



PROTECTIVE LAYERS OF IRON AND NICKEL ALUMINIDES ON STEEL

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Resume

Intermediary phases Ni-Al and Fe-Al are promising materials due to their superior properties such as hardness and good resistance against oxidation at high temperatures. Moreover, Fe-Al phases are resistant in sulphur - containing atmospheres. Because of these characteristics, the above mentioned intermetallic phases seem to be prospective for the use in many technical applications such as energetics, chemical or automotive industry in a form of a bulk material or coatings. Presently, the protective aluminide layer is usually prepared by thermal spraying. Nevertheless, this method is not suitable for complex-shaped components. Therefore, the aim of this work was to find an alternative way to prepare layers consisting of nickel or iron aluminides by other technique than thermal spraying. At first, carbon steel samples were coated using galvanic or electroless nickel plating. Coated samples were subsequently submerged into molten aluminium at various temperatures and process durations. The influence of the temperature and duration on the intermetallic phase growth was studied by scanning electron and light microscopy. Thickness and microhardness of the intermetallic layer was also measured.

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1. Introduction

In recent years, intermetallics based on aluminium and transition metals, e.g. nickel or iron, have been widely studied. Generally, aluminides seem to be interesting materials in a bulk form or coating due to their superior properties, such as low densities, high melting points and corrosion resistance. The strength of some intermetallics remains satisfactory with increasing temperature or can even increase as the temperature increases. Mentioned properties determine aluminides to be used especially for high-temperature applications. Intermetallic phases containing Ni and Al can differ from Fe-Al in some points. The major advantages of nickel aluminides are e.g. resistance to oxidation and carburization in both oxidizing and reducing atmospheres up to 1100 °C, fatigue and wear resistance or superior creep strength. [1, 2] Iron aluminides are promising

while used in sulphur containing atmospheres, have high electric resistivity increasing with temperature and remain stable in many aqueous solutions. Although it seems that aluminides have only advantages, their ductility is limited because of high hardness and brittleness. Manufacturing and processing of intermetallics is also limited. As it was mentioned above, due to the suitable properties of aluminides protective layers formed by Al and Ni or Fe are perspective e.g. for components which are exposed to elevated temperatures or exhaust gases. There are many methods how to prepare aluminide layer, for example by thermal spraying [3, 4], CVD [5-7] or by submersion of the component into molten aluminium. Pre-plating of the substrate material, mostly steel, is usually realized by galvanic Ni plating [8, 9].

Within galvanic nickel plating which is commonly used, electroless nickel coating was

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used in this work to prepare homogeneous nickel coating. The main advantage of this process is that even complex-shaped materials can be coated with nickel of similar thickness on all the parts of the component. The only problem is ecological disposal of waste solution.

Aim of this work was to find an alternative way how to prepare mentioned layers economically and simply with accent on using it on complex machine parts and elements. Replacing thermal spraying process by submersion the sample into molten metal seems to be perspective.

2. Experimental

As a substrate material, plain carbon steel was used in this experiment. Steel contained 0.13 % C, 0.27 % Mn, 0.02 % S. Composition of steel was determined by glow discharge atomic emission spectrometry (GDS).

Surface of rectangle samples (2.5 x 2 x 0.2 cm) was treated by grinding and rinsed by water and ethanol to remove iron oxides and impurities. These samples were consequently coated with nickel by two different procedures - galvanic nickel plating and electroless nickel plating. Required thickness of nickel layer was approx. 10 μm .

2.1. Galvanic nickel plating

Galvanic nickel plating was carried out in nickel plating solution which consisted of 60 g/l NiSO_4 , 120 g/l Na_2SO_4 and H_2SO_4 . The pH value of the bath was maintained at pH = 3. Nickel plating was carried out at 60 °C with current density 50 A/m² and voltage between two lead anodes and steel cathode 4.5 V. Time of electrolysis was calculated to 10 minutes.

2.2. Electroless nickel plating

This method is based on charge exchange reaction in water solution. Nickel is cemented on iron together with a small part of phosphorus (= reduction) and hypophosphite changes into phosphate (= oxidation). Before plating in this nickel bath, the samples were pickled for

3 minutes in HCl 3 : 1 (acid : water) and then three minutes in H_2SO_4 1 : 3, cleaned by ethanol and dried by hot air. Electroless nickel plating proceeded in nickel bath which consisted of 34 g/l $\text{Ni}(\text{C}_3\text{H}_5\text{O}_3)_2$, 31,5 g/l $\text{Ni}(\text{H}_2\text{PO}_2)_2$, 10 ml/l $\text{C}_3\text{H}_6\text{O}_3$ and 5ml of NaOH per every 25 ml of solution. Dissolving the content was taken at 75 °C and coating process was carried out at 90 °C for 120 minutes. After 40 and 80 minutes from start of the procedure, NaOH in required amount was put into the bath. Coating prepared by electroless plating procedure contained 17 at.% phosphorus which was determined by GDS.

2.3. Reaction synthesis of aluminides

Coated samples were submerged into molten aluminium under normal pressure at 700 and 900 °C for various time periods (30 and 240 s). As the reference materials, two steel samples without nickel coating were introduced to the aluminium melt under the same conditions.

As a different variant of the aluminide synthesis, one sample coated by galvanic process was put into aluminium powder and annealed at 650 °C for 8 hours.

2.4. Samples preparation and measurement

After the coating process had finished, samples were air-cooled and metallographic samples were prepared as perpendicular cuts across the layer. Samples were ground using P60- P4000 abrasive papers and polished by D2 diamond paste. These samples were observed by light and electron microscope.

Thickness of produced aluminide layer was measured by image analysis of the light micrograph using LUCIA 4.8 image analysis software. Microhardness (HV 0.05) of aluminide layer was measured by Hannemann microhardness tester.

Chemical composition of aluminides in the layer was determined by Tescan Vega 3 scanning electron microscope using Oxford Instruments INCA 350 EDS analyser and compared with results obtained in [8].

3. Results and discussion

3.1. Microstructure of aluminide layers

In Fig. 1, diffusion process during submersion in molten aluminium is described. Diffusion of aluminium and iron is described by arrows. Text labels mark presence of phases formed in the early state of submersion. Molten aluminium enters the surface of nickel forming nickel aluminide Ni_3Al and then iron. From the surface inwards, iron diffuses into nickel and aluminium forming solid solution Fe-Ni and different types of iron aluminides- FeAl_2 , FeAl_3 , Fe_2Al_5 . Iron aluminide formation is probably a consequence of the delamination of the produced nickel aluminide layer.

At first, samples produced by a combination of galvanic nickel plating and hot dip aluminizing (Ni GAL) were investigated. Electron micrographs show the representation of various intermetallic phases which originate from reactions during submersion. In the case of the sample submerged for 30 seconds (Fig. 2) there still remain small parts of non-reacted nickel. Second nickel-containing phase is NiAl_3 aluminide. Aluminium diffuses towards the steel substrate and forms Fe_2Al_5 as it was

described in [10]. This phase can be found in all the samples submerged for 4 minutes at 700 and 900 °C (Fig. 3 and 4). The difference is in the amount of nickel. There is no nickel in the elemental form or in nickel aluminide. Only small content of nickel (approx. 1 wt. %) was indentified in iron aluminide. Sample submerged at 900 °C contained areas of aluminide FeAl_3 , as seen in the picture.

As well as in the case of samples with galvanic coating submerged for 4 minutes, layers produced by a combination of the electroless nickel plating and aluminizing in the melt (Ni-P) exhibit only very low content of nickel in the intermetallic layer (Fig. 5, 6). Transition zone between iron and aluminium consists of aluminide Fe_2Al_5 , sample treated at 900 °C contained small areas of FeAl_2 included in Fe_2Al_5 .

Low nickel content in prepared layers can be explained as following: Reaction which forms aluminides of nickel is strongly exothermic. Due to a different thermal expansion coefficient of nickel aluminide and steel, the Ni-Al layer delaminates and sinks to the bottom of the melting crucible due to higher density than aluminium.

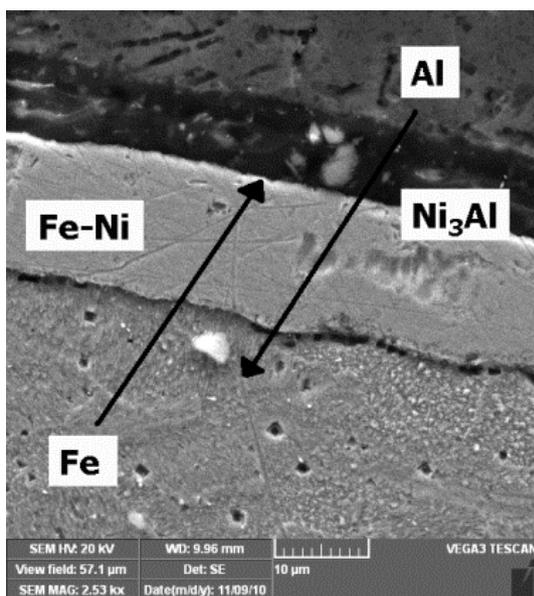


Fig. 1. Diffusion process during submersion.

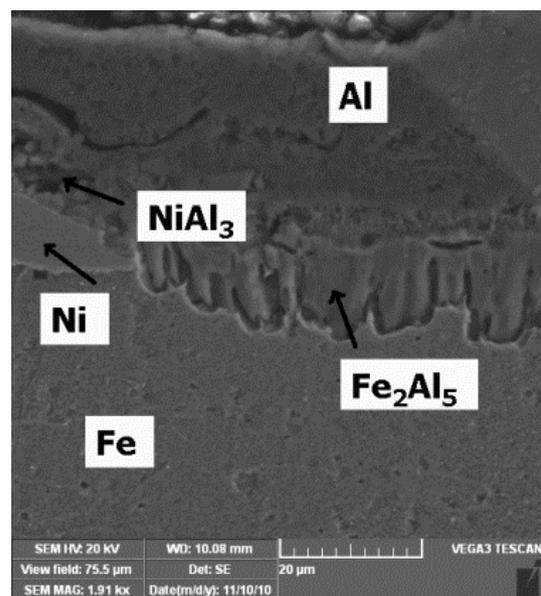


Fig. 2. Ni GAL 700 °C / 0.5 min.

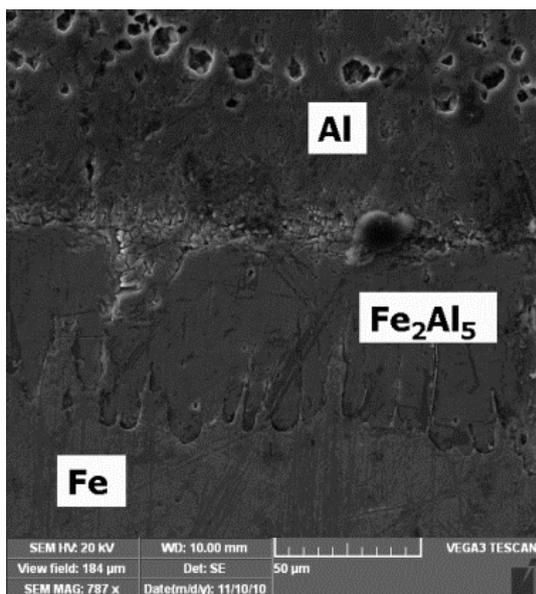


Fig. 3. Ni GAL 700 °C / 4 min.

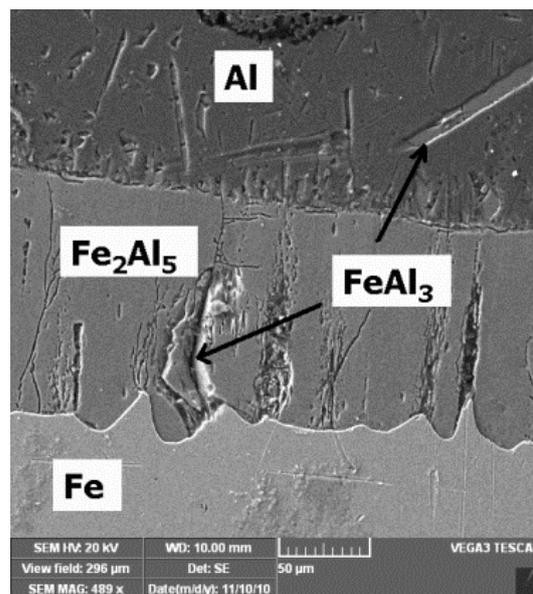


Fig. 4. Ni GAL 900 °C / 4 min.

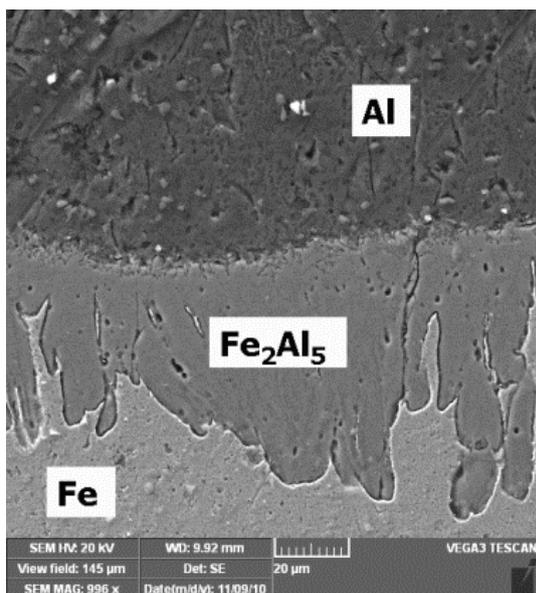


Fig. 5. Ni-P 700 °C / 4 min.

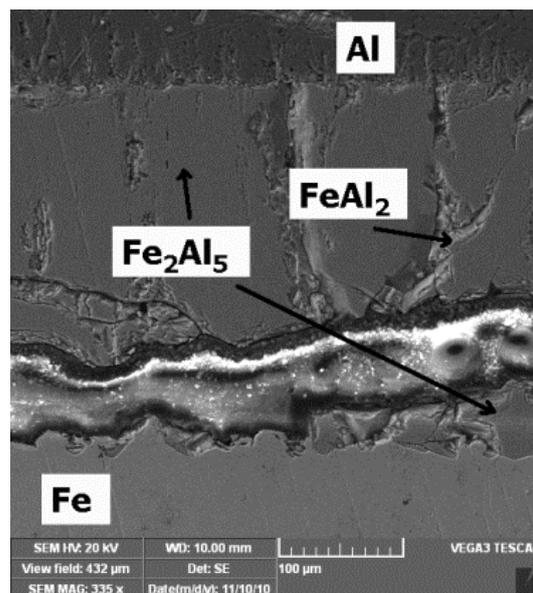


Fig. 6. Ni-P 900 °C / 4 min.

Due to extreme heat generation of Ni + Al reaction, nickel aluminide can be even molten and dissolved in the melt. As longer is the submerging time that less nickel remains on steel. Heat produced by the Ni+Al reaction then supports the formation of iron aluminides. Samples without nickel coating were submerged at 700 °C. Layer originated on sample submerged for 0.5 minute consists of a thin Fe_2Al_5 phase. Sample treated for longer time period included layer of Fe_2Al_5 , about 50 µm of

thickness. Third technology – combination of galvanic plating and powder aluminizing – produced layers of Fe_2Al_5 of different thickness which may depend on amount of powder present on surface of steel.

3.2. Thickness and microhardness of aluminide layers

Light micrographs reveal that the thickness of the Fe_2Al_5 layer increases with process duration and temperature.

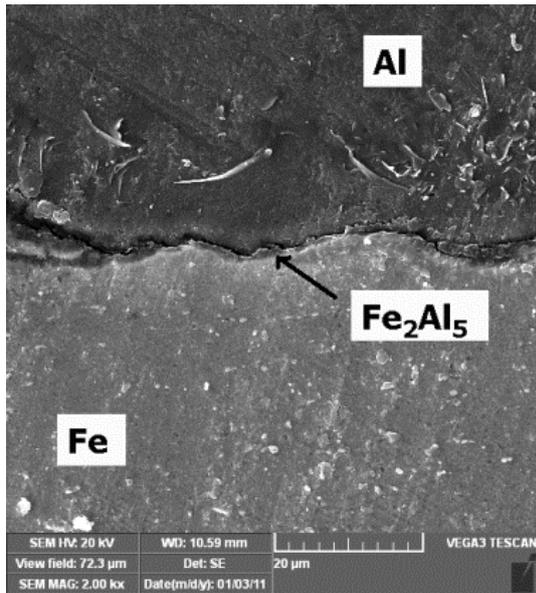


Fig. 7. Fe 700 °C / 0.5 min.

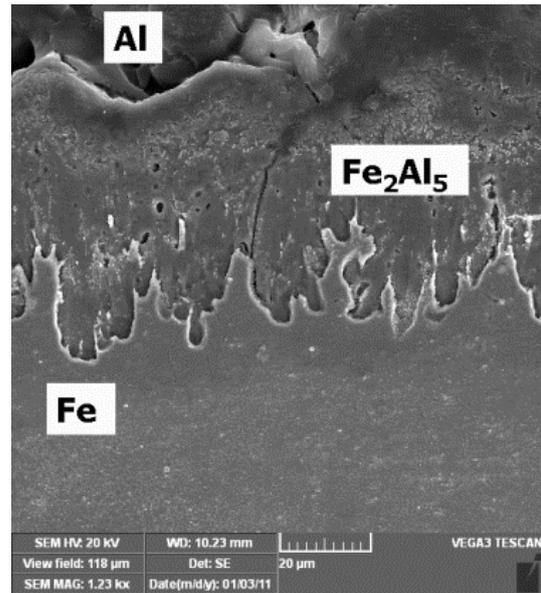


Fig.8. Fe 700 °C / 4 min.

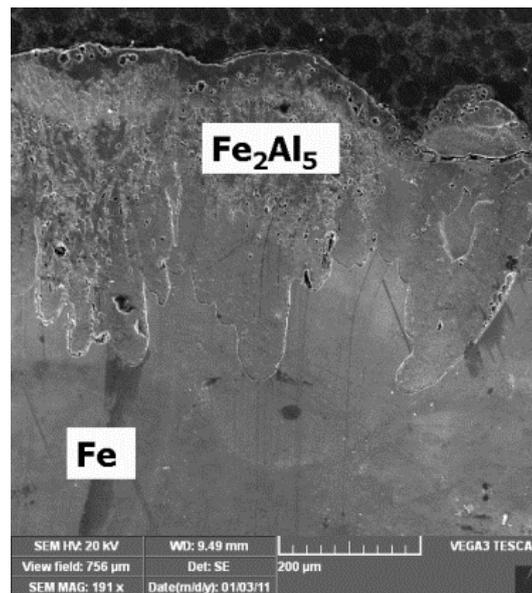


Fig. 9. Fe_2Al_5 made with Al powder.

An increase of the process temperature improves the diffusion of aluminium into substrate material is much faster and as a result, the penetration depth is higher. Thickness of the layer used in graphs was created as the mean value of 30 values measured at different places on the sample (Fig. 10).

Presented microhardness HV 0.05 (Fig. 11) was averaged from 10 measurements.

It could be seen that layers prepared at 900 °C reach higher values of hardness. It could be explained so, that formed aluminide of iron Fe_2Al_5 can exist in wider range of Al and Fe concentration. Ratio of iron and aluminium forming Fe_2Al_5 can differ a little bit from aluminide originating at 700 °C. If there is little more iron included, microhardness can increase. Influence of phosphorus in electroless nickel coating is discussed.

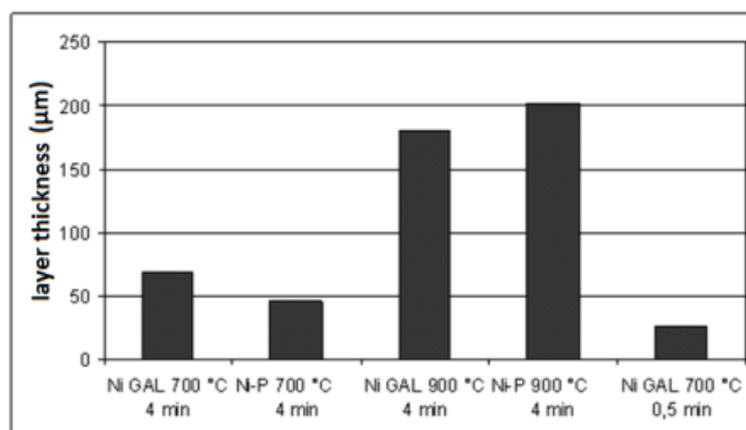


Fig. 10. Thickness of Fe_2Al_5 .

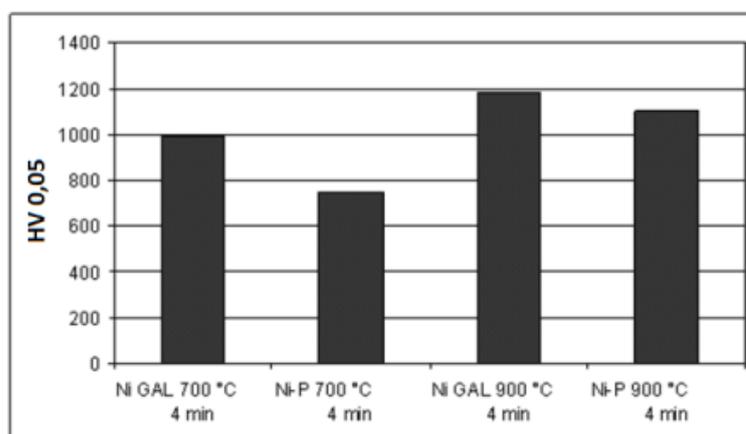


Fig. 11. Microhardness of Fe_2Al_5 .

4. Conclusions

Introduced methods are not suitable for producing compact layers containing aluminides of nickel. Only in the case of sample submerged for 0.5 minute there was a small amount of $NiAl_3$ and nickel in elemental form. Because of intensive exothermic reaction, originating aluminides of nickel delaminate from steel and dissolve in molten aluminium. On the other hand, these methods are promising for creating Fe-Al layers. It was demonstrated that there is an influence of temperature and submersion duration on thickness and microhardness of layer. Samples submerged for the same time at higher temperature are characterized by thicker layer composed mainly of Fe_2Al_5 with small parts of $FeAl_2$ or $FeAl_3$. Thickness of layer varies in range of 30- 200 μm. There is also a difference between microhardness of layers

produced on galvanic and electroless nickel coatings. Layers produced at higher temperatures are harder because of different aluminium- iron ratio in Fe_2Al_5 . There may be an influence of phosphorus present in the case of electroless nickel coatings, which may form hard phosphides. Presence of nickel coating may influence kinetics the iron aluminide layer formation. Powder aluminizing produced the layer formed by Fe_2Al_5 as in the case of melt submersion process, but the laik, yers are less homogeneous.

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