The structure of aluminide coatings on alloy steels in the area of the welded joints

Agnieszka Kochmańska*, Paweł Kochmański Michał Kawiak

West Pomeranian University of Technology Szczecin, Faculty of Mechanical Engineering and Mechatronics, Institute of Materials Science and Engineering, *agnieszka.kochmanska@zut.edu.pl

Preparation of aluminide coatings is used to increase the heat resistance. The coating must be frequently applied to details that were previously welded. The description of the structure of the coating in the area of the welded joint can be important when choosing the proper welding techniques. Butt joints were made using tungsten inert gas, arc welding — the method 141. The main differences between the joints are a kind of parent material and production technology (welding with or without a filler material). Parent materials for making the joints are 1.4749 (X18CrN28) and 1.4404 (X2CrNiMo17–12–2) steels. On prepared samples with joints the silicon-aluminide coating by the slurry method were produced. Samples covered by the slurry were annealed in a furnace with a protective atmosphere of argon at two temperatures 800 and 1000°C for 2 hours. To characterize the structure of the coatings electron microscopy, SEM and EDS X-ray microanalysis were used. It was found that the coatings were formed on the whole test surface. There are strong similarities between the structure of coatings produced in a given temperature despite the use of different substrates and various welded joints. Generally, the coatings produced at a temperature of 800°C are characterized by a three-layer structure, while those at 1000°C have two layers. The thickness of the coating produced at 800°C is from a range of 40 to 65 μm depending on the substrate. The thickness of coatings annealed at 1000°C is in the range of 100 to 200 μm. It is noted that the thickness of the coatings on the parent material is in any case higher than on the weld.

Key words: aluminide coating, slurry method, alloy steel, welded joint.

1. INTRODUCTION

Preparation of aluminide coatings is used to increase the heat resistance of Fe and Ni based alloys. The iron and nickel aluminides improve the resistance to many aggressive environments [1–4] including oxidising [5–10], sulphidising [11] and carburising [12, 13] agents. The method of the coating formation should be easy to apply on complex shaped parts and the cost should be as low as possible. One of these methods is the slurry cementation. Commercially available slurries manufactured on the base of aluminium powder (as an active component) and of the solution of an organic binder are widely used [14]. The slurry method used by the authors is a modification of the classical one. The slurry used in this modified method consists of a metal powder (aluminium and silicon), a binding material (the aqueous solution of sodium silicate) and halides as a flux. The aqueous solution of sodium silicate (inorganic binder) in the slurry allowed for annealing in one single step without additional heating when the organic binder is used.

The main parameters determining the aluminide coating properties and usefulness are its chemical and phase composition and the thickness. The chemical composition of the aluminide coatings is characterized mainly by the aluminium content of these coatings. The thickness assessment and the analysis of the content of the coating are of primary importance for testing coating quality and protective properties [15].

The majority of final products working under a high temperature regime like equipment of furnaces for thermochemical treatment is made of high-alloyed steels and welding is the basic technology of joining of these materials. From a technological point of view, the first operation should be welding followed by manufacturing of a protective coating.

Therefore, the characterization of the coating in the area of the welded joint can be important when choosing the proper welding techniques. The main objective of this work is verification of feasibility of Al–Si coatings production on welded joints of high alloyed steels.

2. EXPERIMENTAL PROCEDURES

The materials used for the investigation were two kinds of high-alloyed steels. The first was ferritic heat resisting steel type 1.4749 (X18CrN28) containing: 0.15–0.2 wt % C, 26–29% Cr, max. 1% Mn, max. 1% Si, max. 0.04% P, max. 0.015% S, 0.15–0.25% N. The second material was austenitic stainless steel 1.4404 (X2CrNiMo17–12–2) containing: 0.03 wt % C, 16.5–18.5% Cr, 10–13% Ni, 2–2.5% Mo, max. 2% Mn, max. 1% Si, max. 0.11% N, max. 0.045% P, max. 0.015% S.

Butt joints were made by the 141 method. The differences between the joints were mainly in the used parent material (sample 1 and samples 2–4) and welding technology (with or without a filler material). Filler materials in the form of welding rod were austenitic filler metal dedicated to the implementation of the above-mentioned joints for the parent material. Generally, common to all welded joints were: the welding method – 141, the welding position – PA, the kind of joint – BW, the kind of current – DC (+), the shielding gas – Ar 100%. The differences between the joints (kind of welded joint) are shown in Table 1. None of a heat treatment removing a potential stresses was applied after welding for all welded joints.

The slurry method was used to produce the silicon-aluminide coating on the samples with joints. The active slurry was prepared from silicon and aluminium powders, the binder consisting of an aqueous solution of sodium silicate, and a composition of sodium and potassium salts (NaF, NaCl and KCl) as the activator. The ratio of the sodium silicate to (Al + Si) powders was 38/100 and the ratio of the salts to (Al + Si) powders was 24/100. The quantitative composition of the slurry was determined experimentally. The samples were immersed several times in the water slurry and dried until the value of the covering mass amounted to 0.2 g/cm².

The samples with dried slurry were loaded into an alumina tube furnace and the temperature was raised to the required temperature 800 and 1000°C respectively with a heating rate of 20°C per minute. The samples were annealed in an argon atmosphere. The powder residues of the slurry were removed from the samples after
3. RESULTS AND DISCUSSION

Coatings are formed using all the assumed parameters. Generally, the coating consisted of two or three major layers depending on the temperature and the parent material. The results of thickness measurements of all coatings are presented in Figure 1.

The coatings produced at 1000°C are considerably thicker than the ones produced at 800°C. Thickness depends also on the kind of parent material. The thickness is lower for the coatings produced at 800°C, albeit there is no nickel in the substrate (steel X18CrN28). The first layer of the coating on the weld has the similar chemical composition as the first one on the base material (Table 2 point 1 and 2), while the second layer of the coating in the area of the weld contains nickel (steel X18CrN28). As previously, the cracks are observed in the coatings produced at 1000°C have a two-layer structure (Fig. 3a, e). As previously, the cracks are observed in the HAZ. It should be emphasized that in this case the cracks are across the whole coating. It is possible that cracks are induced by residual stresses after the welding process.

Differences in the structure of the coatings formed at both 800 and 1000°C on the base material and weld have been observed (Fig. 4). Moreover, differences in the chemical composition of the weld and the parent material have been confirmed (Tab. 2). It was found that the structure of the coatings produced at 800°C is three-layer because of the substrate containing nickel in the weld while double layer because of the substrate without nickel (steel X18CrN28). The cracks in the outer layer of coating in the heat affected zone (HAZ) are visible. The cracks are mainly located in the outer layer of coating. Coatings produced at temperature 1000°C have a two-layer structure (Fig. 3a, e). As previously, the cracks are observed in the HAZ. It should be emphasized that in this case the cracks are across the whole coating. It is possible that cracks are induced by residual stresses after the welding process.

Cracks through the coating as a continuation of the fusion line and in HAZ has been observed. Cracks may occur due to the fact that the chemical composition of the weld is slightly different than the substrate because the nickel content. The filler material used for welding contained nickel contrary to X18CrN28 steel (Table 2, point 1 and 4). Also in all the previously described layers, the nickel content is higher in the coatings formed on the weld than on the base material.

The difference in the chemical composition causes that another aluminides be created in these areas. This in turn leads to a difference in the properties and generates cracks.

For the same reason the difference in the thickness between coatings formed on the weld and the parent material is large where X18CrN28 steel was used. This is especially noticeable for the coatings produced at the temperature of 1000°C (sample 1B). Coatings of greater thickness are formed on the substrate containing more nickel at this temperature. The large difference in the thickness of the coatings formed on the parent material and the weld can also induce crack generation in HAZ.

Table 1. The kind of the parent material and the weld joint and the parameters of coatings production

<table>
<thead>
<tr>
<th>No. of sample</th>
<th>Parent material</th>
<th>Kind of weld joint</th>
<th>Filler material</th>
<th>Welding parameters current/voltage, A/V</th>
<th>Temperature, °C</th>
<th>Time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>X18CrN28 1.4749/AISI 446</td>
<td>141 P BW t8 PA ml bs</td>
<td>W2520</td>
<td>80÷120/18÷20</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>2A</td>
<td>X2CrNiMo17–12–2 1.4404/AISI 316L</td>
<td>141 P BW t3 PA sl ss</td>
<td>316LSi</td>
<td>55÷60/15÷17</td>
<td>800</td>
<td>2</td>
</tr>
</tbody>
</table>

3.1. Coatings on X18CrN28 ferritic steel

In the case of coatings prepared on the X18CrN28 steel at 800°C, three-layer structure of the coating on the weld is observed (Fig. 2a) and the double layer structure on the parent material is observed (Fig. 2e). The cracks in the outer layer of coating in the heat affected zone (HAZ) are visible. The cracks are mainly located in the outer layer of coating. Coatings produced at temperature 1000°C have a two-layer structure (Fig. 3a, e). As previously, the cracks are observed in the HAZ. It should be emphasized that in this case the cracks are across the whole coating. It is possible that cracks are induced by residual stresses after the welding process.

Differences in the structure of the coatings formed at both 800 and 1000°C on the base material and weld have been observed (Fig. 4). Moreover, differences in the chemical composition of the weld and the parent material have been confirmed (Tab. 2). It was found that the structure of the coatings produced at 800°C is three-layer because of the substrate containing nickel in the weld while double layer because of the substrate without nickel (steel X18CrN28). The cracks in the outer layer of coating in the heat affected zone (HAZ) are visible. The cracks are mainly located in the outer layer of coating. Coatings produced at temperature 1000°C have a two-layer structure (Fig. 3a, e). As previously, the cracks are observed in the HAZ. It should be emphasized that in this case the cracks are across the whole coating. It is possible that cracks are induced by residual stresses after the welding process.

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For the same reason the difference in the thickness between coatings formed on the weld and the parent material is large where X18CrN28 steel was used. This is especially noticeable for the coatings produced at the temperature of 1000°C (sample 1B). Coatings of greater thickness are formed on the substrate containing more nickel at this temperature. The large difference in the thickness of the coatings formed on the parent material and the weld can also induce crack generation in HAZ.
Fig. 2. Microstructure of Al–Si coating produced at 800°C in the area of the weld joint: a) 1A, b) 2A, c) 3A, d) 4A; in the area between the weld joint and parent material: e) 1A, f) 2A, g) 3A, h) 4A; BEI

Rys. 2. Mikrostruktura warstw Al–Si wytworzonych w 800°C w obszarze złącza spawanego: a) 1A, b) 2A, c) 3A, d) 4A; w obszarze pomiędzy złączem i materiałem rodzimym: e) 1A, f) 2A, g) 3A, h) 4A; BEI

Fig. 3. Microstructure of Al–Si coating produced at 1000°C in the area of the weld joint: a) 1B, b) 2B, c) 3B, d) 4B; in the area between the weld joint and parent material: e) 1B, f) 2B, g) 3B, h) 4B; BEI

Rys. 3. Mikrostruktura warstw Al–Si wytworzonych w 1000°C w obszarze złącza spawanego: a) 1B, b) 2B, c) 3B, d) 4B; w obszarze pomiędzy złączem i materiałem rodzimym: e) 1B, f) 2B, g) 3B, h) 4B; BEI

Table 2. The results of EDS point analysis (at. %) according to Figure 3

<table>
<thead>
<tr>
<th>Point</th>
<th>Sample 1A 800</th>
<th>Sample 1B 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Si</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>48.1</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>70.4</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>4.6</td>
<td>4.1</td>
</tr>
<tr>
<td>6</td>
<td>48.7</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>68.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig. 4. Microstructure of Al–Si coating produced on X18CrN28 steel in the area between the weld joint and parent material; BEI

Rys. 4. Mikrostruktura warstw Al–Si wytworzonych na stali X18CrN28 w obszarze pomiędzy złączem i materiałem rodzimym; BEI
3.2. Coatings on X2CrNiMo17–12–2 austenitic stainless steel

It was observed that coatings formed at 800°C have a three-layer structure on both the weld and the parent material X2CrNiMo17–12–2 (Fig. 2b÷d, f÷h). The morphology of these coatings is very similar. Coatings produced at temperature 1000°C have a two-layer structure (Fig. 3b÷d, f÷h). The cracks appear only in the external layer of the coating on sample 2 in HAZ (Fig. 2f, 3f).

Elemental mappings and quantitative point analyses (EDS) results of the coatings of the coating produced at 800 and 1000°C are shown in Figures 5, 6 and Tables 3, 4.

The results of chemical composition analyses showed that the coatings produced at 800°C contain more aluminum in the external (2nd) layer, than those produced in the 1000°C. The presence of phases in which content of aluminium is higher than 58% at. in the coating structure produced at 800°C suggests an inward diffusion of aluminium [15]. Chromium and silicon are nearly immobile under these conditions. Due to their low solubility in the growing aluminides, they form their own phases (Fig. 5). The composition of the second layer of coatings produced at 800°C (Table 3, point 4) is similar to that of the 2nd layer of the coatings produced at 1000°C (Table 4, point 1). Similarly the chemical composition of the first (diffusion) layer in the coatings produced at 800°C approximates to that of the first layer of the coating produced at 1000°C (Table 3, point 5 and Table 4, point 3). The chromium content in the layer closest to the substrate is slightly higher than in the substrate. Increased silicon content is also observed here. Precipitates containing Si and Cr are not observed in the coatings produced at 1000°C. Here, silicon and chromium dissolve in the solution and are located mainly in the first layer. There are also visible minor precipitates containing a high content of nickel. The above description applies to the structure of the coatings produced at the weld, but the same situation is on the parent material (X2CrNiMo17–12–2 steel). There were no obvious differences in the content of elements of the substrate material and the weld metal. All three types of samples (No. 2, 3, 4) promote the formation of coatings with a similar structure, both on the weld and the base material coatings.

![Fig. 5. Elemental mapping in cross-section of coating on weld joint; No. 4A (X2CrNiMo17–12–2; 800°C) with points of EDS X-ray microanalysis.](image)

![Rys. 5. Rozmieszczenie powierzchniowe pierwiastków na przekroju warstwy uformowanej na spoinie; nr próbki 4A (X2CrNiMo17–12–2; 800°C) z punktami mikroanalizy EDS](image)

![Fig. 6. Elemental mapping in cross-section of coating on weld joint; No. 2B (X2CrNiMo17–12–2; 1000°C) with points of EDS X-ray microanalysis.](image)

![Rys. 6. Rozmieszczenie powierzchniowe pierwiastków na przekroju warstwy uformowanej na spoinie; nr próbki 2B (X2CrNiMo17–12–2; 1000°C) z punktami mikroanalizy EDS](image)
The differences in thickness of the coatings are insignificant where X2CrNiMo17–12–2 steel is applied as a substrate. This is because the differences between the chemical composition of the parent material and the weld are minor. All coatings produced at temperature 1000°C are of comparable thickness (sample 2B, 3B, 4B) ca. 200 μm. However, this comparison looks differently for the coatings produced at 800°C on the same steel (sample 2A, 3A, 4A). Samples 3 and 4 are made from the same material of the sheet thickness of 2.77 mm (Table 1). The coating thickness is nearly the same (sample 3A and 4A), but the first layers lying close to the substrate is thinner on the sample 4 where no filler material was applied. 

The thickness of the coatings produced at a temperature of 800°C is in the range of 20÷60 μm depending on the substrate type. The thickness of the coatings produced at 800°C is in the range of 40÷65 μm depending on the substrate type. The thickness of the coatings annealed at 1000°C is in the range of 100÷200 μm. It is noted that the thickness of the coatings on the parent material is in any case higher than on the weld. This difference is minor for the coatings produced on the austenitic X2CrNiMo17–12–2 steel (about 5÷10 μm), while much more higher for coatings produced on ferritic X18CrNi28 steel (from 5 to 50 μm). The use of the filler material of different chemical composition of the substrate material causes differences in the thickness of the coating and can also generate cracks through the coating in the HAZ.

### 4. SUMMARY

The aluminide protective coatings by the slurry method were successfully formed on the whole surface of alloyed steels and the welded joints. There are strong similarities between the structure of coatings produced in a given temperature despite the use of different substrates and various technologies of welding. Generally, the coatings produced at a temperature of 800°C are characterized by a three-layer structure, while those at 1000°C have two layers. The thickness of the coatings produced at 800°C is in the range of 40÷65 μm depending on the substrate type. The thickness of the coatings annealed at 1000°C is in the range of 100÷200 μm. It is noted that the thickness of the coatings on the parent material is in any case higher than on the weld. This difference is minor for the coatings produced on the austenitic X2CrNiMo17–12–2 steel (about 5÷10 μm), while much more higher for coatings produced on ferritic X18CrNi28 steel (from 5 to 50 μm). The use of the filler material of different chemical composition of the substrate material causes differences in the thickness of the coating and can also generate cracks through the coating in the HAZ.

### REFERENCES

Struktura warstw aluminiidkowych na stali wysokostopowej w obszarze złącza spawanego

Agnieszka Kochmańska*, Paweł Kochmański, Michał Kawiak

Zachodniopomorski Uniwersytet Technologiczny w Szczecinie, *agnieszka.kochmanska@zut.edu.pl

Słowa kluczowe: warstwy aluminiidkowe, metoda zawiesinowa, stałe stopowe, połączenia spawane.

1. CEL PRACY


2. MATERIAŁ I METODYKA BADAŃ

Do badań użyto dwóch gatunków stali wysokostopowych: ferrytoczną żaroodporną 1.4749 (X18CrN28) i austenityczną kwasoodporną 1.4404 (X2CrNiMo17−12−2). Złącza docelowo wykonano metodą spawania lukołowego elektrodą nietopliwą w osłonie gazów obojętnych. Złącza wykonano z wykorzystaniem materiału dodatkowego oraz bez niego. Materiałami dodatkowymi w postaci próbek było spowo austenityczne dedykowane do wykonania złączy dla wymienionych stali stali. Dla wszystkich złączy zastosowano metodę 141, pozycję spawania PA, rodzaj złączy BW, gładka 1.4404 (X2CrNiMo17−12−2). Różnice miedzy wykonanymi złączami przedstawiono w tabeli 1. Na przygotowanych materiałach ze złączami wytworzone warstwy krzemkowo-aluminidkowe metodą zawiesinową. Zawiesina zawierała proszki Al i Si, materiał wąski (wodny roztwór krzemianu sodu) oraz topniki w postaci mieszaniny soli. Masa zawiesziny na powierzchni próbek wynosiła ok. 0,2 g/cm². Próbki z nałożoną zawiesiną były wygrzewane w atmosferze ochronnej argonu w temperaturze 800°C i 1000°C przez 2 godziny. Potem resztki zawiesiny były usuwane. Określenie wpływów temperatury na strukturę warstw jest ważne, ponieważ w każdej zażytowanej temperaturze otrzymuje się inną skład fazowy warstw. Parametry wytwarzania warstw przedstawiono w tabeli 1. Do opisu warstw użyto metodę SEM/EDS.

3. WYNIKI I ICH DYSKUJSJA

 Wyniki badania grubości przedstawiono na rysunku 1. Warstwy mają budowę dwu- lub trójstrefową. Grubość warstw wytworzonych w temperaturze 1000°C (100÷250 μm) jest większa niż warstw wytworzone w temperaturze 800°C (od 40 do 100 μm). Grubość warstw wytworzonych na stali austenitycznej jest również większa niż na stali ferrytocznej. We wszystkich przypadkach zauważono, że grubość warstw na materiale rodzimym jest większa niż na spoinie. Mikrostrukturę otrzymywanych warstw przedstawiono na rysunkach 2 i 3, odpowiednio dla warstw wytworzonych w 800°C i 1000°C.

Warstwy na stali ferrytocznej X18CrN28

Warstwy wytworzono w temperaturze 1000°C, charakteryzują się trójstrefową budową na spoinie, natomiast dwustrefową na materiale rodzimym. W SWC obserwuje się zanik strefy położonej najbliższej podłoża. W tym obszarze warstwy pojawiają się pęknięcia w jej zewnętrznej części. Warstwy wytworzone w temperaturze 1000°C mają dwie strefy. W SWC pojawiają się przebiegające na wszytsko pęknięcia w warstwie. Różnice w strukturze warstw na spoinie i na materiale rodzimym przedstawiono na rysunku 4, na którym pokazano również miejsca punktowej mikroanalizy SEM/EDS z wynikami ilościowej analizy składu chemicznego w tabeli 2. Swierdlenie zwiększoną zawartość Ni na spoinie ze względu na zastosowany materiał dodatkowy podczas spawania. Wpływa to na większą zawartość Ni we wszystkich strefach warstw na spoinie i sprzęży powstania budowy trójstrefowej. Ze względu na różnice w składzie chemicznym powstają różne aluminiidki, co może generować naprężenia na linię wtopienia prowadzące do pękania.

Warstwy na stali austenitycznej X2CrNiMo17−12−2

Warstwy wytworzono w temperaturze 800°C mającą strukturę trójstrefową na spoinie i na materiale rodzimym, a te wytworzone w 1000°C strukturę dwustrefową. Mapy rozmieszczenia pierwiastków na przekroju warstw przedstawiono na rysunkach 5 i 6, a skład chemiczny w tabelach 3 i 4. Różnica w grubości warstw na spoinie i materiale rodzimym jest niewielka, rzędu 5÷10 μm. Grubość warstw w obszarze złącza spawanego i materiału rodzinnego jest porównywalna w wszystkich przypadkach. Brak materiału dodatkowego przy spawaniu również nie wpływa znacząco na grubość warstw. W SWC nie obserwuje się pęknięć na wszytsko warstw. W zewnętrznej części warstwy wytworzonej w 1000°C obserwuje się pęknięcia w SWC na próbkach spawanych w próbkach spawanych w bojemstwie.

4. PODSUMOWANIE

Najlepsze rezultaty otrzymano, stosując jako podłoże stałe austenityczne. Nie obserwowano w SWC pęknięć na wszytsko warstw, które ma płynne przejście z obszaru na spoinie do obszaru materiału rodzinnego. Skład chemiczny spoiny jest zbliżony do składu materiału rodzinnego. Warstwy na złączach jednostronnich charakteryzują się zwartą budową, bez pęknięć. W przypadku złącza spawanego bez materiału dodatkowego (stałe austenityczne) również otrzymano warstwy dobrej jakości. Wytwarzanie warstw na stali ferrytocznej z zastosowaniem materiału dodatkowego zawierającego nikiel może powodować zmiany w SWC i pęknięcie na wszytsko.