Diffusion Processes of Aluminium Coatings for the Protection of Austenitic Stainless Steels

A. ALDERISIO, B. BREVAGLIERI and S. NATALI - Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia - Facoltà di Ingegneria - " La Sapienza " University, Rome, Italy
A. DANG and G.A. CAPUANO - Department of Chemistry, University of Quebec in Montreal - Montreal, Quebec, Canada.

Abstract

An aluminium-coated austenitic stainless steel has been subjected to heat treatments of various durations. The process has led to the formation of interdiffusion zones with characteristic non-directional and columnar structures.
The formation of intermetallic compounds such as NiAl or Ni$_3$Al prevails in the non-directional type, while substitutional solid solutions occur in the "columnar" type.
One or both these structures can be obtained by balancing and regulating process activity through adequate heat treatments.
The development of one or both structures can heighten the characteristics of the coating as regards coating protection or oxidation resistance at high temperatures.

Riassunto

Sono stati effettuati trattamenti termici di durata variabile su un acciaio inossidabile austenitico rivestito con alluminio; questo processo ha portato alla formazione di fasce di interdiffusione.
Queste fasce si presentano con caratteristiche strutture: una di tipo non direzionale e l'altra di tipo colonnare.
Nel tipo a struttura non direzionale prevale la formazione di composti intermetallici come NiAl o Ni$_3$Al, mentre nel tipo "colonnare" si hanno soluzioni solide sostituzionali.
Bilanciando e regolando l'attività del processo con adeguati trattamenti termici si possono ottenere in prevalenza l'una o l'altra struttura.
Lo sviluppo di una delle due strutture o di entrambe può esaltare le caratteristiche protettive del rivestimento per quanto riguarda la protezione dalla corrosione o dall'ossidazione a caldo.

Introduction

The protective capacity of surface coatings depends not only on the type concerned but also on the formation of oxides and the interdiffusion between coating and substratum with the formation of solid solutions and intermediate phases owing to the effect of heat treatments. Intermediate phases are composed of metals with particular lattice structures which differ from those of the components. Such structures form because there is a very strong bonding between dissimilar atoms resulting in particular chemical and physical properties.

High hardness is correlated with high heat resistance, so the intermediate phases have been evaluated with a view to the development of new structural materials for high-temperature applications.

The chemical and petrochemical industries have used such materials for the construction of gas turbines, valves, exhaust pipes and combustion chambers to provide corrosion protection and oxidation resistance at high temperatures [1-4].

Typical surface coverings are aluminium coatings.

Stress corrosion experiments conducted on aluminium-coated stainless steels have demonstrated that the formation of intermetallic compounds provides very good protection against this form of local corrosion [5, 6]. The purpose of the work reported here was to study the effect of temperature and treatment time on the structure and composition of the intermediate phases which are formed, and especially the development of diffusion zones between the aluminium coating and the matrix of a stainless steel.

Materials, treatments and apparatus

The experiments were run on AISI 304 austenitic stainless steel whose composition (% wt) is C 0.041, Cr 18.60, Ni 8.80, Mn 1.05, Si 0.30, P. 0.004, S 0.005 and Mo 0.35 coated with about 12 μm of aluminium electrolytically deposited from organic solutions.

The electrolyte consists of aluminium bromide and a mixture of alkylbenzenes. The detailed preparation and use of the electrolyte has been described elsewhere [7-10]. The resulting aluminium coatings are ductile and are obtained with cathodic efficiencies approaching 100% at cathodic current densities of 5-40 mA/cm^2.

Samples of steel 10 mm long and 8 mm in diameter have been subjected to combined heat treatments at 600°C and 800°C for 24, 48 and 72 hours in air. Twenty-four hour treatments at 600°C and 800°C have also been performed in an argon atmosphere.

The experimental conditions are detailed ahead.

After the heat treatments the samples were cleaned with CSi paper to N° 800, wet-polished with aluminium powder to 0.05 μm and then cleaned and electrolytically etched in 10% oxalic acid to reveal the structure of the steel and that of the diffusion zone.

Experimental results

The heat treatments performed are summarized in Table 1 where the duration of the heat treatment at 600°C increases from the top downwards (24, 48 and 72 hours), while that of the treatment at 800°C increases from left to right. The symbol 24/24 indicates heat treatment at 600°C for 24 hours followed by treatment at 800°C for 24 hours. Similar symbols are used for the other treatments.

TABLE 1

Heat Treatment 24/24

Elements	E	A		B		M
Al	63	45	35	9	1	0
Cr	3	8	9	24	24	22
Fe	33	38	46	62	70	69
Ni	1	9	10	5	5	9

Heat Treatment 24/48

Elements	E	A	B		M
Al	83	29	3	Absent	0
Cr	5	9	22		22
Fe	11	30	70		70
Ni	1	32	5		8

Heat Treatment 24/72

Elements	E	A	B		M
Al	79	39	3	Absent	0
Cr	4	8	22		21
Fe	16	28	70		70
Ni	1	25	5		9

Heat Treatment 48/24

Elements	E	A	B		M
Al	31	Absent	17	6	1
Cr	13		16	22	21
Fe	47		55	68	69
Ni	9		12	4	9

Heat Treatment 48/48

Elements	E	A		B		M
Al	53	44	44	5	6	0
Cr	13	10	8	24	23	21
Fe	32	43	43	64	67	70
Ni	2	3	5	7	4	9

Heat Treatment 48/72

Elements	E	A	B		M
Al	80	28	5	Absent	3
Cr	8	10	21		20
Fe	11	35	68		68
Ni	1	27	6		9

Heat Treatment 72/24

Elements	E	A	B		M
Al	22	Absent	10	8	0
Cr	13		22	21	21
Fe	60		65	61	70
Ni	5		3	10	9

Heat Treatment 72/48

Elements	E	A	B		M
Al	47	Absent	22	14	0
Cr	10		13	17	21
Fe	40		56	63	70
Ni	3		9	6	9

Heat Treatment 72/72

Elements	E	A	B		M
Al	66	Absent	12	3	3
Cr	8		18	23	20
Fe	20		57	68	68
Ni	6		13	6	9

Two phases are formed owing to the effect of the various heat treatments. These may appear simultaneously (24/24 and 48/48) or individually (24/48 A, 24/72 A, 48/72 A, 48/24 B, 72/24 B, 72/48 B and 72/72 B).

Under the scanning electron microscope one phase appears to have a darker, non-directional structure which will be referred to as Type A, while the other phase has a "columnar" structure, this is Type B.

Part of the external aluminium deposit (E) is transformed into alumina (Al_2O_3), and part remains as metallic aluminium, active as far as diffusion is concerned.

Nickel-rich oxides ($NiAl_2O_4$ and $NiCr_2O_4$) characteristic of oxidation processes [11] have also been identified within the scale, while the matrix (M) remains unaltered.

The average values of the analyses expressed in % at, performed near the interfaces of the various diffusion zone, are reported in the same table.

Figs 1, 2 and 3 reveal the particular situations that occur with the diverse heat treatments. With the 24/24 treatment (Fig. 1) the two phases appear simultaneously, with the 24/48 treatment (Fig. 2) only the A phase is seen, while with the 48/24 treatment (Fig. 3) the B phase is present.

Fig. 4 refers to the 24/24 treatment in an argon atmosphere and reveals only the A phase.

Discussion of results

As can be seen from Figs 1, 2 and 3, the different heat treatments produce two zones of diffusion and an external alumina scale with diverse active aluminium contents.

One of the two diffusion zones has the characteristic "columnar" structure (Type B) proposed by Drewett for substitutional solid solutions, with axis parallel to the direction of growth [12].

The other zone, with non-directional structure (Type A) always occurs close to the pure metal coatings from which it draws its supplies [13, 14].

The analyses conducted on a given zone, at the same distance from the separation interface with the adjacent zone, give composition values in % at of the various elements that are always comparable (Fig. 5).

Furthermore, the analytical values for the two interfaces of the same diffusion zone indicate concentration gradients for the various elements which, with good approximation, lie in the compositional range of the individual phases represented by their binary diagrams with aluminium.

This signifies that the two zones can be considered to be formed by a component and a pseudo-component (Fe, Cr or Ni); hence the layers formed will be single-phase regions [13, 15].

Inspection of the analyses indicates that in the "columnar" structure, when this occurs alone or when it is together with the non-directional structure, the % at of aluminium — whose diffusion is the cause of the formation of these zones — never attains values (20%) such as to form intermetallic compounds either with Fe or with Ni or Cr.

The aluminium remains in substitutional solid solution α with Ni and with Fe, and β with Cr.

In the non-directional structure, instead, the aluminium attains much higher concentrations (45%).

Observation of the binary diagrams also indicates the formation of substitutional solid solutions with Fe and with Cr, while with Ni the aluminium can give intermetallic compounds of the NiAl (34-43% Al) and Ni_3Al (10-34% Al) types.

The probable formation of these intermediate phases emerges from inspection of Fig. 6 where it is noted that in the Type A zone when the Type B zone is absent, a sudden improverishment in iron is matched by a simultaneous increase in Ni to values much higher than those found in the matrix; there is also a parallel increase in aluminium concentration.

In the formation of interdiffusion zones (intermetallic compounds and/or substitutional solid solutions), the types of diffusion that may occur play an important role (16).

In the first type — diffusion towards the inside — the bands that appear are mainly those that occur by diffusion of the aluminium towards the interior of the substratum.

In the second type — diffusion towards the outside — the zones are principally those obtained by diffusion of the Ni and the other elements of the substratum.

By balancing and regulating process activity, fostering diffusion towards the inside, thanks to a high active aluminium content, an aluminium concentration is attained such as to favour the formation of intermetallic compounds, especially with nickel.

If aluminium oxide predominates in the outer layer, there is little or no diffusion of aluminium, while nickel, iron and chromium spread towards the outside; at this point only substitutional solid solutions can form.

Following the events that occurred during the process, it is evident that with heat treatment at 600°C for 24 hours a large quantity of active aluminium remains on the surface. With subsequent heat treatment at 800°C for 24 hours, owing to the shortness of the time involved, the aluminium does not manage to penetrate completely into the inside in high concentrations and meet up with alloy elements coming from the substratum. Hence an intermetallic compound and a substitutional solid solution will form.

With longer heat treatments at 800°C (48 h) the diffusion of the aluminium is greater, and a concentration is attained such as to form an intermetallic compound similar to NiAl or Ni_3Al.

With heat treatments at 800°C for 72 h, further diffusion of the aluminium is possible with the formation only of the Type A zone which is thicker than those obtained with shorter heat treatments.

Treatment at 600°C for 48 hours, producing a larger quantity of γ Al_2O_3, results in a smaller concentration of active aluminium [11]. In this case, during subsequent treatment at 800°C diffusion will not be favoured; longer times will be required for the intermetallic compound to form together with the "columnar" phase (48 h) and alone (72 h) (Table 1).

With treatment at 600°C for 72 hours the active aluminium content is further reduced. In this event, though the aluminium spreads at 800°C it does not manage to attain values such as to permit the formation of intermetallic compounds; it only forms substitutional solid solutions represented by the "columnar" type diffusion zone.

The foregoing is confirmed by heat treatments in an argon-protected environment (Fig. 4). With a 24/24 h treatment, in fact, only the non-directional zone has been encountered. This can be explained by assuming that this treatment leads to a further increase in active aluminium on the surface, such as to attain values during diffusion at 800°C that can immediately generate only the Type A zone.

Conclusions

The use of low cost ferrous materials is limited owing to their poor oxidation resistance at high temperature.

A study has been made of the effects of the electrodeposition of aluminium on austenitic stainless

steels with the aim of developing protective metallic structures suitable for prolonged high-temperature operation. This is an alternative to the use of aluminium coatings on superalloys that have already been tried or are in course of experimentation.

It is possible to select heat treatments that differ in duration and temperature with a view to inducing by diffusion the formation of specific intermediate phases having satisfactory mechanical properties and protective capabilities.

References

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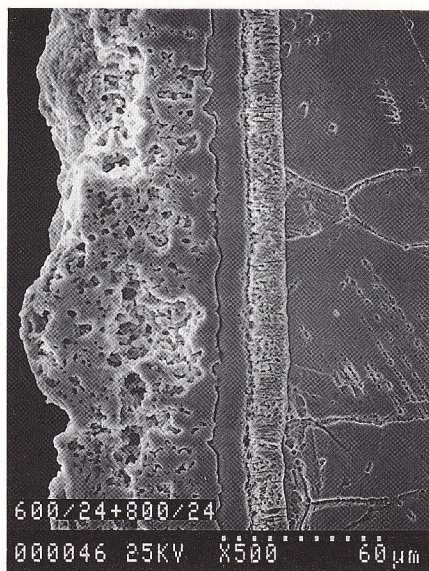[16] G.W. Goward, *Jour. of Metal*, 31-39, october 1970.

Fig. 1:
Heat treatment in air 600/24+800/24 -
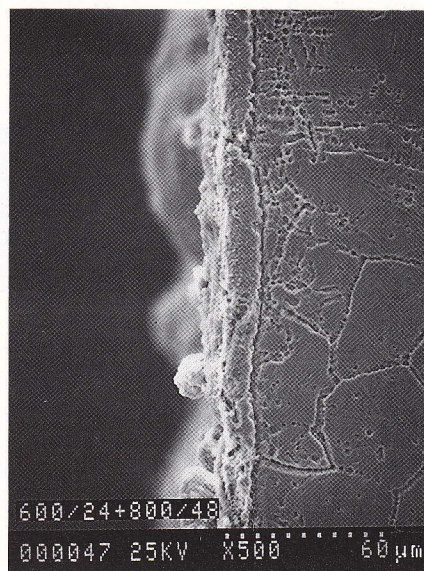Type A and Type B zones.

Fig. 2:
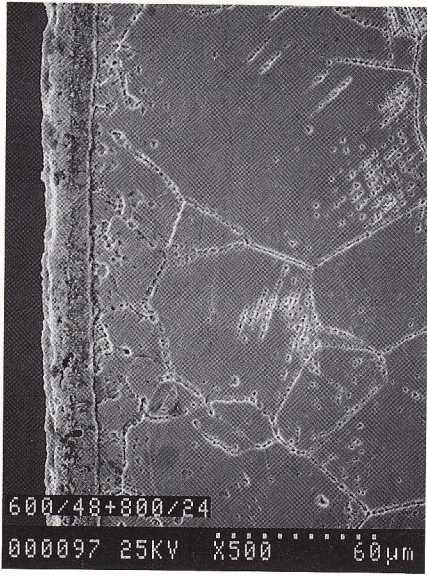Heat treatment in air 600/24+800/48 -
Type A zone.

Fig. 3:
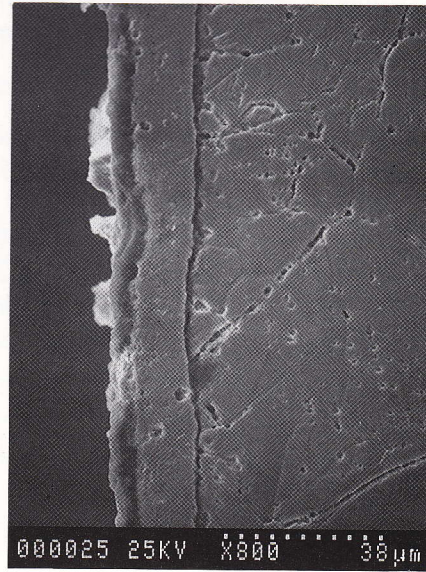Heat treatment in air 600/48+800/24 -
Type B zone.

Fig. 4:
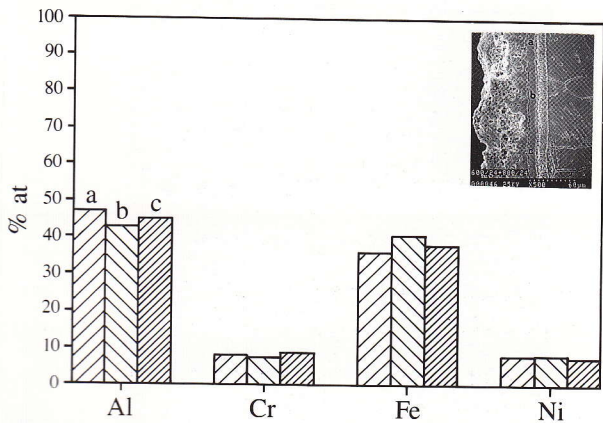Heat treatment in argon 600/24+800/24 -
Type A zone.

Fig. 5:
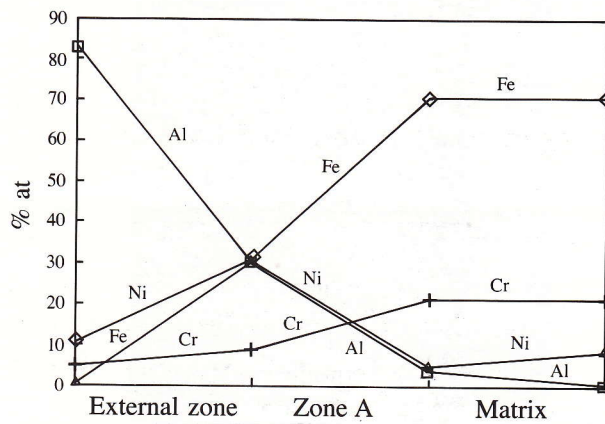Concentration of elements in points equidistant
from the interface.

Fig. 6:
Diffusion of elements during heat
treatment 600/24+800/48.