Effect of Chromium on the Diffusion Rate of Aluminium on Fe-Cr-Ni Alloys

A. ALDERISIO, B. BREVAGLIERI, S. NATALI - Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia - Facoltà di Ingegneria - Università "La Sapienza" - Rome, Italy

Abstract

Syntetic alloys with various contents (12%, 14%, 16%) and a constant nickel content of 6% were produced, with aluminium electroplated. These alloys were subjected to heat treatments of various duration.

A substitutional solid solution was recognized, as was an intermetallic phase which occurs as islands and/or an intermetallic phase in form of a continuous layer.

It can be seen from experimental results that the chromium affect the delicate transformation and precipitation rate of aluminides especially the rate of the transformation front.

The stability of austenite, controlled by the chromium content, is the most important factor affecting the thickness, distribution and continuity of the interdiffusion compounds.

Riassunto

Sono state fabbricate leghe sintetiche a tre diversi tenori di cromo (12%, 14%, 16%) e con tenore costante di nichel del 6%, elettrorivestite con alluminio.

Su queste leghe sono stati effettuati trattamenti termici di durata variabile.

Sono stati individuati, mediante analisi EDS, mappature a raggi X, analisi di immagine, una soluzione solida sostituzionale e una fase intermetallica che si presenta sotto forma di isole e/o una fase intermetallica sotto forma di strato continuo.

Dai dati sperimentali ottenuti si nota che il cromo incide sulle delicate cinetiche di trasformazione e di precipitazione degli allluminuri e in particolare sulla velocità del fronte di trasformazione.

La stabilità dell'austenite, controllata dal tenore del cromo, è il più importante fattore che caratterizza lo spessore, la distribuzione e la continuità dei composti di interdiffusione.

Introduction

Aluminium coatings, followed by specific heat treatments, lead to the formation of intermediate layers of aluminium-based intermetallic compounds on the surface of metallic materials.

Such processes produce a surface with improved resistance to hot oxidation and corrosion, the aim being to extend the service life of the materials thus coated [1,2].

This methodology has also been applied to stainless steels, especially for protection against sulphur dioxide in industrial environments and for corrosion resistance in the salt baths used in fuel cells.

For these applications it is uneconomical to utilize high-alloy materials such as Hastelloy and Inconel, while intermediate materials like AISI 304 and 316 austenitic stainless steels do not have adequate hot corrosion resistance unless they are coated [3,4].

Heat treatments at 800 °C performed on aluminium-coated austenitic stainless steels do not result in diffusion and the formation of continuous intermetallic compounds consisting of β NiAl [5].

Chromium has been identified as the main factor responsible for the continuity of protective coatings and for influencing the composition of Ni-Al alloys. In fact, this element varies the intermetallic compound formation mechanism, promoting the stability of one phase rather than another and increasing the activity of the aluminium [7].

The purpose of the work reported here was to characterize the microstructure and composition of the coatings obtained by the diffusion of aluminium on stainless steels and also to study process parameters and the influence of the substrate.

In particular, it was wished to confirm the fact that chromium represents an inhibiting factor in the formation of "continuous", protective intermetallic compounds, and also to ascertain whether intermetallic compounds like NiAl and Ni_3Al can still be formed when lower nickel contents lower than those normally adopted in stainless steels are used. Hence, synthetic alloys with various chromium contents (12%, 14% and 16%) and a constant nickel content of 6%, were produced.

Materials, heat treatments and equipment

The experiments were performed on round bars of Fe-Cr-Ni alloys having various known chromium contents and a constant nickel analysis. The percentage composition of the alloys is given in Table I.

The alloys were prepared by vacuum smelting in an Edwards High Vacuum "Speedivac" furnace, care being taken to keep the melt under a vacuum of $2\text{-}3 \times 10^{-5}$ mm Hg for thirty minutes.

The ingots were hot-hammered to ensure uniform composition and reduce the grain size. They were then subjected to solution heat-treatment at 1050 °C for one hour and water-quenched.

Round bars were obtained from each ingot. These were given an aluminium coating some 12 μm thick by electrolytic deposition from organic solutions. Cylinders 10 mm thick and 10 mm in diameter were then derived from these bars.

The cylinders were subjected to the following heat treatments: pretreatment at 600 °C for 24 h followed by diffusion heat treatment at 800 °C for 24, 48 and 72 h.

After the heat treatments the flat faces of the samples were cleaned with CSi paper down to n° 1000 and wet lapped with 1.0, 0.3 and 0.05 μm alumina powder; they were then electrochemically etched with 5% H_2SO_4 at room temperature so as to reveal the structure of the Fe-Cr-Ni alloys.

The samples were examined under an S2500 Hitachi Electron Scanning Microscope. Chemical analyses were then performed in % at on the interdiffusion compounds, while X-ray mapping and image analysis were adopted to characterize the morphology of the intermetallic compounds.

TABLE 1 - Alloys composition, % w

Nominal composition	Cr	Ni	C
12/6	11.93	6.08	0.006
14/6	14.42	5.87	0.005
16/6	16.18	6.04	0.010

Methodologies and experimental results

a) SEM examination

A substitutional solid solution (Al 12-4, Cr 12-16, Ni 6, Fe = bal.) was recognized, as was an intermetallic phase which occurs as islands (average composition in % at being Al 27, Cr 5, Fe 37 and Ni 31) and/or an intermetallic phase in the form of a continuous layer with average composition Al 34, Cr 4, Fe 22 and Ni 40.

The phase distribution and the microchemistry of these three compounds show that the interdiffusion layer is a "compound" formed by a dispersion of a hard nickel aluminide phase and a solid substitutional solution with zones of probable ferritic matrix.

Continuous intermetallic compounds — whose thickness increases with the duration of the heat treatments — and scattered islands form in the synthetic alloys containing 12% chromium. This sequence is illustrated in Figs 1a, 1b and 1c.

In the synthetic alloys containing 14% Cr there is an increase in the scattered islands, whose size becomes larger with the length of the heat treatment without, however, resulting in the formation of a continuous profile. Figs 2a, 2b and 2c illustrate this trend.

In the synthetic alloys containing 16% Cr, occasional scattered islands of intermetallic compounds

are found. The number of islands and the size thereof increases with the duration of the heat treatment. Figs. 3a, 3b and 3c illustrate the trend.

b) Characterization of the form and continuity of the intermetallic compounds by image analysis

Three independent factors have been adopted to characterize the shape, size and possible formation of continuous layers:

1) Size factor (f_d): the reciprocal of the average of the perimeters has been considered as the factor directly proportional to the increase in the size of the precipitates

2) Shape factor (f_f): the ratio of the average height to the average thickness has been considered, because an increase in this expresses a morphology close to continuity

3) Position factor (f_p): the reciprocal of the average distance between the centre of mass of the individual precipitates and the edge of the sample has been considered, since this indicates the movement of the intermetallic compounds towards the edge of the sample.

The product $f_d \times f_f \times f_p = IC$ (Index of Continuity) has been determined as the value representing a morphological situation of continuity close to the edge of the sample.

Discussion of results

As the particular heat treatments employed are processes involving high aluminium activity, they favour the diffusion of the aluminium towards the inside, with the probable formation of compounds like β-NiAl and γ'Ni$_3$Al (brittle) [8,9].

Examination of the Fig. 1 micrographs (Cr 12%) reveals the formation of a continuous layer of intermetallic compounds alternating with numerous islands dispersed in a substitutional solid solution; the thickness of the continuous layer increases with the duration of the heat treatment.

Examination of the Fig. 2 micrographs (Cr 14%) reveals the formation of a intermetallic compounds like β-NiAl and γ'-Ni$_3$Al as small scattered islands; the number and size of the islands increases with the duration of the heat treatment, without ever resulting in the formation of a continuous film.

Examination of the Fig. 3 micrographs (Cr 16%) reveals the formation of islands whose size increases with the duration of the heat treatment.

It is evident that the increase in chromium concentration hinders the formation both of a continuous layer and of islands, though the formation of these is favoured by the high activity of the aluminium [10,11].

It is apparent that intermetallic compounds are formed in all cases, even when the nickel content is very low (6%).

The formation of a continuous layer in the first of the three alloys studied can be explained by assuming that the aluminium diffuses in the substrate during the diffusion processes. This diffusion modifies the delicate balance of the austenite stability [12].

Indeed, this is attributable to two important factors:

1) the solubility of the aluminium in the austenite is extremely limited, while in the ferrite it is very high [13], hence diffusion of the aluminium causes the formation of local ferrite on the surface.

2) the nickel in these alloys prevents the transformation of the austenite and it also forms very stable intermetallic compounds, because it has a strong affinity for the aluminium.

The formation of aluminides results in the nickel substrate being impoverished in nickel, thus further favouring the formation of ferrite.

The rate of diffusion of the aluminium in the ferrites is two orders of magnitude greater than in the austentite [13], so the diffusion favours the phase transformation to ferrite and, in its turn, assists the diffusion of the aluminium.

An austenite/ferrite transformation front is thus formed. If the rate of formation and growth of the aluminides is comparable with the rate of migration of the transformation front, the precipitates grow in elongated form, creating needle-shaped particles. However, in the zones where the velocity of the transformation front is substantially higher, the particles of aluminium are spherical in shape. On the other hand, if the velocity of the transformation front is lower than the rate of formation of the aluminides, these nucleate behind the transformation front and mass together to form continuous layers.

It can be seen from the experimental results that the chromium affects the delicate transformation and precipitation rates of the aluminides, especially the velocity of the transformation front.

Fig. 4 illustrates how — as a function of the duration of the heat treatment — the thickness of the interdiffusion band diminishes as the chromium content decreases and the index of stability (I.S.) of the austenite increases [13]. The Index is determined on the basis of the ratio of the Ni_{eq} and the Cr_{eq} derived by means of empirical equations [14].

The depth of penetration of the aluminium in samples with different austenite I.S. values is documented by the Fig. 5 mapping where it is noted that for a low chromium content the aluminium diffuses with greater difficulty than in the higher-chromium alloys because it is in the presence of more stable austenite.

Moreover, a low chromium content (12%), which is associated with a decreased tendency for austenite/ferrite transformation, slowing the advance of the front, favours the formation of continuous layers (high Index of Continuity) (Fig. 6). As the percentage chromium increases (14%, 16%) these layers evolve into rounded precipitates (Figs 2 and 3 micrographs), a phenomenon which occurs when the velocity of the transformation front is markedly greater than that of precipitate growth.

The chromium also governs the formation of the type of intermetallic compounds involved, favouring the dissolution of $\beta NiAl$ in $\gamma'Ni_3Al$ [15], which expels the nickel from the substrate and thus increases the amount of austenite/ferrite transformation, as well as boosting the velocity of the transformation front.

Conclusions

The microstructure and the composition of diffusion coatings in stainless steels depends markedly on the composition of the substrate.

The stability of the austenite, controlled by the chromium content, is the most important factor affecting the thickness, distribution and continuity of the interdiffusion compounds.

The importance of the natural compound, formed by hard aluminide phases dispersed in a soft ferrite phase, depends on the strength and the corrosion resistance of these coatings. Firstly, because the aluminides form a "reserve" of aluminium when the oxide scale is attacked, and secondly because of the formation of a highly protective continuous layer or alternatively a fine dispersion of aluminides which foster better adherence.

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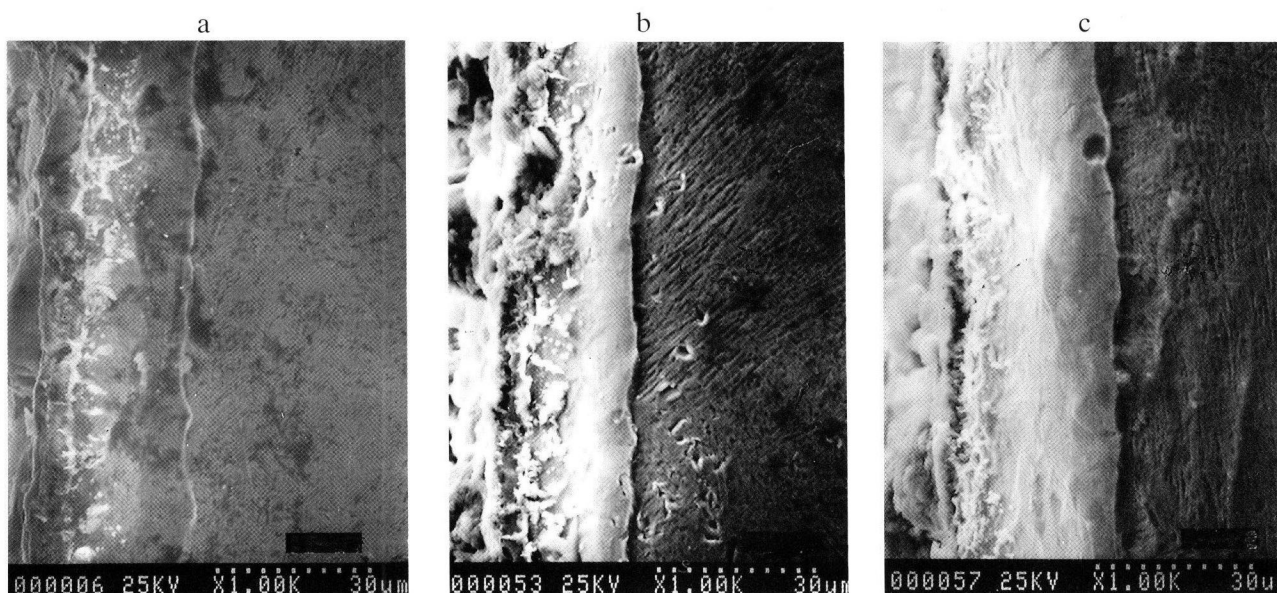
Fig. 1:
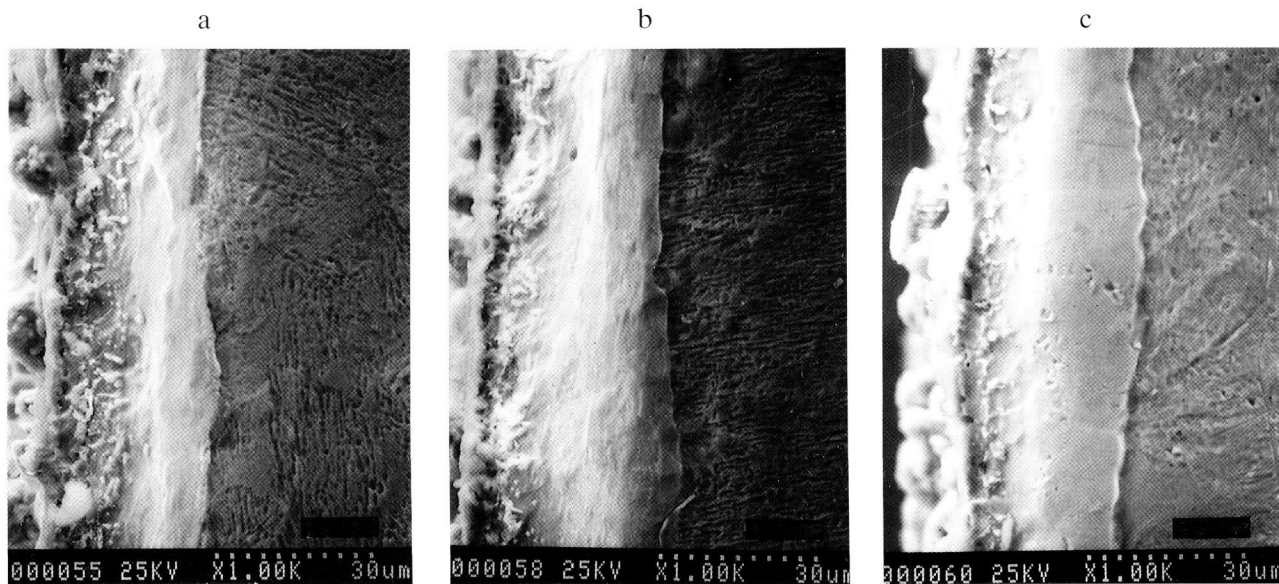12% chromium alloys: a - 800°C 24 h;
b - 800°C 48 h; c - 800°C 72 h.

Fig. 2:
14% chromium alloys: a - 800°C 24 h;
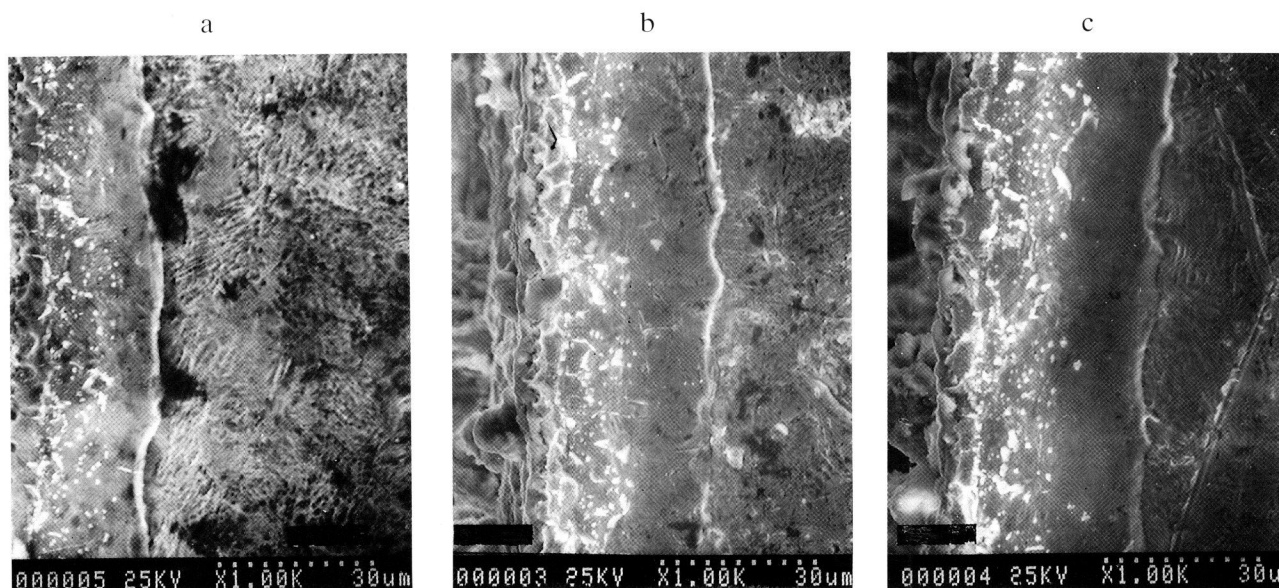b - 800°C 48 h; c - 800°C 72 h.

Fig. 3:
16% chromium alloys: a - 800°C 24 h; b - 800°C 48 h;
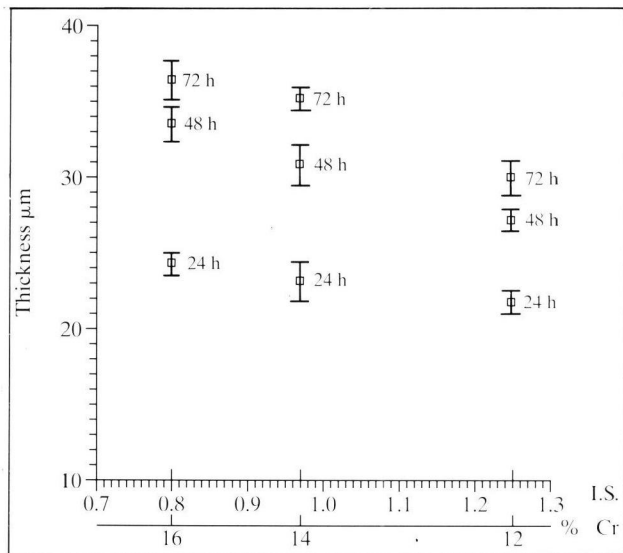c - 800°C 72 h.

Fig. 4:
Effect of austenite stability and duration of heat
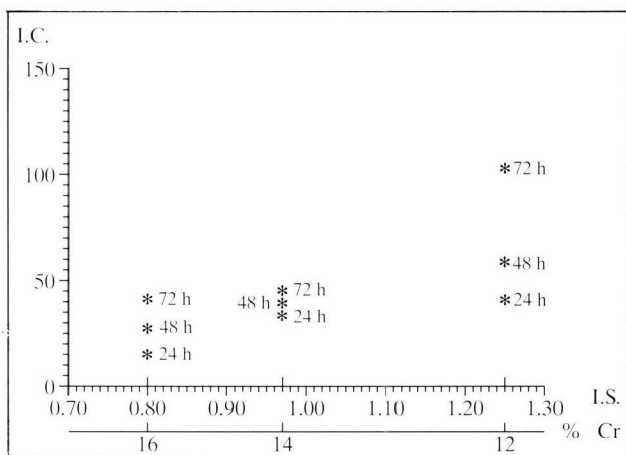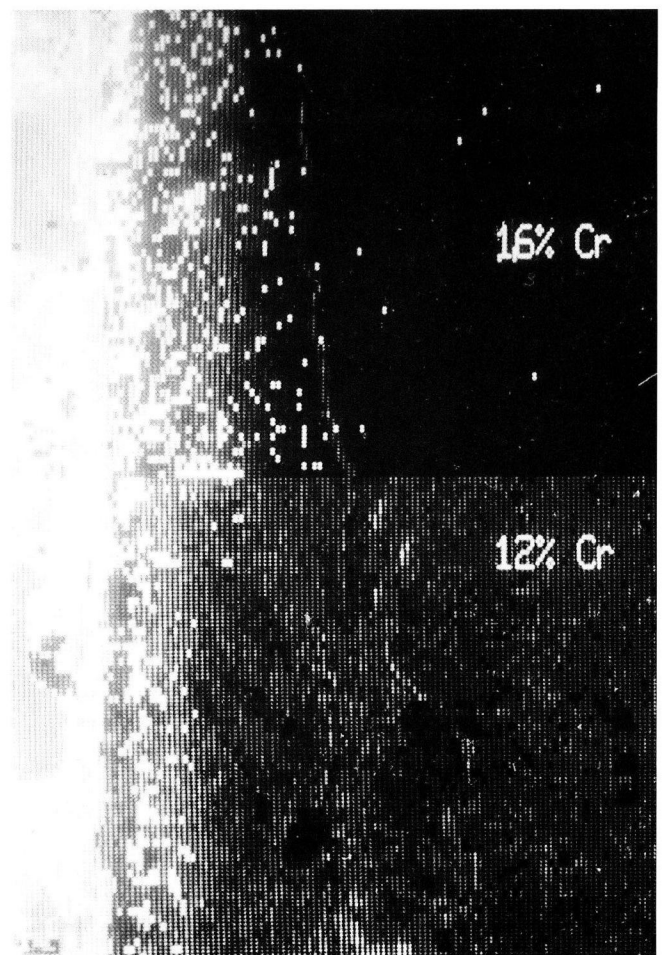treatments on trend of thickness of interdiffusion
zone.

Fig. 5:
Diffusion of aluminium in the 16% and 12%
chromium alloys.

Fig. 6:
Effect of austenite stability on trend of Index of
Continuity.