

Isothermal oxidation of metallic coatings deposited by a water-stabilized plasma gun

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Abstract

Plasma deposits of two high-alloy steels, nickel and a Ni-Cr alloy were studied from the point of view of their isothermal oxidation at elevated temperatures. Deposits separated from the substrate were measured by a gravimetric method after mechanical treatment of both faces of each sample followed by oxidation at 1000–1150 K for various periods of time up to 144 hours. In spite of the irregular growth of the oxide layers due to the defect structure of plasma sprayed deposits as well as of the oxide layers, the oxidation kinetics could be taken for approximately parabolic. The study of the composition of oxide layers on all alloys showed that they contained very low amounts of chromium. This is in a strong contrast to oxides growing during plasma spraying, which are significantly enriched in chromium as compared to the alloy composition. The preferential oxidation of chromium during plasma spraying results in chromium depletion of the alloy phases in plasma deposits. This depletion is the main reason for rapid oxidation of steel deposits during isothermal oxidation tests, which was shown also by comparing one of the plasma deposited high-alloy steels with bulk steel of similar starting composition. The plasma deposits of nickel and the Ni-Cr alloy exhibited significantly better oxidation resistance.

Key words: plasma spraying, metallic coatings, oxidation tests, oxidation kinetics, oxide structure, element distribution

1. Introduction

Protective properties of thermally sprayed deposits are important in industrial applications. The usual aim of applying thermally sprayed coatings is the protection of coated components against aqueous corrosion or high temperature oxidation as described in the review [1]. Among the thermal spraying techniques, plasma spraying is particularly versatile because it enables deposition of metallic, ceramic or composite coatings. The plasma deposition and the coating properties of elemental metals such as Cu [2], Mo [3, 4] or Ni [5, 6] as well as a number of alloys (e.g. Ni-based alloys [7, 8], Fe-based alloys and steels [9–12] or cast iron [13–15]) have been referred to. The aqueous cor-

rosion of thermal and, in particular, plasma deposits has been studied extensively.

The resistance against high-temperature oxidation is an important feature of thermal sprayed coatings. Some cases are described in [16–21], referring mainly to bond coats between metallic substrates and thermal barrier coatings. The additional high-temperature oxidation of previously deposited coatings must be distinguished from oxidation occurring during spraying and inherent to the spraying process itself. The mechanisms of the two reactions and the properties of their products are quite different.

In contrast to the previous work in this field where in most cases gas-stabilized plasma guns or high-velocity oxy-fuel techniques have been used for metal

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Table 1. Results of chemical analysis [% by mass] of steels

Material	C	Cr	Mn	Mo	Ni	P	S	Si	Ti
Feedstock powder 17 021	0.15	14.1	0.27	0.04	0.29	0.022	0.024	0.10	0.44
Feedstock powder 17 346	0.03	18.5	0.21	3.00	13.3	0.020	0.015	0.17	0.17
Bulk steel 17 346	0.08	18.3	1.17	3.48	11.3	0.012	0.009	0.26	0.43

Table 2. Results of chemical analysis [% by mass] of Ni and Ni-Cr alloy

Material	C	Co	Cr	Fe	Mn	Si
Feedstock powder Ni	0.003	0.087	0.057	0.71	0.011	0.007
Bulk Ni	< 0.01	0.003	< 0.005	0.010	0.002	0.010
Feedstock powder Ni-Cr	0.04	0.025	20.0	0.47	0.64	0.81

deposition, all coatings referred to in the present paper were plasma deposited using a water-stabilized plasma gun. The aim of the present paper is to give data obtained in high temperature oxidation tests of several types of plasma-deposited metallic coatings (two high-alloy steels, nickel and a Ni-Cr alloy). Prior to oxidation, the as-sprayed deposits were separated from the substrate, which was followed by adjustment of their dimensions and mechanical treatment of both faces. Afterwards, the plasma deposits were heated in air at temperatures up to 1150 K for up to 144 hours. Bulk samples of some of the materials were tested too to compare their oxidation resistance with the plasma deposits. The oxygen uptake was determined by weighing. The morphological features, composition and structure of oxidation products were studied by scanning electron microscopy, X-ray microanalysis and X-ray diffraction analysis.

2. Experimental

2.1. Materials

Two high-alloy steels ČSN 17 021 (equivalent of AISI 410) and ČSN 17 346 (equivalent of AISI 316), nickel and a Ni-Cr alloy (20 % Cr) were chosen as plasma deposit materials. Feedstock powders produced by gas atomization were used in the experiments. The dimensions of feedstock powder particles were 100–140 μm .

To compare the oxidation behaviour of plasma deposits with that of bulk metals, plates of Ni and steel ČSN 17 346 were tested simultaneously. Other bulk alloys were not available.

The elemental compositions of materials used in the experiments are given in Tables 1 and 2.

2.2. Plasma spraying and surface treatment of the samples

The powder particles were sprayed onto mild steel substrates by a 160 kW water-stabilized plasma gun

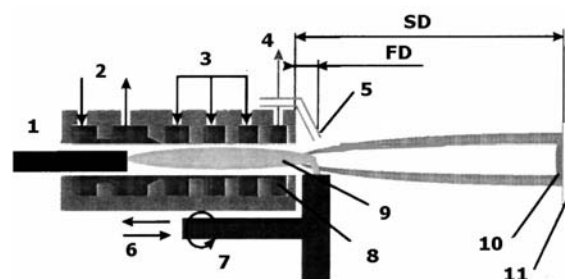


Fig. 1. Scheme of the water-stabilized plasma gun (drawing delivered by P. Ctibor, Institute of Plasma Physics ASCR). 1 – cathode, 2 – cathode cooling, 3 – water inlets, 4 – water outlet, 5 – powder feeder, 6 – anode cooling, 7 – rotary anode, 8 – water vortex, 9 – arc, 10 – plasma deposit (coating), 11 – substrate, SD – spraying distance, FD – feeding distance.

WSP[®] Pal 160. A simplified scheme of the gun is shown in Fig. 1. The principle of the plasma gun function consists in heating and evaporation of water from the internal “wall” of the water vortex surrounding the d.c. arc. This is followed by water dissociation and ionization. The high-pressure plasma is blown from the nozzle to give rise to the plasma jet.

Characteristic distances: spraying distance SD (plasma gun nozzle – substrate) 400 mm, feeding distance FD (nozzle – powder injector) 65 mm.

After plasma spraying, the coated substrates were cut into samples 20 mm long. The width of the samples was chosen so as to be characteristic of each coating material to ensure easy identification after the high temperature test. The plasma deposits were detached from the substrate, which enabled avoiding any interference of the substrate in the reaction between the coating and atmospheric oxygen. The surfaces of both sample faces were mechanically ground to ensure the same properties of the two surfaces. The average thickness of the samples prepared in this way was about 1.5 mm. The geometric surface area of the samples including the edges was 650–800 mm². The average rough-

ness characteristics were as follows (Ra is the mean deviation from the centre line of the profile throughout the sampling length, $Rmax$ is the maximum peak-to-valley height of the profile within the sampling length, which was 25 mm):

Parallel to the grinding direction:

$$Ra = 0.8 \mu\text{m}, Rmax = 24.7 \mu\text{m}$$

Perpendicular to the grinding direction:

$$Ra = 1.0 \mu\text{m}, Rmax = 25.3 \mu\text{m}.$$

2.3. Oxidation experiments and analytical techniques

The samples were positioned in corundum boats so as to ensure equal access of oxygen to both sample faces. An appropriate number of boats were located in a furnace. In each oxidation run, 6 samples of each material (4 types of plasma deposits and 2 bulk metals) were treated in air at atmospheric pressure and at a constant temperature (1000, 1050, 1100 and 1150 K). After 24 h, 48 h, etc., one sample of each material was removed from the furnace and its mass gain was determined. The entire oxidation run lasted 144 hours. As shown later, some oxidation products crack and spall easily. However, neither their cohesion nor adhesion to the substrate failed during the oxidation runs. The gravimetric results were used for assessment of oxidation kinetics. There appeared two possible ways how to describe the oxidation kinetics observed in the experiments: either the linear or the parabolic law can be applied. The linear law is adequate if the major part of the metallic surface is exposed to the oxidizing atmosphere during the whole oxidation run. This can occur due to oxide vaporization or lack of adhesion exposing a bare metallic surface. The oxidation rate would then be equal to the chemical reaction rate on the surface. In spite of some anomalous properties of most oxide layers grown during isothermal oxidation, this was not the case. The parabolic law governed by diffusion appeared to fit better to the oxidation data. To simplify the statistical treatment, the parabolic law was linearized and the least squares fit was applied to the equation

$$\Delta m = a + bt^{1/2}, \quad (1)$$

where Δm is mass gain per unit area, t is time; a , b are parameters.

It follows:

$$k_p = b^2, \quad (2)$$

where k_p is the parabolic rate constant.

To see the morphological features of the plasma deposits and to carry out their local chemical analysis, cross sections were prepared by a conventional metallographic technique. After a thin carbon film deposi-

tion, they were studied by a scanning electron microscope CamScan 4DV and an energy dispersive X-ray microanalysis system LINK AN 10000. The analysed points were chosen as distant as possible from all inclusions, interfaces or boundaries. This was not always possible in oxides grown during plasma spraying because they have mostly the shape of thin envelopes of alloy splats. It follows that the true concentrations of the alloying elements may be somewhat higher than indicated in Figs. 3–5 (see chapter 3), “Oxides A”.

As-oxidized samples were also analysed by an X-ray diffractometer Siemens D 500 to detect the oxide phases present in the oxidation products.

3. Results

The experimental data obtained from isothermal oxidation of plasma sprayed deposits and bulk metals were fitted by parabolic plots. The values of k_p obtained from all samples are given in Table 3. It follows that the temperature dependence of k_p was not always monotonic. This may be due to inhomogeneous growth of oxide layers.

Plasma deposits of steel ČSN 17 021 were chosen to show typical experimental results, calculated plots and 95% confidence bands (Fig. 2).

In Figs. 3–6, typical cross sections of plasma deposits with surface oxide layers grown under selected oxidation conditions can be seen. X-ray microanalysis

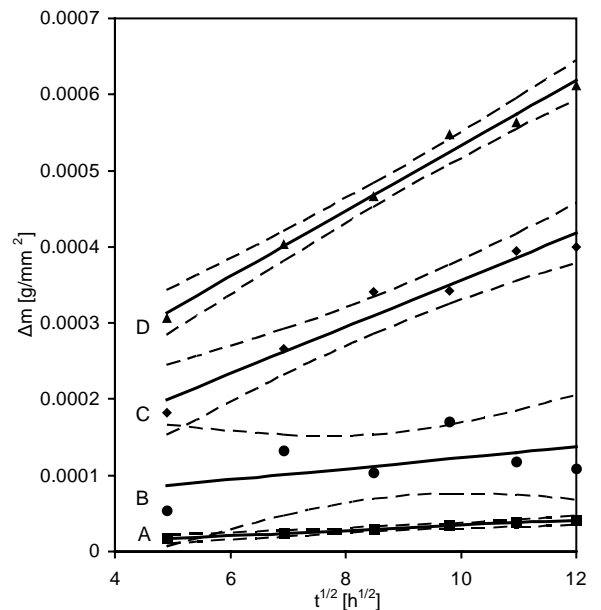


Fig. 2. Oxidation kinetics of steel 17 021 plasma deposits at 1000 (A), 1050 (B), 1100 (C), and 1150 K (D). Confidence bands 95 %.

Table 3. Parabolic rate constants of isothermal oxidation of plasma deposits and bulk metals

Material	Temperature [K]	k_p [$\text{g}^2 \cdot \text{mm}^{-4} \cdot \text{h}^{-1}$] (plasma deposit)	k_p [$\text{g}^2 \cdot \text{mm}^{-4} \cdot \text{h}^{-1}$] (bulk)
Steel 17 021	1000	1.20×10^{-11}	
	1050	5.18×10^{-11}	
	1100	9.52×10^{-10}	
	1150	1.86×10^{-9}	
Steel 17 346	1000	6.20×10^{-12}	3.59×10^{-15}
	1050	3.33×10^{-11}	5.21×10^{-15}
	1100	2.72×10^{-10}	3.3×10^{-14}
	1150	2.82×10^{-10}	1.54×10^{-13}
Ni	1000	1.10×10^{-11}	1.75×10^{-11}
	1050	4.15×10^{-13}	3.24×10^{-12}
	1100	2.24×10^{-11}	8.01×10^{-12}
	1150	8.18×10^{-11}	1.31×10^{-11}
Ni-Cr alloy	1000	1.68×10^{-15}	
	1050	3.22×10^{-11}	
	1100	1.95×10^{-11}	
	1150	8.06×10^{-12}	

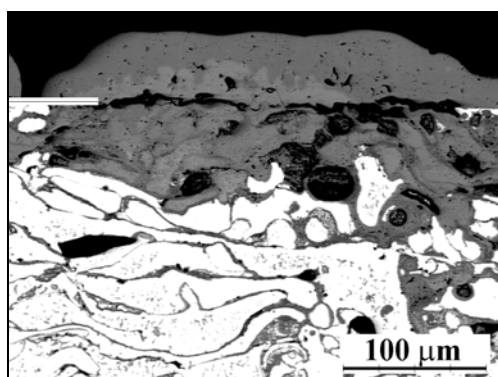


Fig. 3. Cross section of steel 17 021 plasma deposit oxidized 120 hours at 1150 K in air. The X-ray microanalysis resulted in the following average concentration values [% by mass]:

Analysed objects/element	Alloy splats	Oxides A	Oxides B
Cr	3.1	41.2	2.6

was conducted in a number of points. To see clearly the scanning electron patterns, the analysed points are not indicated in Figs. 3–6. Instead, the average concentration values obtained from typical objects are given. These are alloy splats, oxides grown during plasma spraying (oxides A) and reaction products resulting from the isothermal oxidation conducted after plasma spraying (oxides B). The sum of the dominant metallic element concentrations was taken for 100 %, whereas

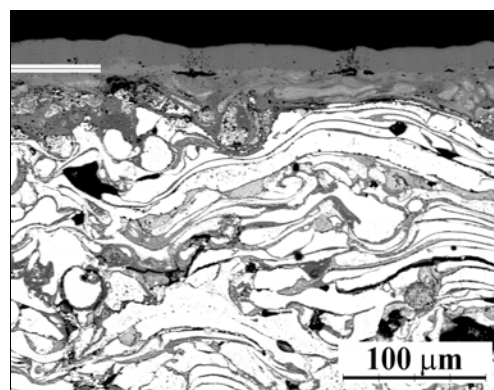


Fig. 4. Cross section of steel 17 346 plasma deposit oxidized 120 h at 1150 K. The X-ray microanalysis yielded the following average concentration values [% by mass]:

Analysed objects/element	Alloy splats	Oxides A	Oxides B
Cr	10.9	27.2	0.9
Mo	2.9	2.0	0.1
Ni	15.3	7.1	2.4

the minor alloying elements and impurities were neglected. This means that steel 17 021 and the Ni-Cr alloy were taken for binary alloys, steel 17 246 for an Fe-Cr-Mo-Ni alloy. In the oxides, the average concentrations of metallic elements were only taken into consideration (irrespective of their possible concentration gradients). The results are indicated in the captions of Figs. 3–6. The alloying elements are mentioned, not the base metals (Fe or Ni), whose concentrations are

Table 4. Qualitative description of oxide phases obtained during plasma spraying

Material	Dominant phase(s)	Minor phase(s)
Steel 17 021	Spinel-type oxide, approx. composition $\text{Fe}_{1.1}\text{Cr}_{1.9}\text{O}_4$ [11, 22]	Fe_3O_4 with small amount of dissolved Cr [22]
Steel 17 346	The same as in steel 17 021	The same as in steel 17 021
Ni	NiO	—
Ni-Cr alloy	Cr_2O_3 with small amount of dissolved Ni; Cr_3O_4 with small amount of dissolved Ni [23]	NiO [23]

Table 5. Qualitative description of oxide phases grown during isothermal oxidation of plasma deposits

Material	Dominant phase	Minor phase(s)
Steel 17 021	$\alpha\text{-Fe}_2\text{O}_3$	In most cases ill-defined spinel oxides ($\gamma\text{-Fe}_2\text{O}_3$, FeCr_2O_4)
Steel 17 346	The same as in steel 17 021	The same as in steel 17 021
Ni	NiO	—
Ni-Cr alloy	NiO	NiCr_2O_4

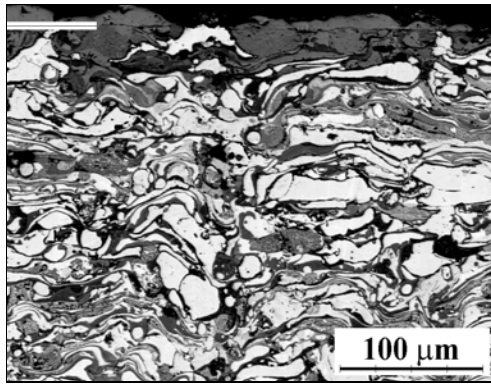


Fig. 5. Cross section of Ni-Cr alloy deposit oxidized 120 h at 1150 K. The X-ray microanalysis yielded the average concentration values [% by mass] as follows:

Analysed objects/element	Alloy splats		
	Oxides A	Oxides B	
Cr	5.9	47.2	14.2

complementary to 100 %. The “pure” nickel deposit (Fig. 6) was not analysed because no alloying element was present.

During isothermal oxidation of all alloys under consideration, the oxide-gas interface moved to the outside and at the same time the metal-oxide interface penetrated to the depth of the splats. The network of oxide films enveloping the splats was embedded in the latter part of the newly grown oxide layer. The position of the metal surface before the isothermal oxidation is mostly “decorated” by rows of voids. In each micrograph relating to an alloy (i.e. except pure nickel), this position is approximately indicated by a double horizontal white bar.

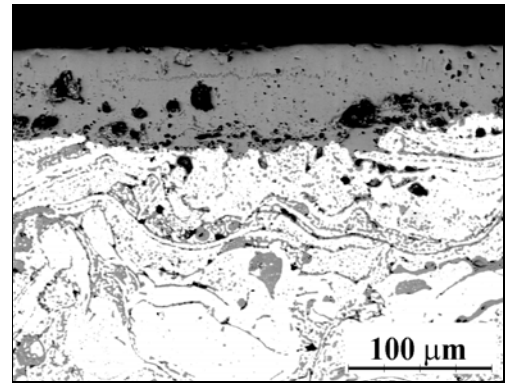


Fig. 6. Cross section of nickel plasma deposit oxidized 120 h at 1150 K. The X-ray microanalysis was not carried out.

The X-ray diffraction results enabled identification of the phases present in the oxides. For most materials, the oxide phases differed significantly from those having grown previously during plasma spraying. A survey of qualitative results is given in Tables 4 and 5. In most cases, the diffraction patterns of metallic phases ($\alpha\text{-Fe}$, $\gamma\text{-Fe}$, Ni) were also obtained (not mentioned in Tables 4 and 5). In Fig. 7, an example of a typical X-ray diffraction pattern of the Ni-Cr alloy surface after isothermal oxidation is given to see qualitatively the phases present in the sample. A more detailed analysis shows a shift of Ni diffraction lines due to dissolved Cr and the shifts of Cr_2O_3 and Cr_3O_4 lines due to dissolved Ni. In NiCr_2O_4 , some deviation from stoichiometry may exist, too. In Table 5, this also relates to FeCr_2O_4 , whose ill-defined diffraction lines did not enable a precise analysis, whereas $\text{Fe}_{1.1}\text{Cr}_{1.9}\text{O}_4$ has been determined previously by a combination of X-ray diffraction and spectroscopic methods [11].

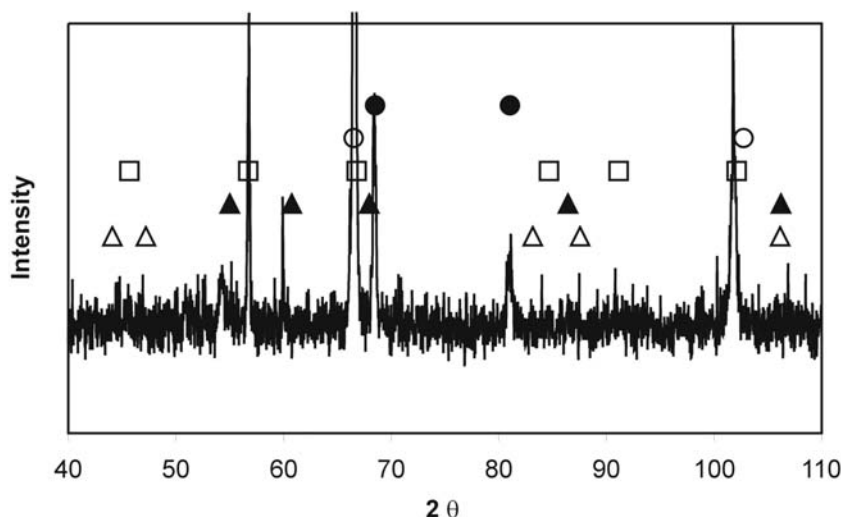


Fig. 7. X-ray diffraction pattern of Ni-Cr alloy plasma deposit oxidized 144 hours at 1150 K: ● Ni, ○ NiO, ▲ Cr₂O₃, △ Cr₃O₄, □ NiCr₂O₄. Some weak diffraction lines of the oxides were identified by magnification of the pattern and reduction of the background. Most diffraction lines are shifted from their indicated regular positions due to alloying or deviation.

4. Discussion

The isothermal growth of oxide layers on plasma deposited metals studied in this paper was highly inhomogeneous. This was apparently due to the structure of plasma deposits composed of splats, oxides originating from the deposition process, and a number of defects. In spite of this, the overall oxide growth was mostly parabolic. It can be assumed that the isothermal growth of oxide layers on the surface of the alloys deposited by a gas-stabilized plasma gun would be similar because of the same defect structure of the deposits.

Strong Cr-depletion was observed in the alloy splats. The depletion was a consequence of preferential oxidation of Cr during plasma spraying. Selective evaporation of elements might also contribute to this effect. In as-sprayed steel 17 346 and a Ni-Cr alloy, the Cr-depletion has been investigated more thoroughly in [24] where merely the situation in as-sprayed deposits has been studied, i.e. no additional oxidation has been conducted. The same phenomenon in steel 17 021 is a matter of a paper to be published elsewhere. These studies have shown that in as-sprayed deposits, the Cr-concentrations were not as low as in the present paper where the samples were analysed after the additional isothermal oxidation. The number of splats selected for analysis was small just to show qualitatively that the Cr-concentrations in the metallic phases fell significantly during plasma spraying.

“Pure” nickel was the simplest case investigated in this paper. Relatively homogeneous oxide layers were obtained on the deposits, however, they contained a number of large voids, in particular near the interface between the metallic splats and the surface oxide layer.

There is an essential difference between the oxides grown during plasma spraying and those resulting from isothermal oxidation. During the flight of molten alloy particles in the plasma stream at very high temperatures, oxide melts grow on the alloy drop surfaces, and preferential oxidation of chromium takes place due to the high affinity of chromium to oxygen. The resulting oxides are very rich in this element. On the contrary, the outer parts of the oxides grown during isothermal oxidation at lower temperatures are poor in chromium. The concentrations of chromium in the inner parts grown into the surface layers of splats are slightly higher; nevertheless they are still much lower than in the oxides grown during preceding plasma spraying. This appears to be due not only to the alloy surface strongly depleted during previous plasma spraying, but also to quite different conditions of isothermal oxidation where the diffusion rates of the elements through the solid oxide layers are decisive.

Thermodynamic aspects of chromium steel and Ni-Cr alloy oxidation during plasma spraying have been discussed in [11, 23]. Plasma spraying, in particular its in-flight stage, is a very rapid process. However, at high temperatures above the melting points of all species present, the in-flight stage is long enough to approach the thermodynamic equilibrium. It follows that the thermodynamic analysis of the in-flight oxidation reaction yields data describing the reality to an acceptable approximation. A necessary condition is a homogeneous mixture of all reacting components. This can be approximately assumed at the in-flight stage, but not in solid-state oxidation where the metal is detached from the reacting atmosphere by an oxide layer and the reaction is governed by diffusion. It fol-

lows that an analogous thermodynamic approach is not applicable in the latter process.

Among the plasma sprayed deposits under consideration, two of them were compared with bulk materials: Ni and steel ČSN 17 346. Whereas the parabolic rate constants for plasma deposited Ni were somewhat higher than for bulk Ni, steel ČSN 17 346 exhibited the differences by three orders of magnitude. This clearly shows the effect of Cr-depletion in steel during plasma spraying as compared with bulk steel. The behaviour of plasma sprayed nickel and Ni-Cr alloy appeared to be more favourable. In particular, Ni-Cr showed to be relatively oxidation resistant, though the Cr-concentration due to depletion fell considerably and the oxide layers grown during subsequent oxidation were not quite compact. It is well known that the porosity of coatings is a phenomenon inherent to the plasma spraying process. This may also affect the porosity of surface oxide layers. Another reason for pore and crack formation in the oxides are the internal stresses in the oxides. It can be assumed, though this could not be verified quantitatively, that the mechanical properties of Ni-based oxides are more favourable than those of Fe-based oxides.

5. Conclusions

1. Isothermal oxidation of metallic plasma deposits was studied in the temperature range 1000–1150 K in air. The exposures were up to 144 hours.

2. Strong Cr-depletion due to plasma spraying was observed in Cr-containing alloys.

3. The plasma deposits of nickel exhibited better oxidation resistance than both high-alloy steels. The same holds for the Ni-20%Cr in spite of the inhomogeneity of the growing oxide layer.

4. The oxide layers grown on plasma sprayed high-alloy steels were prone to cracking and spallation after cooling down to room temperature.

5. The outer regions of the oxides grown on the alloy deposits during isothermal oxidation in the given range of temperatures were poor in chromium in contrast to oxides originating from the reactions during plasma spraying.

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