Materials Science-Poland, *Vol. 28*, *No. 1*, *2010*

Structure and properties of iron aluminide layers fabricated by the chemical vapour deposition on 316L steel

R. SITEK[1*], J. KAMIŃSKI[1], P. SALLOT[2], K.J. KURZYDŁOWSKI[1]

[1]Faculty of Materials Science and Engineering, Warsaw University of Technology, ul. Wołoska 141, 02-507 Warsaw, Poland

[2]Ecole Nationale Supérieure des Mines de Saint-Etienne, 158 Cours Fauriel, 42000 Saint-Etienne, France

The paper presents results of studies of structure and properties of the NiAl + FeAl type diffusion layers fabricated on 316L steel (00H17N14M2) by the chemical vapour deposition using aluminium chloride ($AlCl_3$) in a hydrogen atmosphere as a carrier gas. The layers were examined using light and scanning electron microscopy. Chemical composition analyses were carried out by EDS and phase content was investigated by XRD. Corrosion resistance was tested using the potentiodynamic method in 0.5 M NaCl, and layer/structure adhesion was tested by the scratch test. The results obtained indicate that the 50 μm thick layers fabricated on the 316L steel substrate show very good adhesion combined with very good corrosion resistance.

Keywords: *iron aluminides; FeAl; CVD; austenitic stainless steel; intermetallics*

1. Introduction

Austenitic stainless steel 316L, due to its high corrosion resistance, is frequently used in implant materials [1–5] and for surgical instruments. There is also a constant increase in the number of other fields of application, in the nuclear, shipping, chemical, power and food industries. Wider use of 316L steel in industry is limited by its low operating temperature (up to ca. 400 °C), unsatisfactory resistance to abrasive wear, and insufficient resistance to pitting corrosion (e.g., physiological fluids). To improve these properties, various technological processes are used, e.g. introduction of sufficient amounts of nitrogen and molybdenum, special heat-treatments [6] or surface treatments, i.e. nitriding or oxygen nitriding [7–10]. The advantage of the surface treatment is the ability to fully control the process used to produce layers with a spe-

*Corresponding author, e-mail: rsitek@inmat.pw.edu.pl

cific microstructure, phase content, and chemical composition. Fe-Al type intermetallic phases are increasingly more commonly used in the automotive, aircraft, and shipping industries because they have good heat resistance, are strongly resistant to abrasive wear, have a relatively low density compared with conventional iron and nickel alloys, and because of their high resistance to corrosion in environments containing sulphur or oxygen. It has been predicted [11] that Fe-Al type intermetallic phases can replace in future austenitic steels, used in the food industry, that contain chromium and nickel harmful to organisms. The feature that limits the application of bulk intermetallics is their fragility at room temperature, and hydrogen embrittlement caused by a high affinity of aluminium to water in vapour. These properties can be improved by the addition of alloy elements such as Mo, Si, Cr, Ta, or by grain refinement: this significantly increases the production cost of bulk intermetallic materials [11]. The fabrication of Fe-Al type intermetallics in the form of layers on austenitic steels is both simple and economical [12, 13]. Accordingly, this paper presents the results of research on the fabrication, using the chemical vapour deposition (CVD) method, of Fe-Al type intermetallic layers on 316L steel. Aluminium chloride ($AlCl_3$) was used as the source of aluminium, and the carrier gas was hydrogen.

2. Experimental

Samples for tests were cut out from a 4 mm thick cylindrical bar (diameter 20 mm) made of 316L steel (00H17N14M2) having the chemical composition presented in Table 1.

Table 1. Chemical composition of the 316L steel

Element	Cr	Ni	Mo	Si	Mn	C	Cu	P	S	Fe
Concentration [wt. %]	17.47	12.7	2.55	0.8	2.0	0.03	0.015	0.045	0.03	balance

Sample surfaces were polished using sandpapers (grit: 600, 800, and 1200) and were degreased using an ultrasonic washer in ethyl alcohol. The layers were deposited using the chemical vapour deposition (CVD) method in the IonBond device, in two stages, of one cycle. The first stage involved deposition of aluminium from $AlCl_3$ vapours with the addition of chromium in an hydrogen atmosphere at a temperature of 950 °C for a period of 1.5 h under the pressure of 350 hPa. The second stage entailed baking at 950 °C for 3 h under the pressure of 350 hPa in a N_2 atmosphere. This was to assure diffusion between the deposited aluminium and the steel substrate. In this process, an FeAl diffusion layer was formed. Sections of the samples were examined under scanning electron microscopes HITACHI 2600 and HITACHI 3500 equipped with a microarea microanalysers EDS from Thermo Noran. Cross sections were polished to a mirror-like finish using 0.05 μm silicate slurry. All samples were ultrasonically degreased in acetone and ethanol.

The phase analyses were performed with a Bruker D8 X-ray diffractometer using Cu K_α radiation. The samples were examined in a parallel beam from a parabolic mirror (Gobel Mirror Bruker) under the fixed angle $\omega = 10°$. A corrosion resistance test was conducted using impedance and potentiodynamic methods on an AutoLab PGSTAT 100 device in a deoxidised 0.5 M NaCl solution at room temperature. A deoxidised environment was obtained by running chemically pure argon through the solution. Oxygen concentration was measured using an Elmetron CO 401 oxygen meter. Impedance tests were performed in a three-electrode system (tested electrode –reference electrode (saturated calomel electrode – SCE)–counter electrode (platinum)) within the frequency range of 10^5–10^{-3} Hz at the sinusoidal signal amplitude of 20 mV. The impedance spectra for steel were analyzed using the equivalent circuits (EC). Figure 1a presents the EC for the one time constant model (R(RQ)) and Fig. 1b shows the EC for two time constants model R(Q[R(RQ)]).

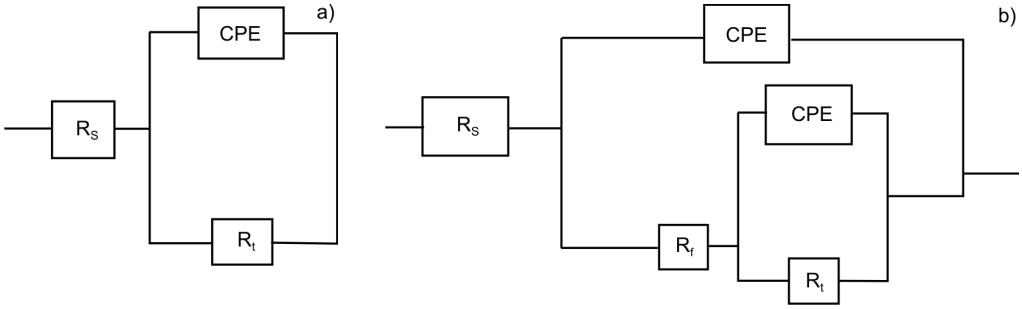

Fig. 1. Equivalent circuits: a) R(RQ), b) R(Q[R(RQ)]); CPE – constant phase element, R_s – solution resistance, R_f – resistance of the porous layer, R_t – charge transfer resistance through a double layer

The spectra were studied with the Baukamp's EQUIVCRT software. The potentiodynamic tests were performed in the same three-electrode system within the potential range from –400 mV to 500 mV in the anodic direction at the rate of 0.2 mV/s. Surface topography tests were conducted using a VEECO scanning profilometer. The microhardness measurements were carried out using the Vickers method and a ZWICK (Materialprüfung 3212002) hardness meter under the load of 200 g. The layer adhesion test was measured on a Micro-Combi-Tester device, with a variable load in the range from 0 to 100 N.

3. Results

The CVD method used in the study, employing $AlCl_3$ as an aluminium donor in a hydrogen carrier gas atmosphere, was good enough to produce a 50 μm layer on the 316L steel substrate. These layers of a complex substructure consisting of elongated grains exhibited geometrically perfect adhesion to the substrate (Fig. 2).

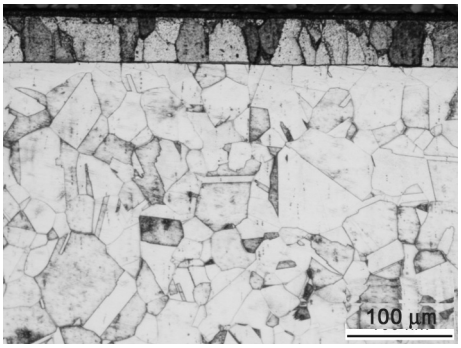

Fig. 2. Microstructure of the layer after the process at 950 °C on the 316L steel substrate

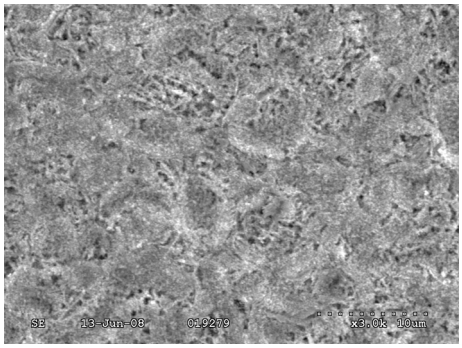

Fig. 3. Morphology of the surface of the layer at 950°C

Figure 3 shows that the surface of the layer was relatively smooth with an average surface roughness parameter R_a not exceeding 0.5 µm. Details on the data roughness is provided in Table 2. R_a is R_a is the average arithmetic standard deviation of the roughness profile, R_q is the average square deviation of the roughness profile and R_t is the maximum height of the roughness profile peak.

Table 2. Roughness parameters [µm] of the 316L steel surface before and after the CVD process

Materials	R_a	R_q	R_t
Before treatment	0.095	0.129	4.53
After treatment	0.412	0.526	6.18

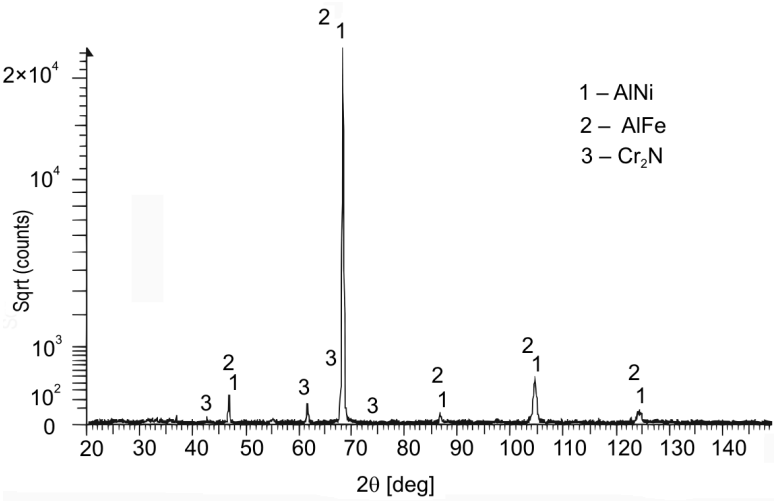

Fig. 4. Spectrum of the X-ray diffraction pattern from the layer produced in the CVD process at 950 °C on the 316L steel substructure

The surface microhardness of the layers was about 430$HV_{0.2}$. The results of X-ray analysis (Fig. 4), performed in the 20–150° range (2θ) revealed the presence of the AlFe, AlNi and Cr_2N phases.

The analysis of the chemical composition focusing on microareas of the transverse sections of the layers (Fig. 5, Table 3) showed the presence of two sub-layers. The outer sublayer is enriched in nickel appearing together with iron and aluminium. In the inner sublayer, the nickel content decreased while the iron content increased.

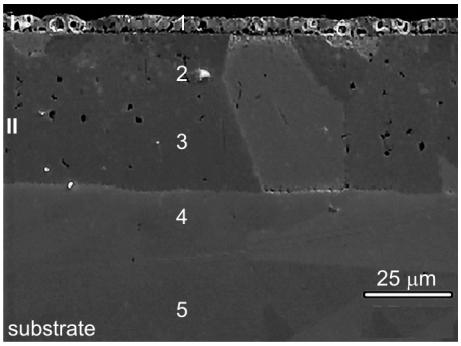

Fig. 5. SEM image of sublayer revealed on the transverse sections of the layers fabricated on the 316L steel in the CVD process at 950 °C (for details, see Table 3)

Table 3. Chemical composition in microareas of the transverse section of the layer produced on 316L steel in the CVD process at 950 °C

Microarea	Chemical composition [wt. %]					
	Fe	Cr	Ni	Mo	Al	C
1	47.61	9.80	23.77	1.70	10.02	6.84
2	67.51	17.19	6.63	2.30	3.42	2.87
3	68.99	18.86	5.06	2.17	2.02	2.91
4	67.01	16.81	8.79	2.07	-	3.21
5	66.67	16.69	9.32	1.87	-	2.88

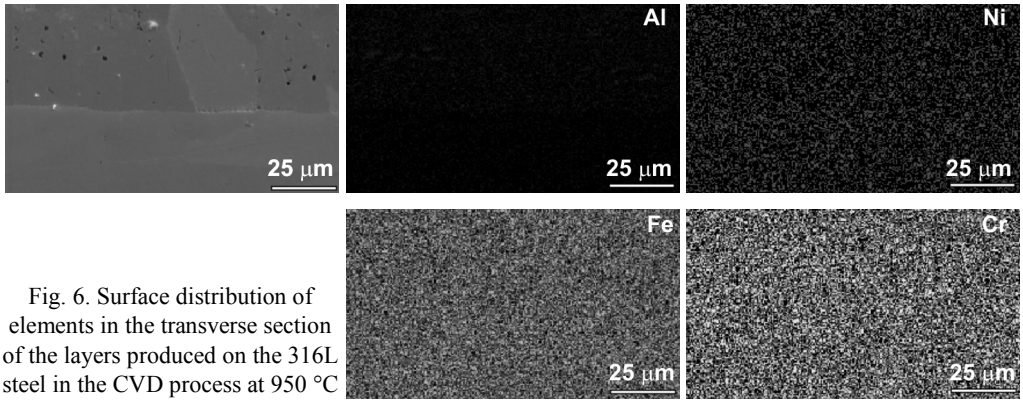

Fig. 6. Surface distribution of elements in the transverse section of the layers produced on the 316L steel in the CVD process at 950 °C

The distribution of the elements on a transverse section of the layer is shown in Fig. 6. It reveals that the layer was made mainly of aluminium, iron, chromium and nickel. The increased concentration of aluminium and nickel in the outer part of the layer indicates the formation of an intermetallic layer containing those two elements. The inner sublayer consists most probably of an intermetallic layer made of iron, and aluminium. However, the presence of some Cr_2N in both sublayers cannot be excluded.

The polarization curves for the 316L steel substrate and samples with the layer (FeAl) produced upon it are shown in Fig 7. Table 4 presents the characteristic electrochemical parameters of the tested materials; i_{corr} is the corrosion current density, E_{corr} – corrosion potential, and E_{np} – nucleated pit.

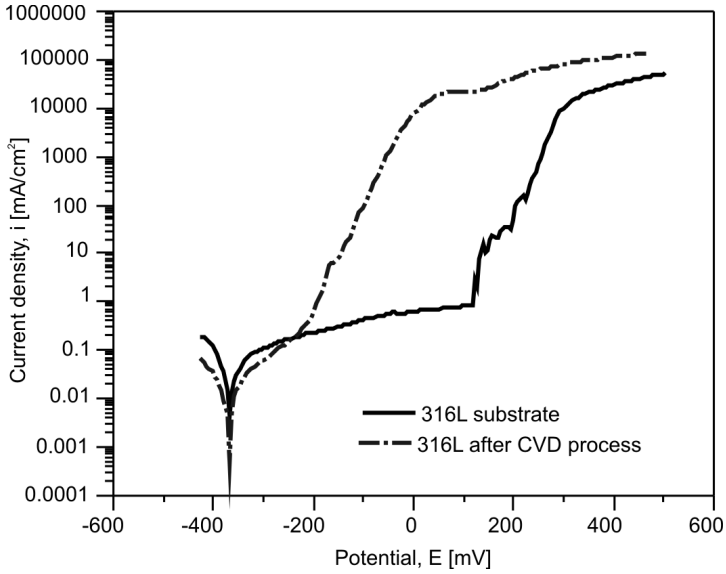

Fig. 7. The anodic polarisation curve in 0.5 M NaCl for NiAl + FeAl type diffusion layer and for 316L steel substrate

Table 4. Corrosion parameters describing the influence of layers fabricated in the CVD process on the corrosion resistance in comparison with the 316L steel

Material	i_{corr} [μA/cm^2]	E_{corr} [mV]	E_{np} [mV$_{SCE}$]
316L steel without a layer	0.08	–370	120
316L steel with a layer of the NiAl + FeAl type	0.028	–330	–180

As results from the data in Table 4 the layers of the NiAl + FeAl type increase the corrosion resistance of 316L steel. It is evidenced by a reduction in the density of corrosion currents with a simultaneous increase in the corrosion potentials. The durability

of this state was significant, as proved by both the low current densities in the passive area (ca. 0.8 μA/cm^2) and the relatively high breakthrough potentials (E_k = 120 mV), with pitting corrosion observed above this potential (Fig. 8a).

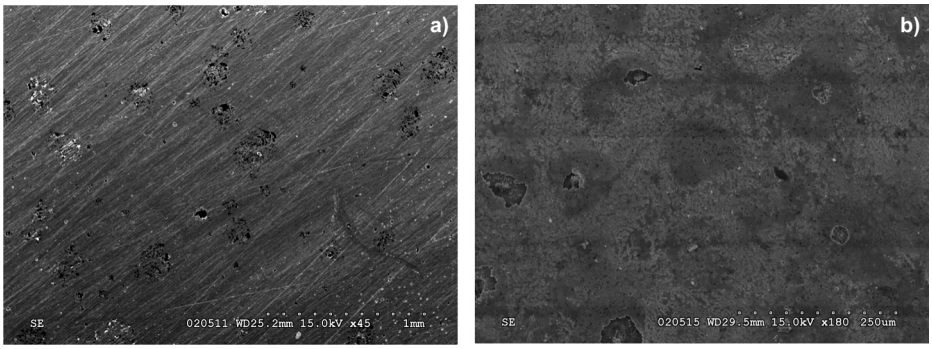

Fig. 8. Morphology of steel after potentiodynamic tests in deoxidised 0.5 M NaCl of the 316L steel substrate (a) and after the CVD process (b)

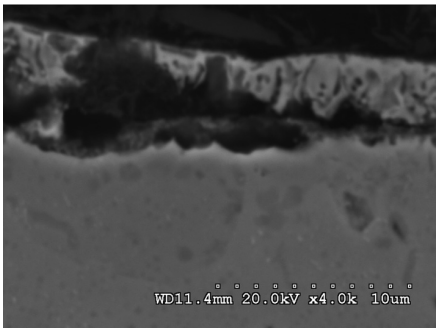

Fig. 9. Under-layer corrosion after being revealed by the potentiodynamic test in deoxidised 0.5 M NaCl solution in transverse sections

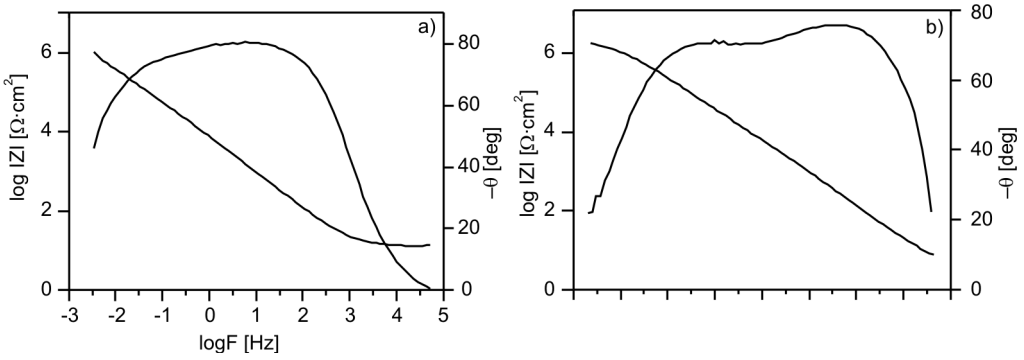

Fig. 10. Impedance spectra (Body's diagram) for the 316L substrate (a) and after the CVD process (b)

The FeAl layers had a significant influence on the 316L steel corrosion resistance. Although the data in Table 4 indicates an improvement in the corrosion resistance, the potentiodynamic tests showed that the durability of the passive state is very low.

A constant increase in densities of currents in the passive area was observed with a simultaneous reduction in the breakthrough potential. Moreover, the produced coatings have a cathodic potential with respect to the substrate which caused the material to be sensitive to underlayer corrosion (Fig. 9). The non-metallic intrusions observed on the layer surface seem to act as local corrosion initiation spots (Fig. 8b).

Table 5. Results of impedance measurement tests of the 316L substrate before and after the CVD process

Material	R [Ωcm^2]	Q_{CPE} [F/cm^2]	n
316L steel without a layer	1.47×10^{6}	7.04×10^{-6}	0.88
316L steel with layer of the NiAl+FeAl type	1.58×10^{6}	6.26×10^{-7}	0.82

Analysis of the spectra shown in Fig. 10 indicates a one time constant characteristic for a single electrochemical process taking place on the surface (i.e., the passage of an electron through a double layer). High angle values (ca. 80°) in a broad frequency range (10^{2}–10^{-1}Hz) confirmed the presence of the passive layer on the steel substrate.

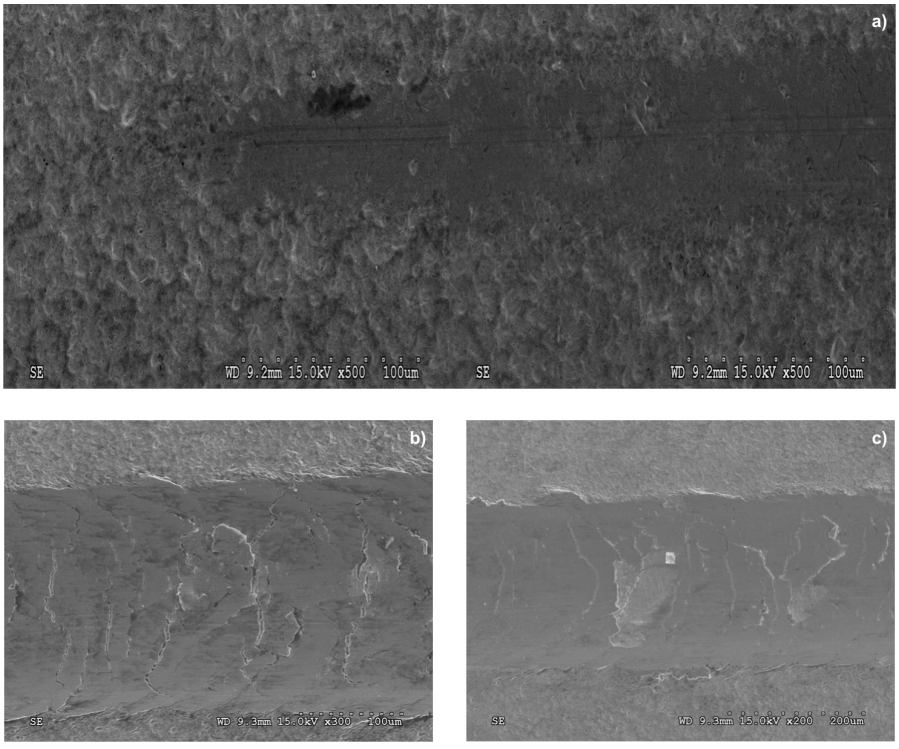

Fig. 11. Results of the scratch test of the resistance to abrasive wear. Details in the text

The layer characteristics (Table 5) were close to the values obtained for permanent passive layers. The impedance spectrum shown in Fig. 10b is different. The presence of two peaks in the impedance spectrum means that two electrochemical processes occurred on the surface, one of them being related to the passage of electrons through the double layer and the other to the electrochemical processes at the heterogeneous outer layer (zone 1 enriched with Al and Ni). According to the impedance spectrum and Fig. 4, it might be assumed that this layer was discontinuous (porous). This is the most likely explanation for the unsatisfactory durability of passive layers as observed during the potentiodynamic tests. The data in Table 5 (R is the resistance, Q – capacity) indicate that, despite the significant porosity of the outer layer, the Fe-Al coating was characterised by a similar corrosion resistance (slightly better) in comparison with the substrate.

Results of the adhesion tests (scratch-test) are presented in Fig. 11. The tested layers demonstrated a very good adhesion to the substrate and plasticity. The first cracks of the layer were observed under a critical force of Lc_1 = 24.1 N at the distance of 2.23 mm (Fig. 11a). Spalling (non-continuous perforation) was observed under a critical force of Lc_2=38.8 N at the distance of 7.63 mm (Fig. 11b). Continuous perforation and layer removal were observed under a critical force of Lc_3 = 73.57 N at the distance of 7.63 mm (Fig. 11c).

4. Summary

The CVD treatment with $AlCl_3$ vapour and hydrogen as carrier gas at 950 °C is satisfactory to produce ca. 50 μm thick layers of the NiAl + FeAl type 316L substrate in one-step. The layers are characterised by a very good adhesion to the substructure, and can be deposited on surfaces having complicated geometries. The NiAl + FeAl layer has a cathodic character in relation to the substrate. It improves the corrosion resistance of steel 316L but makes it more sensitive to the sublayer corrosion.

References

[1] *Engineering Materials for Biomedical Applications*, Teoh Swee Hin (Ed.), World Scientific, Singapore, 2004.
[2] BORDJI K., JOUZEAU J.Y., MAINARD D., PAYAN E., DELEGOUTTE J.P, NETTER P., Biomater., 17 (1996), 491.
[3] SUDHAKAR K.V., Eng. Fail. Anal., 12 (2005), 249.
[4] LIU C., LIN G., QI D.Y.M., Surf. Coat. Techn., 200 (2006), 4011.
[5] GERINGER J., FOREST B., COMBRADE P., Wear, 259 (2005), 943.
[6] ABDULUYAHED A.-A., ROŻNIATOWSKI K., KURZYDŁOWSKI K.J., Scripta Metal., 33 (1995), 1489.
[7] FOSSATI A., BORGIOLI F., GALVANETTO E., BACCI T., Surf. Coat. Technol., 200 (2006), 3511.
[8] LI G.-J., PENG Q., LI C., WANG Y., GAO J., CHEN S.-Y., WANG J., SHEN B.-L., Surf. Coat. Technol., 202 (2008), 2749.
[9] MINGOLO N., TSCHIPTSCHIN A.P., PINEDO C.E., Surf. Coat. Technol., 201 (2006), 4215.

[10] ZHAO C., WANG L.Y., HAN L., Surf. Eng., 24 (3) (2008), 188.
[11] *Metallic Materials Containing Intermetallic Phases*, W. Przetakiewicz, Z. Bojar (Eds.), Studio Bel, Warsaw, 2006 (in Polish).
[12] ZHANG Y., PINT B.A., COOLEY K.M., HAYNES J.A., Surf. Coat. Technol., 202 (2008), 3839.
[13] KAMACHI MUDALI U., BHUVANESWARAN N., SHANKAR P., RAJ B., Corr. Sci., 46 (2004), 2867.

Received 10 March 2009