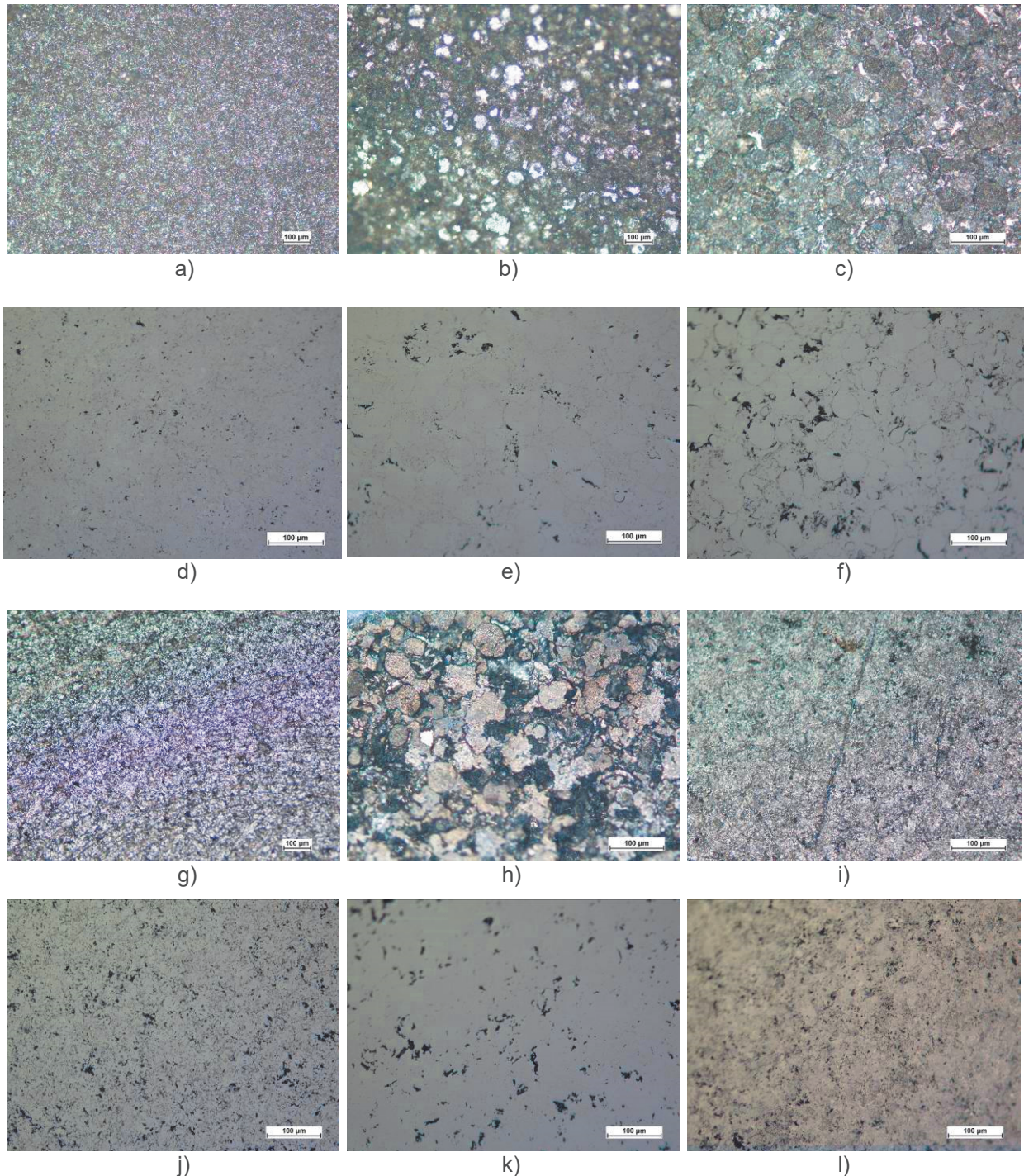
**Fig. 1** Anodic polarization curves in 5% solution of H<sub>2</sub>SO<sub>4</sub> at room temperature from HVOF sprayed coatings

The potentiodynamic tests show that Cr<sub>3</sub>C<sub>2</sub>-NiCr coating exhibited the best corrosion resistance out of all coatings. It was caused by the lowest measured values of  $J_{\text{corr}}$  and  $E_{\text{corr}}$  and also the graph on **Fig. 1** apparently shows its resistance in H<sub>2</sub>(SO)<sub>4</sub> acid. Cr<sub>3</sub>C<sub>2</sub>-CoNiCrAlY coating also showed good anti-corrosion properties in the environment of H<sub>2</sub>(SO)<sub>4</sub>. The third most resistant coating in H<sub>2</sub>(SO)<sub>4</sub> acid was Hastelloy C-276 coating. However, the selective dissolution of some phases initially occurred in this coating (see **Fig. 1**). Phase dissolution was followed by the passivation of the coating in values listed in **Table 1**. The Precise determination of phase dissolution will be the subject of future research. TiMoCN-Ni and Stellite 6 coatings show very similar behavior in this environment (see **Fig. 1**). The worst results were measured by NiCrBSi coating, which greatly degraded in this environment. It is also evident from the position and the shape of its curve in **Fig. 1**. The graph shows that the anticipated dissolution of two phases occurred as first, and subsequently the partial passivation of the coating took place. The low resistance of NiCrBSi coating in this environment has been previously proved using immersion tests in the publication Česánek et al. [6]. The graph for this coating (**Fig. 1**) shows the transition from active to passive state, but the corresponding values of the corrosion current density were too high (see **Table 1**). These values indicate the fact that no protective film was formed on the coating surface, and the surface was therefore still in the active state of corrosion ( $I_{\text{corr}}$  is greater than  $I_{\text{corr}}$  of passivated coating). Studies show that no protective or absorption film is formed on the surface of NiCrBSi coating.

### 3.2. Microstructure change after anodic polarization experiment

The **Fig. 2** represents photos of all evaluated coatings before and after the potentiodynamic corrosion tests. The photos before the test are provided for illustration of the original coatings microstructure. The photos after the test apparently show that the passivation layer was not formed over the entire coating surface by certain coatings (Stellite 6 and TiMoCN-Ni). This assumption is derived from the photos **Fig. 2c** and **Fig 2h**, which clearly show microstructure and maintained boundaries between splats. The oxides and spinels on splat borders were probably not formed by these coatings and particularly this process probably enables coatings to protect the substrate material. Other coatings except NiCrBSi probably created oxide passivation film over

the entire surface see **Fig. 2**. NiCrBSi coating showed the worst passivation ability out of all evaluated coatings. **Fig. 2i** shows the resulting microstructure of this coating after the potentiodynamic corrosion test.



**Fig. 2** Images of evaluated coatings on the surface before and after potentiodynamic tests in 5 % aqueous solution of  $H_2(SO)_4$ , where d)  $Cr_3C_2$ -NiCr coating before and a)  $Cr_3C_2$ -NiCr coating after the test, e)  $Cr_3C_2$ -CoNiCrAlY coating before and b)  $Cr_3C_2$ -CoNiCrAlY coating after the test, f) TiMoCN-Ni coating before and c) TiMoCN-Ni coating after the test, j) Hastelloy C-276 coating before and g) Hastelloy C-276 coating after the test, k) Stellite 6 coating before and h) Stellite 6 coating after the test, l) NiCrBSi coating before and i) NiCrBSi coating after the test

## CONCLUSION

- 1) In general, it can be argued based on the potentiodynamic tests in aggressive environment of 5 %  $\text{O H}_2(\text{SO})_4$  that carbide coatings exhibited better passivation protection to the substrate compared with alloys based coatings.
- 2)  $\text{Cr}_3\text{C}_2\text{-NiCr}$  cermet coating showed the best passivation properties out of all cermet coatings and experimental  $\text{TiMoCN-Ni}$  coating exhibited the worst results.
- 3) Hastelloy-276 coating exhibited the highest passivation protection to the substrate out of all alloy based coatings and  $\text{NiCrBSi}$  showed the worst results, probably due to the lack of stable passivation protective layer formation on its surface.

## ACKNOWLEDGEMENTS

*This paper was prepared with support from grant No. SGS-2013-028 - Ministry of Education, Youth and Sports of the Czech Republic.*

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