Aluminide protective coatings on high–temperature creep resistant cast steel

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Abstract

This paper presents the results of research on aluminide protective coatings manufactured on high–temperature creep resistant cast steel. The main purpose of these coatings is protection against the high temperature corrosion, especially at high carburizing potential atmosphere. Coatings were obtained on cast steel type G–XNiCrSi36–18 with the following methods: pack cementation, paste method, cast method and slurry cementation. The phase composition, thickness and morphology of coatings were determined. Coatings capacity of carbon diffusion inhibition and thermal shocks resistance of coatings were determined with different methods. It was found, that all of the coatings reduce carbon diffusion in different degree and all coatings liable to degradation in consequence cracking and oxidation. Coating life time is mainly dependent on morphology, phase composition and service condition (thermal shocks first of all).

Key words: Anticarburizing protective coatings, Pack cementation, Cast method, Paste method, Slurry method, Thermal shocks.

1. Introduction

High temperature corrosion problems are objective of many investigations world wide to improve reliability and service duration of various equipment.

Austenitic nickel–chromium cast steel is the main material used for creep–resistant parts of carburizing furnaces [1]. Among those parts, the elements used for batch formation and transport of castings to be carburized (e.g. grates, fixtures, etc.) are exposed to the severe conditions. While running, they are heated together with the charge up to 880÷950ºC, to be held next at the carburizing atmosphere and cooled rapidly, usually in oil, at a temperature of about 60ºC. In macro–scale, the effects that the carburizing atmosphere, thermal shocks and charge load exert on the intricate design of these elements results in their deformation and breaking of some fragments. In case of grates, they are damaged as shown in Figure 1a and 1b, that is, mainly on the corners, what obviously makes castings useless in further operations. In micro–scale, on the wall cross–sections, some areas of internal corrosion (Fig. 1c, 1d) are formed, described, among others, by Grabke and Wolf [2].

The susceptibility of cast material to deformation and cracking increases with increasing of its carburizing degree, and therefore all attempts at improving the casting life and performance are mainly aimed to improve carburizing resistance. To improve the resistance to high–temperature corrosion, castings can be coated with diffusion, heat–resistant coatings [3]. In most cases these are the protective diffusion coatings based on aluminium [4, 5], where the main role is played by an intermetallic NiAl phase [6].
To guarantee the best performance characteristics in the mentioned castings, matched to the specific operating conditions, the anticarburizing coatings should satisfy the following general requirements:

- possibly strong forces of adhesion should act the coating and a casting,
- the value of the linear expansion coefficient and of the thermal conductivity of the coating should be similar to that possessed by the cast material,
- the heat resistance of the coatings should be at least the same as that of the substrate,
- application of coating should not change in any significant way the technology of casting fabrication; the cost effectiveness has to be taken into consideration as well.

In this work the results of the studies on the choice of anticarburizing aluminium-based coatings to protect parts of the carburizing furnaces from an adverse effect of the carburizing atmosphere have been described.

2. Experimental and testing procedure

Using as a guideline the preliminary studies done by Christodulu and Piekarski [7, 8, 9] as well as the data collected from reference literature, it was decided to choose for tests and examinations aluminium-based coatings of the Al–Cu, Al–Si and Al–Fe type. It was also decided that the substrate for these coatings will be cast steel of the chemical composition as given in Table 1.

Table 1.

<table>
<thead>
<tr>
<th>Chemical composition of experimental alloy, wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>0.33</td>
</tr>
</tbody>
</table>

The samples were cut out mechanically from the ingots of dimensions 350x150x25 mm; their surfaces after milling were ground with 220 abrasive paper and degreased.

2.1. Pack cementation

Diffusion impregnation of samples in pack mixtures was performed in air-tight containers made from austenitic stainless steel. The composition of the mixture and the conditions of the process are given in Table 2.

Table 2.

<table>
<thead>
<tr>
<th>Coatings fabrication conditions with the pack cementation [7, 8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of coating</td>
</tr>
<tr>
<td>Al–Cu</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>Al–Si</td>
</tr>
<tr>
<td>Al–Fe</td>
</tr>
</tbody>
</table>
To describe structure of the coatings, they were examined using X-ray diffraction and microscopy methods. Thickness of the coatings was measured along with their hardness and mean grain size in an external layer of coating. Examples of coating microstructure as well as detailed results of the metallographic examinations are shown in Figures 2 and 3 – the marked points indicate the spots where the coating layers were examined. The produced coatings, as shown in Figures 2 and 3, are characterized by the presence of two–layers and a heterophase structure [9].

The protective efficiency of the coatings was evaluated from the obtained values of carbon diffusion coefficient. For this purpose an isotopic technique of autoradiography performed on skew sections was applied. This method enables determination of the carbon concentration profile in thin layers. As a maker, carbon isotope $^{14}$C was used. The samples with coatings applied were carburized under the atmosphere produced by methanol and ethyl acetate for a time of 15 hours at temperature of 900ºC. The carbon potential of the atmosphere was $c_p = 0.7-0.8\%$. An example of the carbon concentration distribution in Al–Si coating is shown in Figure 4a, and it is representative of all the samples. From the drawing it follows that in the carburized layer at least two zones can be distinguished: zone I – characterized by a relatively constant carbon concentration, and zone II – of transient character. The coefficient of carbon diffusion in individual zones ($D_1$ and $D_2$, respectively) of the examined coatings was determined using the relationships described elsewhere [10]. The measured values of the coefficient are compiled in Figure 4b.

Since the values obtained for Al–Cu and Al–Si coatings are definitely much lower than the values obtained for Al–Fe coatings, further discussion and evaluation of the structural stability of coatings at carburizing atmosphere and thermal shocks conditions was restricted to the first two coatings only.

The samples with Al–Cu and Al–Si coatings were carburized at temperature 900ºC for 10 hours and cooled in oil at temperature of 60ºC. The cycle was repeated 100 times. The potential of the carburizing atmosphere produced from a mixture of propane and hydrogen was $c_p = 0.7-0.8\%$. The microstructures of samples after 500 hours of the carburizing process are shown in Figure 5.

For 500 hours the coatings were efficiently inhibiting carbon diffusion from the atmosphere, revealing only some minor single cracks and beginnings of oxidation of the carbide layer, which precipitated inside the coating. However, after 1000 hours, the coating degradation process was much more significant (Figure 6).

A measurement of the carburized layer thickness revealed carbon diffusion penetrating to a depth of about 0.5 mm and 0.25 mm underneath the Al–Si and Al–Cu coatings, respectively, while the measured thickness of the carburized layer in a sample without coating amounted to about 2.5 mm. In Al–Si coating numerous cracks were observed as well as an oxidizing effect on both the surface and substrate coating phase boundary. The Al–Cu coating, on the contrary, well preserved its continuity.
2.2. Paste method

By its mere nature, the technique of slurry cementation should provide a powdered composition characterized by appropriate consistency, enabling its direct application onto the casting surface. To the mixed powders some binder was added to obtain a dense slurry characterized by strong adhesion to the surface. As an activator and a flux at the same time a mixture of salts was used (Table 3).
Table 3  
The conditions of the Al–Cu–Si coating fabrication obtained with paste method [11].

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Metal part</td>
<td>45%Al + 45%FeSi + 10%Cu</td>
</tr>
<tr>
<td>B. Binder</td>
<td>Aqueous solution (1:1) of water glass (mₘ=3)</td>
</tr>
<tr>
<td>C. Flux</td>
<td>Mixture of salts (45%NaCl + 45%KCl + 10%NaF) melted at 600ºC</td>
</tr>
<tr>
<td>Process time and temperature</td>
<td>3.5h / 900±10ºC</td>
</tr>
</tbody>
</table>

The Al–Cu coating was additionally enriched with an addition of silicon to improve its heat resistance. The slurry was applied onto the samples; next it was dried in a jet of hot air, and heated with furnace in air atmosphere. The composition of the mixture and the conditions of the coating fabrication process are given in Table 3. The results revealed a three–zonal structure of the coatings, as shown in Figure 7a.

![Figure 7. Microstructure of Al–Cu coating: a) coating in the starting condition and its main phase constituents, b) coating after 340 h test with well visible cracks running through the two external zones [11]](image)

The coating subjected to a carburizing process remains effective for at least 500 hours. The depth of carburizing in a coated sample is three times smaller than that observed in the sample without coating, as illustrated by the results of hardness measurements shown in Figure 8.

![Figure 8. An evaluation of the coating effectiveness by hardness measurements [11]](image)

The studies evaluating the structural stability of coating, performed in similar way as in the previous experiments, have proven, that the coating is characterized by a very strong tendency to crack formation (Fig. 7b) as early as after about 300 hours of the carburizing and thermal fatigue test.

### 2.3. Casting method

Using experience acquired previously, the studies were conducted only on coatings of the Al–Cu type, without an addition of silicon. It has been decided that the studies will be carried out according to the plan of partial experiment, conducted on five levels and for the three variables. The plan provides for making twenty tests with six experiments at a central point [12, 13, 14]. The composition of coatings applied onto the surface of a casting mould included:

- powders of metallic Al and Cu mixed in ratios of Al/Cu = 1.5 ÷ 2.5,
- water glass of modulus 3 in an amount of 12% in respect of the metal powder weight,
- flux (KCl + NaCl + NaF) in an amount of 5% in respect of the metal powder weight.

The coatings were applied onto the surface of cavities in casting moulds. Next the moulds were dried at temperature of 200°C for 40 hours and poured with metal. The density of an active paste onto the mould surface was 0.01–0.3 g/cm³, what corresponded to the layer thickness of 0.11÷0.25 mm.

In the experiments, the variables changing simultaneously were: the density of an active paste on the mould surface, the thickness of casting wall, the temperature of steel pouring, the rate of metal column raising in mould, and the metallostatic pressure. The structure and phase composition of a typical coating in as–cast state are shown in Figure 9. The three–zone structure of the coating is also observable [13].

The coated samples were carburized in powder carburizer at temperature of 900°C for 10 hours and cooled in oil at a temperature of 60°C. The cycle was repeated 40 times. The coating microstructure after the process of carburizing and thermal fatigue is shown in Figure 9b–c. Basing on the results of the studies it has been concluded that coatings are characterized by a good resistance to carburizing and thermal shocks when they:

- contain large amounts of (Al + Cu) wt-%,
- are of thickness 650÷800 μm,
- are characterised by high specific density of Cu on coating surface and contain the following phase components – β′Al(Ni,Fe,Cu), α(Fe,Cr,Ni) and γ(Fe,Ni,Cr).

The above mentioned properties can be obtained when during manufacture of coating the following parameters are maintained:

- volume density of mould coating reaching (1.02÷1.1)x10³ g/mm³,
- metal column raising speed in mould cavity higher than 6 cm/s,
- pouring temperature above 1630°C.
The coatings fabricated by casting are 5 to 10 times thicker than those made by diffusion impregnation method (Fig. 2, 3 and 9) [14]. They also have different structure. In coatings obtained by the powder method the external zone of coating is composed of a continuous layer of (Ni,Fe)Al crystals (Fig. 2), which efficiently inhibits the diffusion of carbon from the atmosphere. On the other hand, the thin (approx. 20 μm) intermediate zone makes the coating less resistant to thermal shocks, what appeared by cracking and intercrystalline corrosion observed after tests (Fig. 5c and 6). In cast coatings the external layer is composed of a mixture of (β(Ni, Fe,Cu)Al, α(Fe,Cr,Ni), γ(Fe,Ni,Cr) phases which makes carbon diffusion less efficient. However, the well developed intermediate zone (approx. 30 μm) should make these coatings more resistant to the effect of rapid changes of temperature. They get destroyed by slow building up of a brittle scale on the whole of their surface.

In this part of research, application of a plan of experiment and mathematical data processing, enabled preparation of a technology of the coating manufacture directly in foundry mould [14] (Fig. 10).
2.4. Slurry method

Occurrence of amount of copper oxide on cast coatings has been found. This finding has caused return to research on aluminum silicon coatings, due to better silicon’s heat resistance than copper’s [7, 13]. It is possible to find confirmation of this thesis in literature as well [15].

The authors decided to modify the paste method by changing the composition and the consistence of the paste used [16]. This part of paper presents the results of manufacturing aluminium–silicon coatings and microstructural examinations describing their morphology, chemical and phase composition.

The samples of high-temperature creep resistant cast steel were prepared. The chemical composition of this cast steel is approximately: 0.2 wt-% C, 18 % Cr, 30 % Ni, 0.7 % Mn, 1.5 % Si [7]. The primary materials for the mixture are: Al and Si powders, water solution of soluble glass as the binder, fused mixture of salts as the flux. The chemical composition of the mixture was determined in a series of test. The aluminium–silicon mixture was put (by immersion) on cast steel. The samples differed in mass density of mixture (0.2 to 2.0 g/cm²) and in surface conditions (machined and as-cast conditions). The samples covered with the mixture were then annealed at the temperature of 900°C for 7 hours.

All of the coatings have continuous and compact structure. The typical coating consists of three zones: the internal zone (1), the middle zone (2) and the external zone (3). The coating microstructure is shown in Fig. 12. This figure presents Al–Si coatings obtained on both machined surface and raw cast surface.

The thickness of the obtained coatings on the whole surface of samples is relatively uniform and the thickness of individual zones is comparable. Results of thickness measurements are shown in Table 4. The grinding of the samples before coatings manufacturing has no influence on the quality of the coatings. The coatings have continuous and compact structure and a similar thickness on both types of surface (in machined and as-cast conditions). The results of Vickers hardness measurements performed in zones 1, 2 and base material are shown in Figure 13. It was found, that the zone 3 is brittle. This zone cracked during hardness measuring and locally dropped off.

Table 4.
Average thickness of Al–Si coatings [17]

<table>
<thead>
<tr>
<th>Thickness [μm]</th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>on raw casting surface</td>
<td>22</td>
<td>62</td>
<td>65</td>
<td>149</td>
</tr>
<tr>
<td>on machined surface</td>
<td>16</td>
<td>48</td>
<td>35</td>
<td>98</td>
</tr>
</tbody>
</table>

Experiment plan was worked out after preliminary tests. The rotatable–universal experiment plan was applied. This plan has five levels with three variable technological parameters. Determination of the influence of technological parameters on coating’s structure and properties was possible thanks to this plan. As variable technological parameters were taken: temperature (X₁), time of annealing (X₂) and ratio aluminium to silicon in the slurry (X₃).

![Fig. 12. Microstructure of Al–Si coatings on: a) machined surface, b) raw casting surface; obtained at parameters: T=900°C, t=7.5h, Al/Si=9 [17]](image)

Fig. 12. Microstructure of Al–Si coatings on: a) machined surface, b) raw casting surface; obtained at parameters: T=900°C, t=7.5h, Al/Si=9 [17]

![Fig. 13. Average microhardness of Al–Si coatings on: (1) raw cast surface, (2) machined surface [17]](image)

Fig. 13. Average microhardness of Al–Si coatings on: (1) raw cast surface, (2) machined surface [17]

The slurry mass density value was 0.3 g(Al+Si)/cm² after drying. The samples covered with the mixture were annealed at temperatures between 732°C and 1068°C for 3.3 ÷ 11.7 hours [18]. The ratio Al/Si was between 4 and 14. The central point for this plan was correspondingly: temperature – 900°C, annealing time – 7.5 hours, Al/Si ratio – 9. Series of twenty different coating
manufacturing processes with different parameters according to the plan of experiment was carried out.

Coatings were examined using the following techniques:

− light and scanning electron microscopy – JOEL JSM–6100;
− XRD analysis – Panalytical X’Pert – PRO, CoKα radiation, identification of phases was performed using Panalytical High Score software;
− microhardness tests – Buehler 2000, 10 G, 15 s, Knoop indenter;
− X-ray microanalysis EDS – LINK ISIS of Oxford, 20 kV, 0.45 nA.

The microscopic observations indicated, that there are no essential differences in microstructure between the obtained coatings. The typical coating consists of three zones: the internal zone (1), the middle zone (2) and the external zone (3). The coating microstructure is shown in Figure 14. Differences in the structure of coatings were observed in thickness and chemical composition. The differences among coatings come from different parameters of coatings manufacturing [18].

XRD phase analysis was performed on sections parallel to the coating surface. Consecutive layers of the coating material were removed. Owing to such preparation of specimens, identification of major phases in each zone was possible [18] (fig.14).

Elemental mappings on coatings cross-sections, line and point quantitative analysis were performed by means of EDS X-ray microanalysis.

Results of the quantitative X-ray microanalysis are presented in Figure 15. On the basis of XRD and point quantitative EDS analysis, the phase composition of coating was determined. Continuation of this paper does not contain the information about 3rd zone, because of its phase composition. There are mainly oxides [11] which do not have protective properties.

Fig. 14. Microstructure of typical Al–Si coating (coating obtained at 900ºC, for 7.5h)

Fig. 15. Metals mapping in Al–Si coating obtained at average parameters: \(X_1=900^\circ C, X_2=7.5h, X_3=9\), mag. 2500x [18]

<table>
<thead>
<tr>
<th>Zone</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1: Al(Fe,Ni), α(Fe,Si), Cr(_2)C(_6), AlNi(_1)</td>
<td></td>
</tr>
<tr>
<td>Zone 2: α(Fe,Cr,Ni), Cr(_2)C(_6), AlNi(_1)</td>
<td></td>
</tr>
<tr>
<td>Zone 3: Fe(_2)SiO(_4), FeAl(_2)O(_4), Fe(_2)O(_3), Al(_2)O(_3), CrSi(_2)</td>
<td></td>
</tr>
</tbody>
</table>

substrate: γ(Fe,Ni,Cr), Cr\(_2\)C\(_6\)
The thickness of the coatings and each zone was measured. The correlations between technological parameters and thickness of the coatings were determined. Dependent variables presented in correlations in figures 16, 17, 18 are: \( Y_1 \) – the thickness of 1st zone, \( Y_2 \) – the thickness of 2nd zone, \( Y_4 \) – the total thickness of coatings; \( R \) – correlation coefficient, \( R^2 \) – matching coefficient, \( F \) – value of Snedecor test.

On basis of statistical calculations, it was found that the thickness of the coatings is dependent on temperature \( (X_1) \) and time of annealing \( (X_2) \) but it is independent on Al/Si ratio.

Thickness of the 1st zone grows with temperature increase, but decreases with time increase at low temperature. Thickness of the 2nd zone increases with growth of temperature and time. The correlation between the thickness of the 3rd zone and technological parameters possess very low matching coefficient and the graph of correlation is omitted because of that. Thickness of the 3rd zone increases with temperature growth only in limited range.

In case of coating produced at temperature ca. 1000°C the 3rd zone was severely cracked and in case of the highest annealing temperature (1100°C) the 3rd zone was not observed at all.

The total thickness increases with temperature and time growth, but the matching coefficient is lower (because of the 3rd zone).

Protective properties of coatings were tested at as close to real working conditions as possible. Samples were divided into 3 identical series consisting of coatings obtained at different technological parameters.

The first and the second series were being carburized at temperature 900°C in powders for 400 hours in 20 hour periods. The second series of samples was oil quenched twice after each carburizing period. The third series was taken to structural investigations (described earlier) at as received state.

\[
Y_1 = 749.9 + 0.001X_1^2 - 1.69X_1 + 0.02X_1X_2 - 18.02X_2;
R = 0.98; R^2 = 0.95; F = 76
\]

\[
Y_2 = \exp(-3.26 + 0.007X_1 + 0.088X_2);
R = 0.9; R^2 = 0.81; F = 31
\]

\[
Y_4 = -237.87 + 0.0004X_1^2 + 0.007X_1X_2;
R = 0.8; R^2 = 0.71; F = 20
\]

Fig. 16. Graph of a correlation between technological parameters and thickness of 1st zone [18]

Fig. 17. Graph of a correlation between technological parameters and thickness of 2nd zone [18]

Fig. 18. Graph of a correlation between technological parameters and total thickness of coatings [18]

Fig. 19. Microstructure of Al–Si coating, obtained at temperature 900°C, in time 11.7h and Al/Si=9 after carburizing and thermal shocks [19]
The coatings on samples after carburizing and after carburizing and thermal shocks consist of two zones. Decomposition of the third zone was observed. Thickness of the 1st and the 2nd zone was increased. Appearance of new intermediate layer between the 1st and 2nd zone was observed (Figure 19).

Thickness of the coatings after carburization and thermal shocks was determined and presented graphically in figure 20. The minimal, maximal and average values of thickness are shown as well.

Appearance of new intermediate layer between the first and second zone was observed. Results of EDS X-ray microanalysis revealed, that this layer was enriched in nickel. Microstructure and elemental mapping of the coating after carburizing and thermal shocks are shown in fig. 21.

In some cases cracks trough the second zone of coatings after carburizing and thermal shocks were observed (fig. 21). Usually, those cracks finish in neighbourhood of intermediate layer and sometimes propagate along the boundary of the first zone and the intermediate layer. It was dependent on kind of coating that is on technological parameters of coating manufacturing.

Efficiency of coatings was assumed as a depth of carburized layer. Obviously, the less depth of carburized layer indicates the higher efficiency of coating. It was found, that depth of carburized layer was different for different coatings’ structures.

Fig. 20. Thickness of Al–Si coatings before and after carburizing and thermal shocks [20]

The XRD results indicated that the main phases of coating after carburizing and thermal shocks were: in the first zone – \( \alpha(Fe,Cr,Ni) \), \((Cr,Fe)_{23}C_6\); in the intermediate layer – \( \beta'Al(Ni,Fe) \), \(AlNi_3\), \(CrSi_2\); in the second zone – \( \beta'Al(Ni,Fe) \), \(Al(Fe,Ni)\), \((Cr,Fe)_{23}C_6\), \(CrSi_2\) [15] (Figure 22).

Fig. 21. Elemental mapping in Al–Si coating (technological parameters 1000°C, 5h, Al/Si=6) after carburizing and thermal shocks [20]

The major phases of coating in each technological stage (before and after carburizing and thermal shocks) are: \( \beta'Al(Ni,Fe) \), \(\alpha(Fe,Cr,Ni)\), \((Cr,Fe)_{23}C_6\), \(AlNi_3\), \(CrSi_2\), \((Cr,Fe)_{23}C_6\) [15]. Changes in structure of coatings after carburizing were observed. The second zone containing \( \beta'Al(Ni,Fe) \) inhibits effectively the carbon diffusion inwards. This is visible as chromium distribution on elemental mapping (Fig. 21). However, thermal shocks cause cracking of 2nd zone. Therefore, very important is presence of the 1st zone containing \( \alpha(Fe,Cr,Ni) \) to prevent coating against cracking.

In work [18], it was found, that hardness of the 1st zone is intermediate between the 2nd zone and the substrate, and moreover crystal lattice of this zone is different from the substrate and from other zones of the coating. Described above features of the 1st zone inhibit cracks propagation.

Investigations performed after carburizing and thermal shocks tests indicate enlargement of both total coatings’ thickness (Fig. 20) and thin intermediate layer between zones 1 and 2 (Fig. 19). In as received state, this layer is enriched in aluminum and nickel and it is composed of fine AlNi3 precipitates located in boundary of zones 1 and 2 (Fig. 15).
This layer is not indicated as a separated zone, but it is counted among the 1st zone (Fig. 14). Thickness increase of this layer is the most likely caused by outwards diffusion of nickel and inwards diffusion of aluminum [17]. Presence of this intermediate layer was very important in case of carburizing and thermal shocks conditions due to mentioned above inhibiting of cracks propagation (Fig. 21).

2.5. Influence of coating on mechanical properties of substrate

Following the assumptions previously adopted, the presence of coatings should protect the base material from getting carburized, however, on condition of not deteriorating its mechanical and physical properties.

For a 38%Ni–18%Cr grade cast steel the changes in the value of the mean linear expansion coefficient $\alpha$ are in very obvious way correlated with changes in carbon contents [8, 12]. This gives the possibility of adjusting the value of the $\alpha$ coefficient of both the base metal and coating. If this is ensured, the process of carburizing will cause quick decrease of mechanical properties in specimens without coating, while the specimens protected by a coating will maintain their properties at a relatively stable and high level (Fig. 23). In spite of a pronounced difference in the properties of coated and uncoated specimens, the coating was observed to be operating for about 500 hours without any “leakages”.

3. Summary

The life time of construction elements and accessories operating in carburizing furnaces usually does not exceed 4000 hours [8]. It is expected that, by applying onto the surface of these castings a coating which at the conditions of a carburizing atmosphere and thermal shocks can provide protection from the carburizing effect, the time of the casting operating life should be prolonged significantly. The studies conducted in this field on various types of aluminium–based coatings fabricated on cast steel type 38%Ni–18%Cr have confirmed this assumption.

The conducted experiments have proven the coatings are to be regarded as protective barriers – they inhibit carbon diffusion for some time which, when exceeded, makes their effect either get weaker or totally disappeared. The loss of protective properties occurs due to intercrystalline corrosion which is promoted by carbon diffusion along the grain boundaries of a (Ni,Fe)Al phase with formation of $M_7C_3$ carbides, which in the course of further performance of the coating are undergoing the process of oxidation.

The evaluation of coating quality should be based on at least three criteria:

- the coefficient of carbon diffusion – it determines the protective properties of coating against the carburizing effect,
- the stability of coating microstructure at operating conditions – it determines the life time of coating,
- the degree of material carburizing – it determines the real effectiveness of coating during performance at industrial conditions.

The presence of coating may have an adverse effect on the mechanical properties of casting, but the drop in these properties and in impact resistance is several times less drastic than in the case of carburizing of casting without coating. At the same time it has been indicated that some possibilities exist to avoid this, highly disadvantageous, tendency through adjustment of the values of the coefficient of thermal expansion in the coating and in base material (using the changing over a wide range of values in function of the carbon content, coefficient of thermal expansion typical of a given type of cast steel).

Coatings of Al–Cu, Al–Si and Al–Fe types fabricated on cast steel by powder method were characterized by good protective efficiency. Originally, these coatings had been used as a
protection against oxidizing but later it was found, that they also have good protective properties at carburizing conditions.

As a continuation of the research, other methods: paste, casting and slurry were applied. Application of different manufacturing methods enabled to determine advantages and disadvantages of both particular type of coating and the used method.

From the point of view of phase stability, resistance to thermal fatigue, and real protective efficiency of a coating (understood as a thickness of the carburized layer on base material), the coating of an Al–Cu type is more stable than coatings of an Al–Si and Al–Fe type, because of phase composition (it is a mixture of β(Ni, Fe,Cu)Al, α(Fe,Cr,Ni), γ(Fe,Ni,Cr)).

A comparison of the properties of the same coating but obtained by various methods enables formulation of the following conclusions:

1. Irrespective of the fabrication process, the coating preserves its temporary ability to inhibit carbon diffusion from the atmosphere to the base material. The efficiency of the coating depends on the initial contents of aluminium, the rate of its oxidation, and the rate of coating dissolution in base material.

2. The method of coating fabrication has an important influence on its thickness and structure as well as morphology of the individual structural components.

3. The good resistance of the coating to a carburizing effect is ensured by the high contents of (Ni,Fe)Al phase in external layer. However, the presence of carbides M₆C₅ or of the α(Fe,Cr,Ni) phase, characterised by properties different than those of the (Ni, Fe)Al phase (e.g. differences in the values of the thermal expansion coefficient and density) affects in a negative way the resistance of coating to thermal shocks.

The authors consider that the slurry method is the most perspective in terms of practical application. The slurry method appeared to be more comfortable, less harmful than classic powder methods [7] and it is also easier to apply than the cast method [13].

Other advantages of this method are: low consumption of substrate materials, possibility of the manufacturing uniform and good quality coatings on complicated–shape elements.

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