

Composition and structural modifications to the Al/AISI 316L sintered steel interface induced by heat treatments

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Abstract

After heat treatment, the aluminium coating, deposited on sintered AISI 316L austenitic stainless steel forms an interdiffusion layer. Aluminium diffuses beyond the layer/steel interface, mostly along the interconnected porosities, penetrating into the sintered steel for about 80µm, and causing a nitrogen exchange reaction with the Cr_2N phase. This leads to the formation of AlN particles. At the beginning these are tiny, then they subsequently coalesce and migrate outwards through the interdiffusion layer. The vapour phase aluminium diffusion is in accordance with thermodynamical data.

At the layer/coated sintered steel interface, on the steel side, the cavity surfaces are covered by aluminium and chromium mixed films. In uncoated heat treated sintered steels, the chromium oxide films are present in all the volume.

The anodic behaviour of aluminium coated and heat treated (700 - 900°C) sintered steels is much better than that of the uncoated steels heat treated at the same temperatures.

The improvement can be attributed to the Cr_2N and Al reaction which makes passivation easier. With 1000°C heat treatment, a worsening is observed compared to the lower temperatures.

Riassunto

Il rivestimento di alluminio, depositato su un acciaio inossidabile austenitico AISI 316L sinterizzato, per effetto di un trattamento termico dà luogo alla formazione di una fascia di interdiffusione. L'alluminio diffonde oltre l'interfaccia fascia/acciaio, preferibilmente lungo le porosità interconnesse, penetrando nel sinterizzato per uno spessore di circa 80µm e dando luogo ad una reazione di scambio dell'azoto con la fase Cr_2N , che conduce alla formazione di particelle di AlN prima finissime, che successivamente coalescono e migrano verso l'esterno attraverso la fascia di interdiffusione. La diffusione dell'alluminio in fase vapore è compatibile con i dati termodinamici.

All'interfaccia fascia/sinterizzato rivestito, lato acciaio, le pareti delle cavità appaiono ricoperte da guaine di ossidi misti di alluminio e cromo. Nei sinterizzati non rivestiti, trattati termicamente, le guaine sono costituite da ossido di cromo, presenti in tutto il volume.

Il comportamento anodico dei sinterizzati alluminati e trattati tra 700 e 900°C è sensibilmente migliore di quello dell'acciaio non rivestito trattato alle stesse temperature.

Il miglioramento può essere attribuito alla reazione tra Cr_2N e Al, da cui deriva una più facile instaurazione dello stato passivo. Nel trattamento a 1000°C si osserva un peggioramento rispetto alle temperature inferiori.

INTRODUCTION

The sintered stainless steels market is in continual growth as the manufactured articles made from them, mainly cams, gears, small components for food industry machinery and filters, have good mechanical properties, moldability and a good external appearance [1].

The sintering process itself constitutes the critical phase in the production of these materials, since production success is strongly conditioned by parameters of temperature, time and sintering atmosphere [1, 2].

The atmospheres used, which contain nitrogen, favour the precipitation of chromium nitrides reducing the passivation properties of the austenitic stainless steels [3].

The considerable difficulty of these steels in forming, therefore, a continuous film of protective oxide [4], is closely linked not only to the presence of the interconnected porosity itself of the sintered steel, but also to the chromium depletion caused by the precipitation of Cr_2N , Cr_7C_3 nitrides and carbides, and by the formation of σ and χ phases at the grain boundary [5].

From what has been said, the need to limit the formation of these phases can be deduced.

Since the Cr_2N nitride has been the most studied by far [1, 3, 5, 6, 7], it seemed useful to focus our attention on the attempt to limit the negative effect of its presence.

Uçock et al.'s research [7], carried out on 316L sintered steel microalloyed with aluminium and subjected to a thermomechanical treatment, has allowed us to ascertain an improvement in the mechanical properties linked to the precipitation of tiny AlN particles.

Using this research as a starting point, the composition and structural modifications of sintered AISI 316L stainless steel were studied. This stainless steel was aluminium coated by metal spraying and heat treated to facilitate the formation of

an interdiffusion layer at the steel/coating interface and the aluminium diffusion inside the steel - this occurring within the prospect of using the aluminium differently since this element has a high affinity for nitrogen and the ability to form a stable nitride competing with Cr_2N , therefore allowing the chromium to free itself and be available to establish a more stable passive state.

This study does not consider a tendency that has recently manifested itself [8, 9], which is to "enrich" the sintered stainless steel with nitrogen, thus obtaining a notable improvement of its mechanical properties, as well as of its resistance to corrosion, as confirmation of the experimental data for this is unavailable in the works cited.

MATERIALS, EQUIPMENT AND HEAT TREATMENTS

The experiments were carried out on a sintered AISI 316L austenitic stainless steel produced by Hoganas and sintered in a continuous industrial oven at 1180°C using a dissociated ammonia atmosphere (25% N_2 , 75% H_2). The average composition of this steel, expressed in % at. is equal to: Cr = 17.2; Ni = 13.4; Mo = 1.1; Si = 1.5 and Fe for the remainder.

The steel was, therefore, coated with commercially pure aluminium deposited by means of a metal spraying process carried out using a type 9E Metco gun.

On both the uncoated and coated samples a preliminary heat treatment at 600°C for 24 h with oven cooling until room temperature and a second heat treatment at 700-800-900- 1000°C for 24 h with successive water quenching were carried out.

The examination of the coating was done using point analysis and mappings carried out on the Hitachi SEM 2500 electronic scanning microscope, X rays and anodic polarization curves.

The polarization curves, in which the potential is measured compared to the saturated mercurous chloride electrode, were carried out in H_2SO_4 1N solution with a scanning speed of 30 mV/min and repeated at least three times. The sample size is $\approx 1 \text{ cm}^2$.

The metallographic preparation of the samples was carried out with SiC paper until n° 1200 and with diamond pastes until $6 \mu\text{m}$; finally, the samples were electrochemically etched with H_2SO_4 .

EXPERIMENTAL RESULTS

An interdiffusion layer (fig. 1a) corresponding to a heat treatment at 800°C for 24 h is visible on the transversal sections of the coated steel; similar situations occur for the other heat

treatments. Fig. 1b shows the aluminium mapping where it is evident how the aluminium has completely diffused inside the layer.

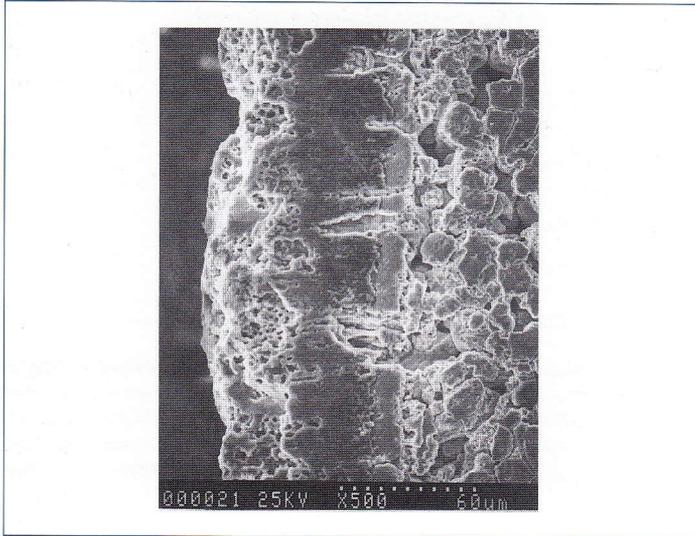


Figure 1a: SEM micrograph (X 500) of the transversal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 800°C for 24 h with water quenching

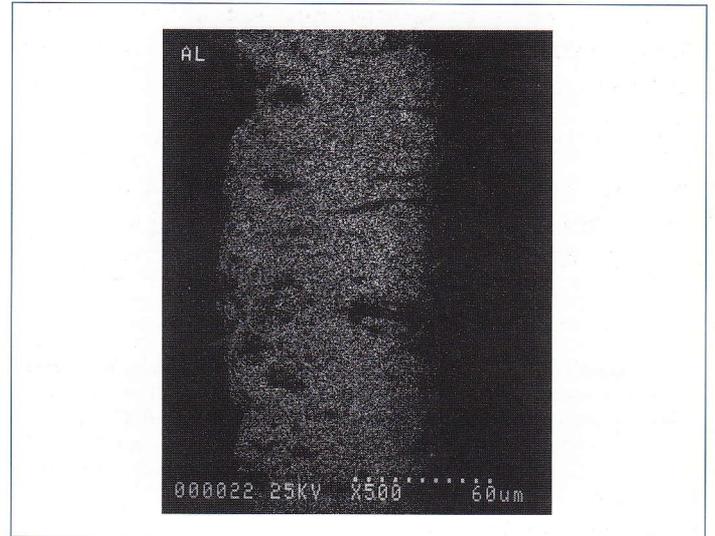


Figure 1b: SEM mapping (X 500) of the aluminium of the transversal section of a sample of aluminium coated sintered AISI 316 austenitic steel heat treated at 600°C for 24 h with oven cooling and at 800°C for 24 h with water quenching

Table 1 shows the average point analyses carried out inside the layer after heat treatment at 700-800-900-1000°C on the surface, in the intermediate area and at the interface with the steel. A heterogeneous structure, in which areas richer in aluminium and chromium compared to the matrix can be observed

TABLE 1 - Aluminium concentrations, % at

T (°C)	surface	intermediate area	interface
700	75	73	68
800	77	64	57
900	78	55	40
1000	81	40	40



Figure 2a: SEM micrograph (X 1000) of the longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24h with oven cooling and at 800°C for 24 h with water quenching. The micrograph refers to the interface of the interdiffusion/matrix area

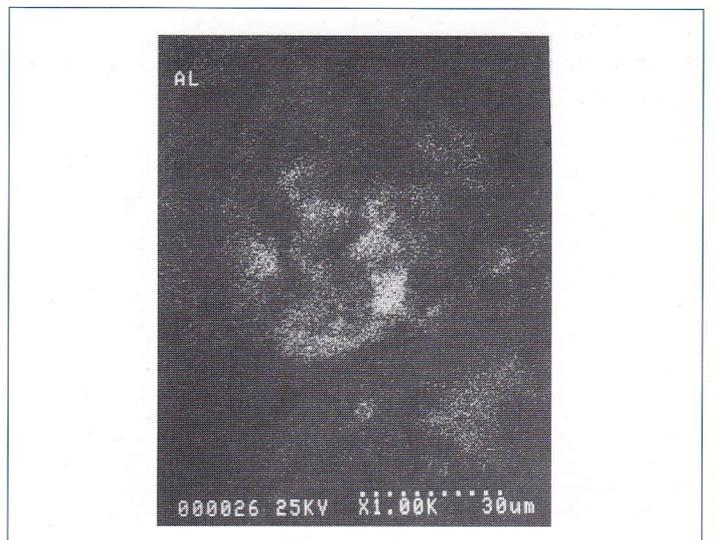


Figure 2b: SEM mapping (X 1000) of the aluminium on a longitudinal section of a sample of aluminium coated sintered AISI 316 austenitic steel heat treated at 600°C for 24h with oven cooling and at 800°C for 24 h with water quenching. The mapping refers to the interface of the interdiffusion/matrix area

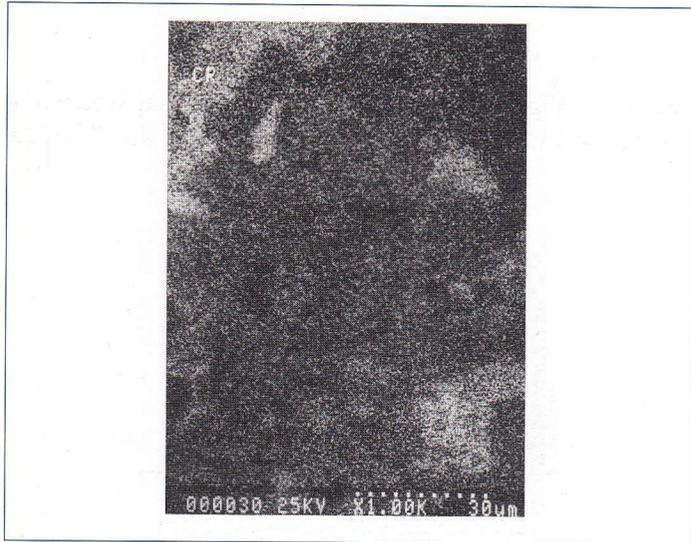


Figure 2c: SEM mapping (x 1000) of the chromium of a longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 800°C for 24 h with water quenching. The mapping refers to the interface of the interdiffusion/matrix area

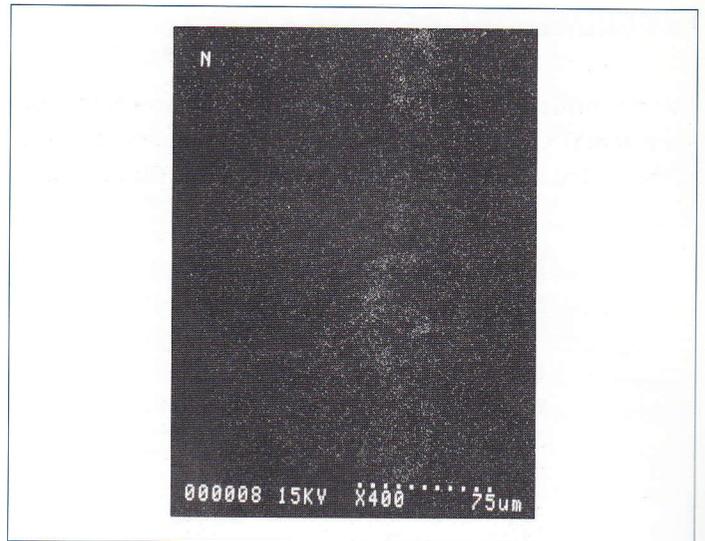


Figure 3: SEM mapping (X1000) of the nitrogen of a transversal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 1000°C for 24 h with water quenching. The micrograph refers to the interface of the interdiffusion/matrix area

(fig. 2a micrograph, figs. 2b & 2c mappings), appears at the layer/steel interface after the electrochemical removal of the layer. Fig. 3 shows the nitrogen mapping at the interface, on

the steel side, corresponding to a heat treatment at 1000°C; an analogous situation also occurs in the other conditions. Aluminium nitrides, more dense at the interface, were often

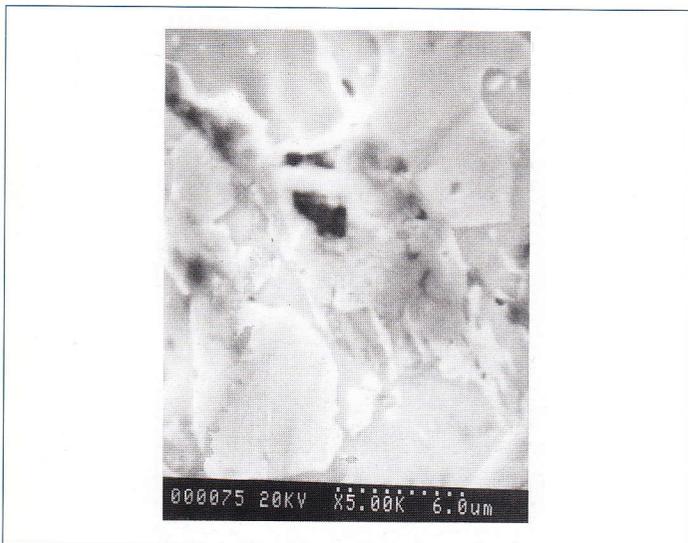


Figure 4a: SEM micrograph (X 5000) of the formation of an aluminium nitride at the interface of the interdiffusion/matrix zone of a longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching

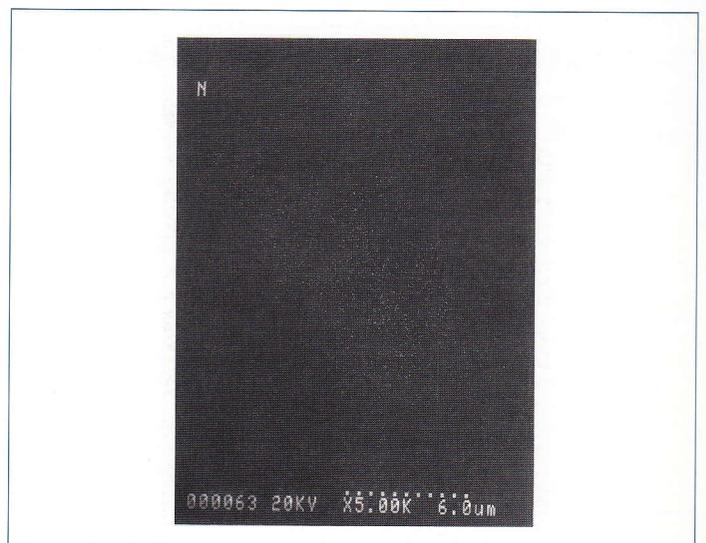


Figure 4b: SEM mapping (X 5000) of the nitrogen in the aluminium nitride at the interface of the interdiffusion/matrix area of a longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching

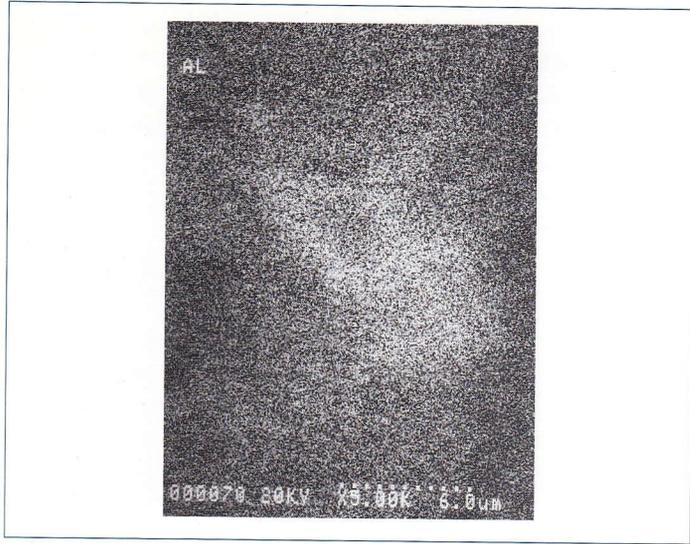


Figure 4c: SEM mapping (X 5000) of the aluminium in the aluminium nitride formation located at the interface of the interdiffusion/matrix area. The mapping refers to a longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching

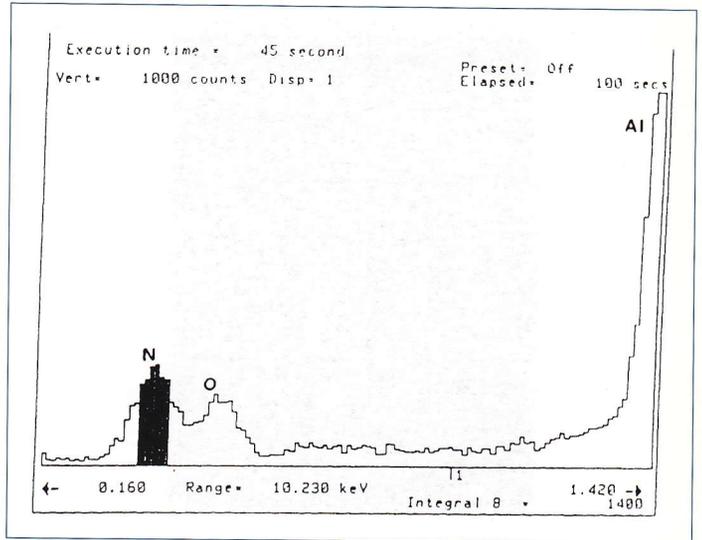


Figure 4d: SEM spectrogram of an aluminium nitride at the interface of the interdiffusion/matrix area of an aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching

identified in the same area. These are documented by the fig. 4a photo, figs. 4b & 4c mappings and by the fig. 4d spectrum, corresponding to 900°C.

The fig. 5 mapping, corresponding to the aluminium diffusion layer at 1000°C, highlights the aluminium rich areas, referable to the interconnected porosities in the steel layer

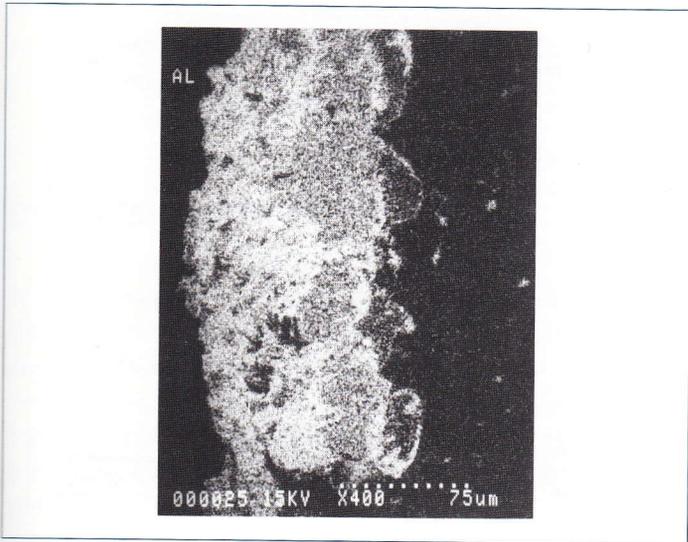


Figure 5: SEM mapping (x 400) of the aluminium of a transversal section of an aluminium coated sintered AISI 316L steel heat treated at 600°C for 24 h with oven cooling and at 1000°C for 24 h with water quenching

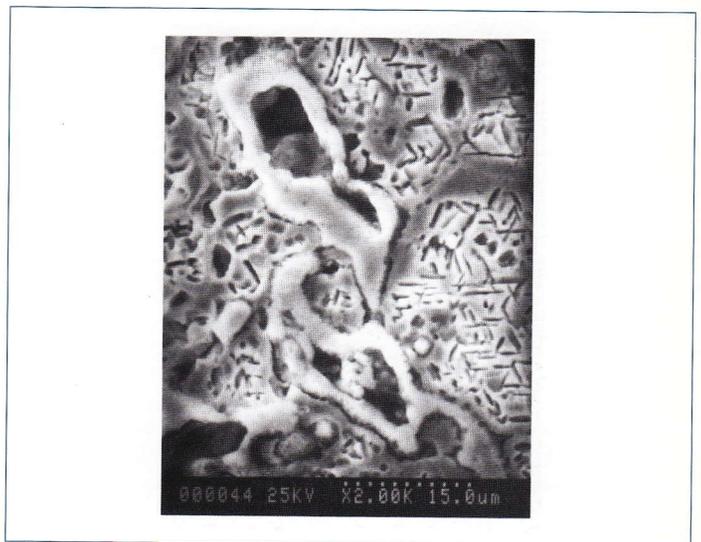


Figure 6a: SEM micrograph (x 2000) of the longitudinal section of a formation of chromium oxides for a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching



Figure 6b: SEM mapping (X 2000) of the chromium of the longitudinal section of a formation of chromium oxides for a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching



Figure 6c: SEM mapping (X 2000) of the oxygen of the longitudinal section of a formation of chromium oxides for a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 900°C for 24 h with water quenching

bordering the interface, which is approximately 80 μm thick. Fig.6a represents the porosity state after heat treatment of uncoated sintered steels. In them chromium oxide film for the temperatures of 800-900-1000°C can be noted, as shown

in the figs. 6b & 6c mappings.

In the same way, fig.7a refers to aluminium coated sintered steels whose porosities also appear coated by chromium oxide “films” as the fig. 7b spectrum and the mappings analo-

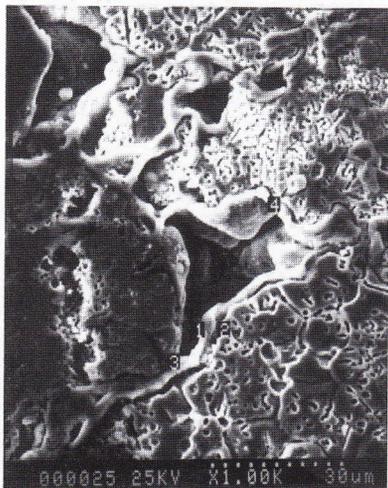


Figure 7a: SEM micrograph (X 1000) of the longitudinal section of an aluminium coated sintered AISI 316L austenitic heat treated steel showing the formation of chromium oxides

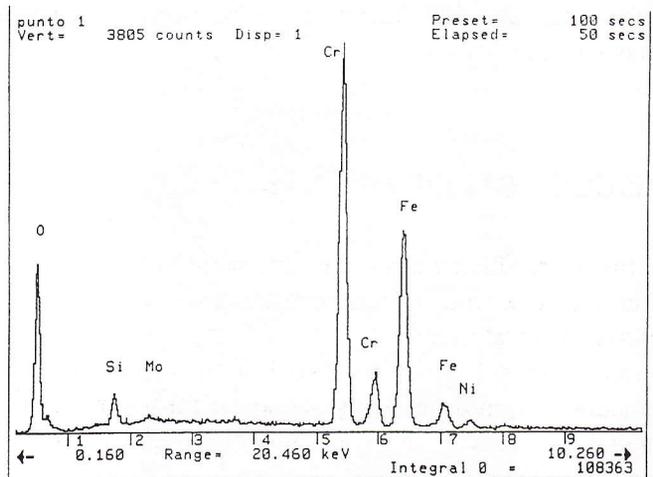


Figure 7b: SEM spectrogram showing the formation of chromium oxides

gous to the preceding ones show.

The diffraction pattern shown in fig.8 is of the surfaces included in the diffusion layer, obtained by successive electrochemical removals, after heat treatments, at 700-800-900-1000°C respec-

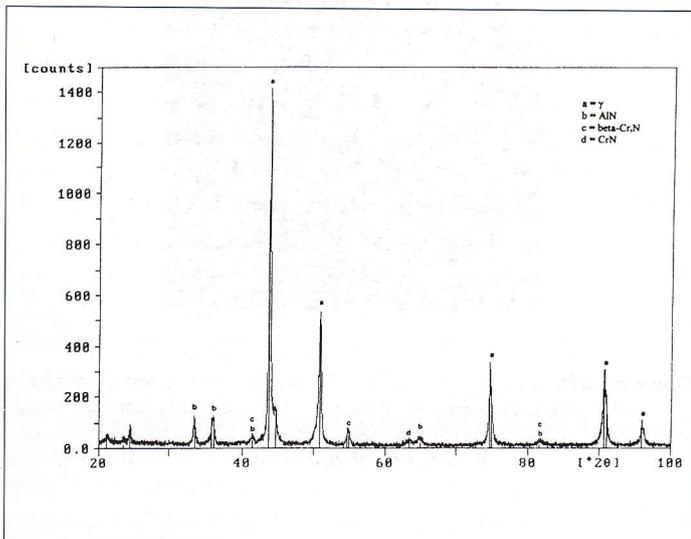


Figure 8: Diffraction pattern of the interface of the interdiffusion/matrix area of an aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C with oven cooling and 900°C with water quenching

steel heat treated in the same conditions as the coated sample. The curves which refer to the coated steel heat treated at 700-800-900°C are included in a band (oblique line) characterized by a passive current which is lower than that of the uncoated steel, as well as of those belonging to heat treated uncoated steels (dots). On the other hand, the curve referring to the coated steel heat treated at 1000°C is located inside the second band.

DISCUSSION OF RESULTS

In the interdiffusion layer, the concentration of aluminium decreases as we move from the external surface to the layer/sintered steel interface.

As shown in table 1, this decrease is more noticeable at high temperatures, most probably due to the formation of intermediate phases with a different composition at different temperatures [10, 11].

The interface is the place where the aluminium/nitrogen reaction takes place - a simple $Cr_2N + Al$ exchange reaction. In reality, the AlN formation in extremely small particles already takes place in the steel layer near the interface which is about ten micrometers thick, as shown by the nitrogen accumulation (fig. 3) and the presence of aluminium "flakes" in the porosities (fig. 5).

tively; aluminium and chromium nitrides are visible.

Fig. 9 shows the anodic polarization curves carried out after successive electrochemical removals of the diffusion layer, in a comparison with the uncoated steel behaviour and the

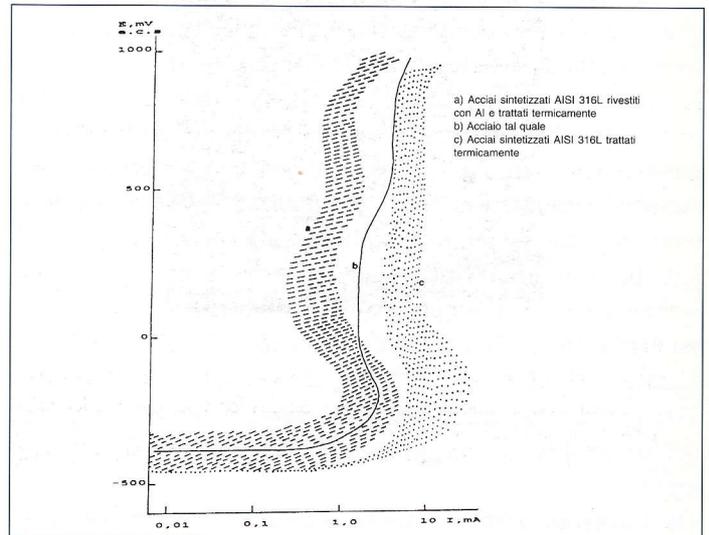


Figure 9: Anodic polarization curves of the sintered AISI 316L stainless steel in H_2SO_4 1N solution

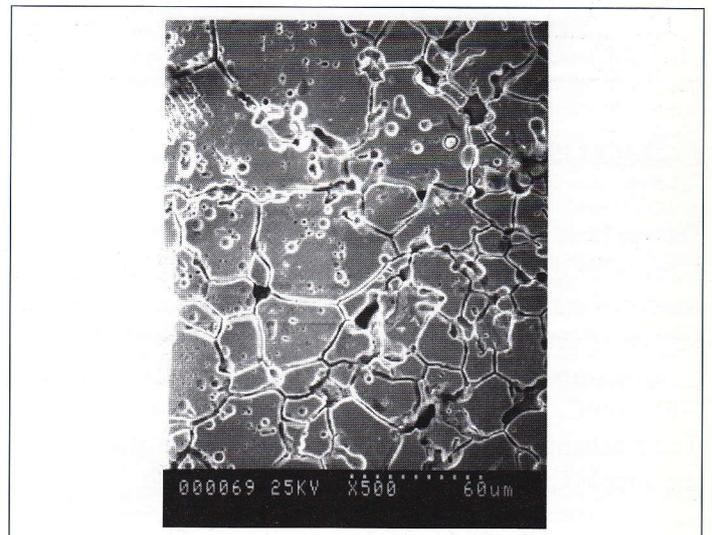


Figure 10: SEM micrograph (X 5000) of the longitudinal section of a sample of aluminium coated sintered AISI 316L austenitic steel heat treated at 600°C for 24 h with oven cooling and at 700°C for 24 h with water quenching

At steady state, the mechanism of the reaction would consist in the aluminium diffusion, activated by the concentration gradient between the layer and the underlying steel, mostly along the interconnected porosities, in the reaction to the interface, in the nitride precipitation in an extremely small form. At the layer/sintered steel interface, bigger azide particles, (figs. 4a, 4b, 4c) deriving from the coalescence of the extremely small particles, can often be observed.

In the same way that Šalák [12] hypothesized for the mechanism with which manganese acts in protecting sintered manganese steels from oxidation, and according to whom, presumably sublimation of the manganese and its reaction to oxygen occur, it can be thought that also in the system studied, the aluminium can spread and react at the vapour state, seeing that the vapour pressure of this element is from 1000 (at 700°C) to 100 (at 1000°C) times lower than that of manganese.

The author cited judges the phenomenon, which in our case occurs weakly in very prolonged heat treatments, to be "intense".

The formation of mixed aluminium and chromium oxides can also be observed at the interface, as shown by the fig. 2a micrograph and figs. 2b & 2c mappings. The reaction proceeds on the internal surface of the pores, coating them. On the basis of this assumption, the aluminium and the chromium, by oxidizing, partially occlude the porosities. Such occlusions have an average composition equal to (% at.): Al = 10 and Cr = 22.

CONCLUSIONS

Due to heat treatments, the formation of an interdiffusion layer with different structures below and above 950°C is observed at the sintered Al/AISI316L interface. This diversity is reflected in a different anodic behaviour at different temperatures compared to uncoated steels: better at 700÷900°C, worse at 1000°C.

The mechanism of this phenomenon has been attributed to the simple $\text{Cr}_2\text{N} + \text{Al}$ exchange reaction which, by freeing

The formation of mixed oxides, observed at 800-900-1000°C, is absent at 700°C (fig. 10).

In sintered steels, manufactured in atmospheres containing nitrogen, Cr_2N particles can be observed; for this reason, as has been said, they are passivated with more difficulty.

The formation of aluminium nitrides, evident at 700-800-900°C (figs. 4a, 4b, 4c), competing with the formation of chromium nitrides, frees some chromium and allows an easier establishment of the passive state. This is confirmed by the pattern of the anodic polarization curves referring to the diffusion layer, which present a lower passivation current compared to those of the corresponding steels heat treated at 700-800-900°C (fig. 9) but which are not aluminium coated.

While the passivation currents for the latter are comprised between 3 and 10 mA, for the coated sintered steels they decrease to values of 200÷300µA, not unlike those for alloyed sintered steels [14].

The behaviour at 1000°C is different from that at lower temperatures. While in cast steels, due to a heat treatment at this temperature, an improvement can be observed in the anodic behaviour due to the complete solubilization of the chromium carbide, which only started for the azide [7], a worsening of the anodic behaviour can be observed in the sintered steel. It was not considered appropriate to investigate the causes of this phenomenon, but certainly the nature of the interdiffusion layer which is modified in composition, structure and continuity, in the passage from 950 to 1000°C, is involved.

the chromium, facilitates the establishment of the passive state. The reaction is activated at the layer/steel interface, on the steel side, thanks to the aluminium penetration at the vapour phase, above all, by means of the interconnecting porosities in a layer which is about ten micrometers thick. From here, extremely small AlN particles migrate, in the opposite direction to that of the aluminium diffusion and they increase in size.

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