Production of aluminium coated ferritic stainless steel by co-rolling and annealing

D. Pilone, F. Felli, U. Bernabai

Ferritic stainless steel enriched with aluminium (>7%) represents the best material for the production of substrates in catalytic converters because of its good corrosion resistance at high temperature (700-1000 °C). Enriching steel surface with aluminium avoids brittleness problems related to the traditional metallurgical process and, due to the high superficial aluminium concentration, enhances the Al_2O_3 scale formation in the early stages of the oxidation process. Among several techniques, the co-rolling process appears to be a promising technology for enriching ferritic stainless steel surface with aluminium. That versatile technology produces, at room temperature, a very adherent aluminium coating without affecting the structural and mechanical properties of the substrate. In this work annealed AISI 430 ferritic stainless steel has been cold rolled together with aluminium foil to form an Al-steel-Al sandwich. The aim of the work was to enhance the oxidation resistance through a controlled oxidation of a thin aluminium layer. The diffusion bonding obtained via an annealing treatment was evaluated studying the concentration profiles as a function of process temperature. Intermetallics and /or solid solutions formed were characterized by X-Ray Diffraction (XRD).

Key words: Alumina coating, co-rolling, iron aluminides, solid state diffusion, catalytic converter

INTRODUCTION

Ferritic stainless steel enriched with aluminium (>7%) represents a promising material for the production of substrates in catalytic converters because of its good corrosion resistance at high temperature (700-1000 °C) and because of the absence of nickel, which is responsible for localized corrosion in sulfidizing environments.

Iron aluminides have been of great interest for many years because of their excellent oxidation and sulfidation resistance, as well as because of their reduced density. Despite that, their use as a structural material has been limited by limited room temperature ductility and a drop in strength at temperature higher than 600 °C [1]. Formation of iron aluminides includes ingot solidification followed by thermomechanical treatment, but over the past 15 years many attempts have been done to form iron aluminides by solid state methods such as hot pressing [2], mechanical alloying [3] or in-situ synthesis for surface coating on conventional metallic materials [4]. One promising method is the formation of aluminides by heat treatment of co-rolled foils [5]. This method has been used over the past few years to produce Al-Ni intermetallics by cold rolling and annealing of Al/Ni alternate foils [6,7]: a reaction in the solid state is promoted by milling together alternate foils of the elements and by low temperature annealing (T<250°C) of rolled composites.

Among several techniques such as hot dipping, pack cementation, electroplating, physical vapour deposition, the co-rolling process appears to be a promising technology for enriching ferritic stainless steel surface with aluminium. That versatile technology produces, at room temperature, a very adherent aluminium coating without affecting the structural and mechanical properties of the substrate. Despite those advantages, avoiding the formation of Fe-Al intermetallics during the sandwich heat treatment can represent a big challenge setting up the process.

Steel surface enrichment with aluminium not only avoids brittleness problem but, due to the high superficial aluminium concentration, enhances the Al_2O_3 scale formation in the early stages of the oxidation process. In fact the high temperature oxidation resistance of Fe-Cr-Al ferritic stainless steels is due to the formation of a continuous alumina layer, which usually spalls during thermal cycling, although the addition of active elements such as Mo, Cu, Zr, Y, Hf and rare earths (R.E.) could improve the oxide layer adherence.

In three previous works [8,9,10] co-rolled and electroplated Al-steel-Al sandwiches, 50 µm thick, have been heat treated over the 300-900 °C temperature range. Al, Fe and Cr concentration profiles as well as microhardness profiles have been determined in order to investigate the relationship between heat treatment conditions and formation of possible intermetallic compounds. The obtained results highlighted that over the temperature range 300-450 °C interdiffusion does not occur, while at 450-750 °C intermetallic phases formation is detected. When the treatment temperature is higher than 750 °C a solid solution is predominantly formed.

In this work annealed AISI 430 ferritic stainless steel has been cold rolled together with aluminium foil to form an Al-steel-Al sandwich. The aim of the work was to enhance the oxidation resistance through a controlled oxidation.

The intermetallics and /or solid solutions formed were characterized by X-Ray Diffraction (XRD) and the oxide morphology, as a function of temperature treatment, was studied by using SEM imaging.

EXPERIMENTAL

Foils of annealed ferritic (17% Cr) stainless steels sheets, 50 µm in thickness, and raffinal aluminium, 15 µm in thickness, were used to produce co-rolled foils. Those foils were

D. Pilone, F. Felli, U. Bernabai
Dip. ICMMPM – Università degli Studi di Roma "La Sapienza", Roma, Italy.

Paper presented at the 2nd International Conference
HEAT TREATMENT AND SURFACE ENGINEERING IN AUTOMOTIVE APPLICATIONS,
organised by AIM, Riva del Garda, 20-22 June 2005

degreased using ultrasonic cleaning. Steel foil was also mechanically brushed in order to activate the metallic surface. Al and steel sheets, having a surface area equal to 25x90 mm, were superimposed in order to obtain an Al-steel-Al sandwich 80 µm thick. The assemblies were cold-rolled in air to reach a final thickness of 50 µm. After co-rolling the assemblies were thermally treated: 1) at 600°C for 12 hours, 2) at 600°C for 12 hours and at 900°C for 40 minutes, 3) at 900°C for 40 minutes.

Polished cross sections of specimens both after reaching the final thickness and after heat treatment were imaged by SEM, while EDS analyses were carried out in order to obtain Al concentration profiles close to Al-steel interface. Small parts of the assembly were sampled and analysed, using X-ray diffraction (XRD), to identify different phases formed as a consequence of heat treatments.

Thermal cycling tests were performed on specimens pretreated at 600 °C for 12 hours. The chosen thermal cycle was: 15 minutes either at 700°C or 800°C or 900°C, 5 minutes at room temperature.

SEM imaging was used to evaluate oxide compactness and morphology after heat treatment as well as after thermal cycling.

RESULTS AND DISCUSSIONS

Al-steel-Al assemblies co-rolling produced, after few rolling passes, a good adherence among layers: initial thickness of different layers and number of rolling passes were determined with great care in order to avoid specimen embrittlement due to cold working as well as cracks formation.

After reaching the desired final thickness a SEM analysis of the specimen cross section revealed that each Al layer was about 10 µm thick. Since the rolling process produced only a cold welding of different layers, heat treatments were performed with the objective of promoting both Al, Fe and Cr diffusion and growth of an oxide protective layer.

1. Isothermal tests

On the basis of previous results [8,9] the sample was held isothermally at 600 °C for 12 hours to activate diffusion and solid state reactions. XRD patterns revealed the presence in the annealed sample of Al-rich intermetallic compounds such as $FeAl_2$ and $FeAl_5$ (Fig. 1a) together with metallic Al and alumina. SEM micrograph of the specimen cross section highlighted that the alumina layer, which appears compact and well adherent to the substrate, has a thickness of about 5 µm (Fig. 2). If a specimen pre-treated in that way is kept for 40 minutes at 900 °C, the alloy phases revealed by XRD are completely different (Figure 1b) from the previous ones. High temperature treatment, favouring both Al diffusion toward the specimen centre and $Al \rightarrow Al_2O_3$ conversion, decreases Al concentration in the outer zone. As suggested by Al-Fe phase diagram, by lowering Al concentration in the alloy, $\alpha 2$ phase formation is favoured although a small quantity of Fe_2Al_5 is still present together with aluminium oxide. If the co-rolled assembly is treated at 900 °C without a preoxidation stage, the phases detected by means of XRD are alumina, Cr_3O and a ternary Al-Fe-Cr intermetallic compound (Fig. 1c). In fact at high temperature chromium easily diffuses through the scale and reacts with oxygen, moreover when Cr concentration increases in the outer zone, it forms intermetallic compounds with Al and Fe.

Treatment temperatures have to be carefully chosen so that aluminium concentration in the ferritic steel reaches 10-14% by weight avoiding the formation of intermetallic compounds, which would determine material embrittlement. Considering that the treatment temperature affects not only the base material structure, but also the oxide growth, determining treatment parameters is the key issue in the process set up. SEM imaging was used to study oxide layer morphology. As it can be observed in Figure 3a, after keeping the specimen at 600 °C for 12 h, the oxide appears to be porous and characterized by ripples and globular morphology. If that specimen is treated at 900 for 40 minutes the nuclei previously formed grow with consequent porosity increase (Fig. 3b). If the cold rolled specimen is treated at 900 °C for 40 minutes, without a pre-oxidation treatment, the oxide morphology is completely different: a naked eye observation reveals the presence of a thin and glassy alumina layer,

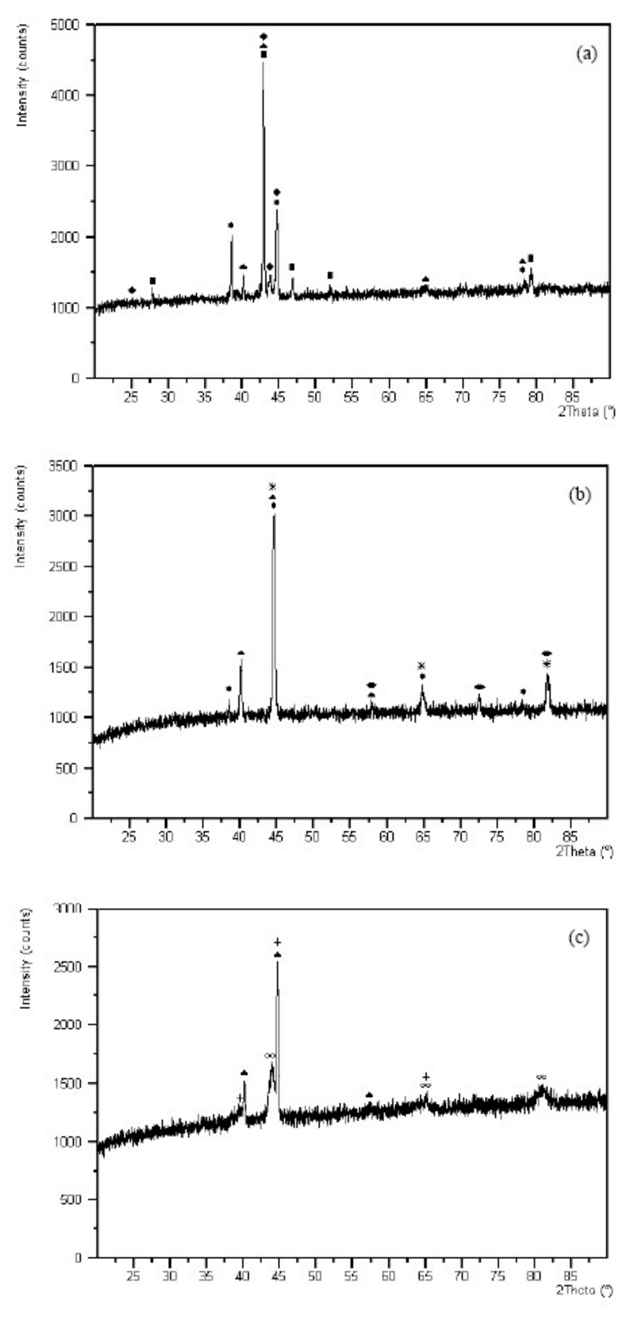

Fig. 1 – X-Ray diffractograms of samples after co-rolling and heat treatment. Key: (a) 12 h at 600 °C, (b) 12 h at 600 °C + 40 min at 900 °C, (c) 40 min at 900 °C. ■ *Al_5Fe_2 orth.,* ◆ *FeAl2,* ✱ *Al,* ▲ *Al_2O_3,,* ✲ *FeAl,* ● *Fe_2Al_5 mon.,* † *Cr3O,* ∞ *$Al_{0.99}Cr_{0.02}Fe_{0.99}$.*

Fig. 1 – Analisi XRD di campioni sottoposti a colaminazione e trattamento termico. (a) 12 ore a 600 °C, (b) 12 ore a 600 °C + 40 minuti a 900 °C, (c) 40 minuti at 900 °C. ■ *Al_5Fe_2 orth.,* ◆ *FeAl2,* ✱ *Al,* ▲ *Al_2O_3,,* ✲ *FeAl,* ● *Fe_2Al_5 mon.,* † *Cr3O,* ∞ *$Al_{0.99}Cr_{0.02}Fe_{0.99}$.*

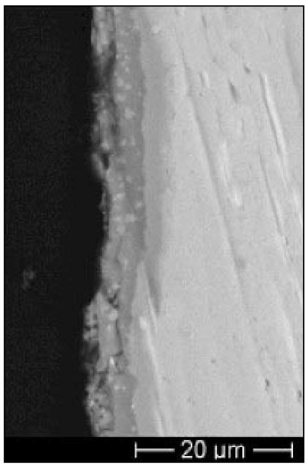

Fig. 2 – SEM micrograph of the specimen cross section after heat treatment at 600 °C for 12 hours,

Fig. 2 – Micrografia SEM della sezione del co-laminato dopo trattamento termico a 600 °C per 12 ore.

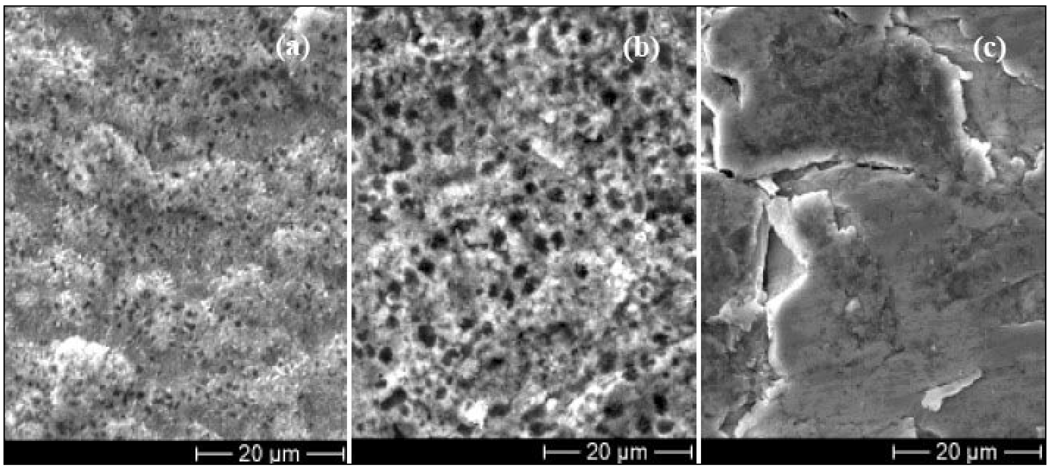

Fig. 3 - SEM micrographs showing the samples surface morphologies after co-rolling and different heat treatments: (a) 12 h at 600°C, (b) 12 h at 600°C + 40 min at 900°C, (c) 40 min at 900°C.

Fig. 3 – Micrografie SEM in cui è mostrata la morfologia superficiale dei campioni dopo co-laminazione e differenti trattamenti termici: (a) 12 ore a 600°C, (b) 12 ore a 600°C + 40 minuti a 900°C, (c) 40 minuti a 900°C.

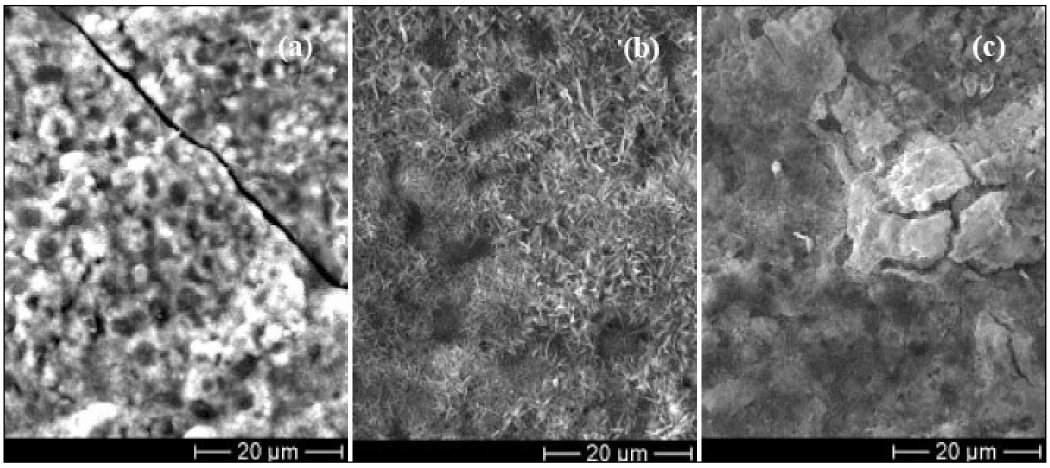

Fig. 5 – SEM micrographs showing the samples surface morphologies after co-rolling, annealing at 600°C for 12 hours and thermal cycling at: (a) 700 °C, (b) 800 °C, (c) 900°C.

Fig. 5 – Micrografie SEM in cui è mostrata la morfologia superficiale dei campioni dopo colaminazione, ricottura a 600°C per 12 ore e ciclaggio termico a: (a) 700 °C, (b) 800 °C, (c) 900°C.

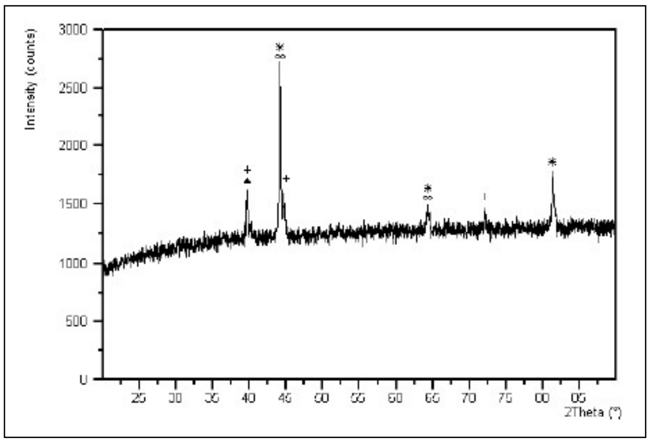

Fig. 4 – X-Ray diffractograms of samples after co-rolling, heat treatment at 600°C for 12 h and 1000 thermal cycles at 700 °C. ▲ Al_2O_3, ✻ $FeAl$, + Cr_3O, ∞ $Al_{0.99}Cr_{0.02}Fe_{0.99}$.

Fig. 4 – Analisi XRD di un campione co-laminato dopo trattamento termico a 600 °C per 12 ore e dopo 1000 cicli in un test di ciclaggio termico a 700 °C. ▲ Al_2O_3, ✻ $FeAl$, + Cr_3O, ∞ $Al_{0.99}Cr_{0.02}Fe_{0.99}$.

which makes the surface really shiny. Figure 3c shows a SEM micrograph of the specimen surface highlighting the formation of a compact oxide layer with evident cracks due to internal stresses arising from metal-oxide transformation. That oxide morphology is not desirable since a tiny and porous structure is essential to produce both a higher catalyst effectiveness and a greater oxide adherence due to reduced internal compressive stresses.

2. Thermal cycling tests

During their life, catalytic converters are subjected to cyclic thermal variations, which are critical since they can produce scale spallation reducing the converter life. The specimens previously isothermally treated at 600 °C for 12 hours, were subjected to thermal cycling tests at 700 °C, 800 °C and 900 °C. As expected the tendency to scale formation increases with increasing testing temperature.

2.1 Thermal cycling at 700 °C

XRD analysis of the sample after 1000 thermal cycles at 700 °C shows that, as interdiffusion proceeds with time, Al-rich intermetallics disappear, while $\alpha 2$ phase is formed (Fig. 4). As far as oxide morphology is concerned, thermal cycling at 700 °C modifies the oxide layer obtained during pre-oxidation forming a more compact scale. That scale has lower internal compressive stresses and then it is more susceptible of deep cracking (Fig. 5a). Chromium oxide found after thermal cycling was probably formed in those areas where the alumina layer cracked, allowing the reaction between chromium and oxygen.

2.2. Thermal cycling at 800 °C

Thermal cycling at 800 °C determines the growth, on the oxide formed during the pre-oxidation stage, of a high number of alumina nuclei that appear acicular in shape (Fig. 5b). XRD analyses show that the phases in the scale are the same that were found in the sample after thermal cycling at 700 °C. In this case, because of acicular growth, the compressive stresses are still present in the oxide layer, so favouring the resistance to scale cracking.

2.3. Thermal cycling at 900 °C

Thermal cycling at 900 °C produces a rapid oxide growth and the formed scale appears quite compact. As it can be observed in Figure 5c the scale, which probably still has internal compressive stresses, cracks only on the top of the ripples because of oxide lateral growth.

XRD patterns revealed that thermal cycling at 900 °C determines the formation, in addition to alumina, of a considerable amount of chromium oxides, more rich in oxygen in comparison with the one found after thermal cycling at 800 °C. As a consequence of high temperature treatment, which promotes aluminium diffusion toward the specimen centre as well as aluminium oxidation, a Cr-Fe intermetallic is formed.

CONCLUSIONS

Annealed AISI 430 ferritic stainless steel has been cold rolled together with aluminium foil to form an Al-steel-Al sandwich in order to obtain a mechanical bonding among the three layers. After co-rolling the assembly was thermally treated with the dual objective of producing diffusion bonding between Al and steel and of obtaining the growth of a porous and adherent oxide layer. Isothermal tests highlighted that alumina films formed at 600 °C have a considerable degree of porosity, while alumina films formed at 900 °C appear thin and glassy. On the basis of those results a preoxidation stage at 600 °C appears essential to obtain a porous oxide coating allowing for relaxation of thermal and growth stresses. Under thermal cycling conditions the oxide layer cracks at 700 °C, while it performs much better at 800 °C since that temperature treatment produces the growth of a tiny acicular structure, which avoids coating spallation. Thermal cycling at 900 °C produces a scale consisting of mixed oxides containing mostly Al and Cr: its morphology, characterised by ripples, is beneficial for thermal stresses compensation and assures good adherence between coating and substrate even at high temperature.

ACKNOWLEDGEMENTS

The authors thank CSM for the financial support.

REFERENCES

[1] C.G. MCKAMEY, J.H. DE VAN et al., J. Mater. Res. 6, (1991), p.1779.

[2] B.H. RABIN and R.N. WRIGHT, Metallurgical transaction A 22, (1991), p.277.

[3] G.H. FAIR and J.V. WOOD, Journal of Materials Science 29, p.1935.

[4] J. DUSZCZYK, J. ZHOU et al., Journal of Materials Science 34, (1999), p. 3937.

[5] J.R. BLACKFORD, R.A. BUCKLEY et al., Scripta Materialia 34, (1996), p. 721.

[6] L.BATTEZZATI, P. PAPPALEPORE et al., Acta Materialia 47, (1999), p. 1901.

[7] L. BATTEZZATI, C. ANTONIONE et al. 3, (1995), p. 67.

[8] G.A. CAPUANO, A. DANG et al., Oxidation of Metals 39, (1993), 263.

[9] U. BERNABAI, A. BROTZU et al., Proc. 4th ASM Heat Treatment and Surface Engineering Conference in Europe, Florence (1998), AIM, p. 383.

[10] U. BERNABAI and F. FELLI, Proc. Materiali: Ricerca e Prospettive tecnologiche alle soglie del 2000, Milano (1997), FAST, p. 1129.

ABSTRACT

COLAMINATI IN FOGLIO SOTTILE ACCIAIO INOX FERRITICO-ALLUMINIO

Parole chiave: acciaio inox, ossidazione, laminazione, diffrattometria, microscopia elettrica

Un acciaio inossidabile ferritico contenente più del 7% di alluminio rappresenta il materiale più idoneo per la produzione di substrati per marmitte catalitiche in virtù della buona resistenza alla corrosione alle alte temperature (700-1000°C). Un arricchimento superficiale con alluminio della superficie dell'acciaio tipo AISI 430 permette di evitare i problemi di infragilimento correlati con il processo metallurgico tradizionale e favorisce la formazione dello strato superficiale di Al_2O_3 nei primi stadi del processo di ossidazione. Tra le varie possibili tecniche di arricchimento superficiale dell'acciaio con alluminio la co-laminazione appare la più promettente.

Nel presente lavoro colaminati in foglio sottile sono stati prodotti a partire da fogli di acciaio inossidabile ferritico, spessi 50 μm, e da fogli di alluminio raffinal aventi uno spessore di 15 μm. Tali fogli sono stati colaminati allo scopo di ottenere un sandwich Al-acciaio-Al avente uno spessore finale pari a 50 μm. Il colaminato è stato trattato isotermicamente 1) a 600 °C per 12 ore; 2) a 600 °C per 12 ore e a 900 °C per 40 minuti; 3) a 900 °C per 40 minuti. Analisi XRD hanno rivelato (Fig.1a) la formazione, per effetto della diffusione e di reazioni allo stato solido, di intermetallici ricchi in alluminio quali $FeAl_2$ e Fe_2Al_5 dopo il solo trattamento a 600 °C. Il trattamento a 900 °C del campione già trattato a 600 °C determina non solo la conversione Al → Al_2O_3 ma anche la diffusione dell'alluminio verso il centro del campione: come suggerito dal diagramma di stato Al-Fe, al diminuire della concentrazione dell'alluminio nella lega, si favorisce la formazione della fase $\alpha 2$ (Fig.1b). Se il colaminato è trattato esclusivamente a 900 °C le analisi XRD rivelano la presenza di ossido di cromo e di un composto intermetallico ternario Al-Fe-Cr (Fig.1c).

Le temperature di trattamento devono essere scelte attentamente in modo che la concentrazione dell'alluminio nell'acciaio raggiunga il 10-14% in peso evitando la formazione di intermetallici fragili. Poiché la temperatura di trattamento influenza non solo la struttura della lega, ma anche la morfologia dello strato di ossido, che dovrà fungere da supporto per il catalizzatore, la determinazione dei parametri di processo è il punto chiave nella messa a punto del trattamento. Dopo il trattamento a 600 °C per 12 ore l'ossido appare poroso e caratterizzato da una crescita globulare (Fig.3a); se il provino pre-ossidato è trattato a 900°C per 40 minuti i nuclei precedentemente formati si accrescono e la porosità dell'ossido aumenta (Fig.3b). Se il colaminato è trattato a 900 °C, senza pre-ossidazione, si forma uno strato di ossido sottile e vetroso caratterizzato da profonde cricche (Fig.3c) causate da sollecitazioni interne conseguenti alla trasformazione metallo-ossido.

Poiché durante l'esercizio i convertitori catalitici sono soggetti a variazioni cicliche di temperatura, che possono produrre un distacco della scaglia di ossido, campioni colaminati, pre-ossidati a 600 °C, sono stati sottoposti a prove di ciclaggio termico a 700, 800 e 900 °C. Dopo 1000 cicli a 700 °C la scaglia di ossido appare più compatta e fratturata rispetto a quella ottenuta dopo la pre-ossidazione (Fig. 5a), mentre dopo 1000 cicli a 800 °C la scaglia di ossido è caratterizzata da un numero molto elevato di nuclei accresciutisi con morfologia aciculare (Fig.5b).

Prove di ciclaggio termico a 900 °C hanno determinato la formazione di una scaglia costituita prevalentemente da ossidi di alluminio e cromo: la morfologia di tale scaglia, caratterizzata da protuberanze (Fig. 5c), appare favorevole per la compensazione degli stress termici ed assicura una buona aderenza tra substrato e rivestimento anche alle alte temperature.