Journal of Alloys and Compounds, 211/212 (1994) 619–624
JALCOM 150

N ageing in aluminized steel sheet: an industrial application of high frequency internal friction measurements to point defect–interface interactions

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Abstract

Aluminized sheet, obtained by a continuous hot-dipping process applied to steel sheet, is widely used because of its favourable high temperature corrosion resistance combined with a high reflectivity and a good formability. It has been known for some time that cold-rolled Al-clad sheet, containing a controlled amount of interstitial nitrogen before cladding, is resistant to the formation of brittle Fe–Al intermetallics. These intermetallics give the material a poor high temperature performance. The aim of the present research was to apply a similar method to improve the high-temperature resistance of continuously aluminized sheet. The mechanism responsible for the better performance was studied by means of internal friction measurements and secondary-ion mass spectroscopy depth profiling. The results strongly suggest that a thin AlN diffusion barrier is formed at the coating–substrate interface.

1. Introduction

Aluminized sheet successfully combines the surface properties of an aluminium–silicon alloy coating with the mechanical properties of the steel substrate. It has a high reflectivity and high electrical and thermal conductivity, which makes it a chosen material for specific applications in automobile manufacturing, the appliances industry and, to a lesser extent, the building industry. The main application for the material is in automotive exhaust systems (centre pipe, muffler and tail pipes).

There are two main technologies to produce aluminized steel sheet. In the Al cladding route a thin Al foil is welded onto the substrate by roll bonding [1]. The Al-clad material is annealed after cold rolling. This results in the degradation of the properties if no special precautions are taken to avoid Fe–Al alloy formation during the annealing procedure. Bahadur *et al.* [2] have recently reviewed the details of the Fe–Al alloy formation and reported that the compound most commonly found was Fe_2Al_5. The formation of this brittle Fe_2Al_5 phase is particularly detrimental to most of the interesting properties of the material. This aluminide is porous and has poor adhesion to the substrate. An Al–Si alloy is therefore used instead of pure Al in order to avoid the thick alloy layer that forms under normal annealing conditions. The silicon is incorporated in the Fe–Al alloy during annealing and slows its growth. Another precaution is the use of substrates of ingot-cast unkilled steel grades [3,4]. These grades are characterized by a high concentration of interstitial N. Their N/Al atomic ratio can be as high as 5, with N contents between 50 and 100 p.p.m. Al-clad steel sheet is a material that ages and its mechanical properties and formability are therefore expected to be time dependent [5].

The alternative route for the manufacture of aluminized sheet is the continuous hot dipping of steel sheet [6]. In this case the substrate is aluminized by hot dipping the steel strip in a molten Al–10%Si alloy bath after continuous annealing of the strip in the same coating line. The substrates used are continuously cast Al-killed low carbon or "interstitial-free" steel grades. The N/Al atomic ratio of the low carbon steel grades is typically 0.2 or less, with N contents in the range 20–60 p.p.m. Usually these low carbon grades are processed so as to contain no N or C interstitials.

0925-8388/94/$07.00
SSDI 0925-8388(94)00150-B

However, a certain concentration of interstitial N can be achieved by careful selection of the substrate chemistry and processing parameters. The interstitial N guarantees that the Fe_2Al_5 phase formation during the high temperature use of the manufactured part will be impeded.

The purpose of the present paper was to show that a considerable improvement in material performance could be achieved on industrially produced commercial grades of hot-dipped aluminized sheet. the microstructural process that causes the suppression of the Fe_2Al_5 phase formation was identified. The results suggest that if sufficient interstitial N is present a continuous AlN diffusion barrier can be formed at the substrate–coating interface.

2. Experimental details

The materials used in the present work were all industrially produced in the Galvalange continuous hot-dipping aluminizing line [7]. The starting material was cold-rolled full-hard low carbon steel that was recrystallized in a reducing atmosphere during the soaking cycle before being coated by immersion in a liquid Al–Si alloy. Figure 1 shows the coating structure of aluminized steel sheet. Even though Si is added to slow the formation of Al–Fe intermetallics, a continuous

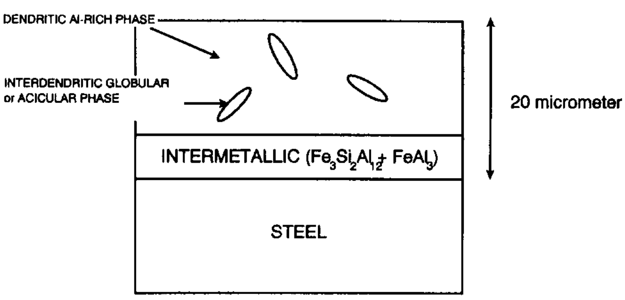


Fig. 1. Schematic cross-sectional view of the coating structure of a continuously hot-dipped aluminized steel sheet. The coating weight varies between 80 and 150 g^f m^{-2} (both faces coated). The coating thickness is around 20 μm for a typical coating weight of 120 g^f m^{-2}.

Fe–Al–Si compound is usually present between the substrate and coating layer. Table 1 reviews the chemical composition of the substrates that were used. Materials 1–5 are low carbon steels and material 6 is an "interstitial-free" titanium steel obtained by means of vacuum degassing and Ti additions.

The N ageing was studied by means of internal friction measurements carried out on an automated 40 kHz composite oscillator [8]. A schematic of the resonator assembly is shown in Fig. 2. It consists of a drive quartz crystal, which acts as longitudinal vibration source, cemented to a gauge quartz crystal, which monitors the vibration, and the specimen. A fused quartz rod, not shown in the drawing, is used to isolate the heated specimen from the quartz crystal. An input voltage V_d is applied across the gold-plated sides of the drive crystal and the output voltage V_g is taken from the gauge crystal. The mechanical damping Q^{-1} of the assembly is related to the ratio of V_d to V_g. The sample temperature is measured via a thermocouple inserted in a dummy specimen identical to the specimen tested. A typical experimental internal friction *vs.* temperature data plot is shown in Fig. 3. The internal friction peak near 450 K can be deconvoluted into an exponential tail of a Snoek–Köster cold-work peak at higher temperatures and the two overlapping single-relaxation-time Debeye peaks for interstitial N and C in b.c.c. Fe. A In τ–$1/T$ analysis of the internal friction data was also carried out to test for the presence of two components in the observed internal friction peak at 450 K. An example (Fig. 4) shows a typical dispersion of the relaxation constant located between the In τ–$1/T$ plots for high purity Fe doped with C or N based on recent data obtained by Weller [9]. The τ values are close to the τ value for N at low temperatures. At higher temperatures the τ value shifts towards the τ value for C.

3. Results

The different materials were compared by performing annealing experiments at 450 °C. The internal friction

TABLE 1. Composition (wt.%) of the substrates of the aluminized steel sheet

Material	C	Mn	P	S	N	Al	Ti	N/Al
1	0.021	0.206	0.008	0.004	0.0060	0.065	–	0.178
2	0.055	0.316	0.009	0.014	0.0044	0.049	–	0.173
3	0.043	0.289	0.011	0.014	0.0067	0.087	–	0.149
4	0.042	0.289	0.016	0.008	0.0043	0.082	–	0.104
5	0.038	0.225	0.007	0.007	0.0020	0.149	–	0.026
6	0.005	0.188	0.011	0.006	0.0027	0.147	0.0800	0.027[a]

[a]N/(Al+Ti) ratio.

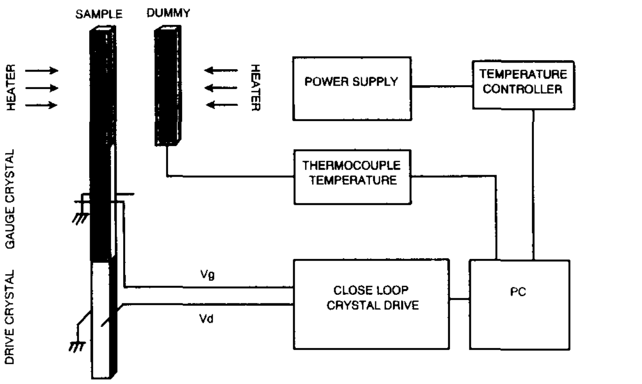


Fig. 2. Schematic of the high frequency composite oscillator used for the internal friction measurements.

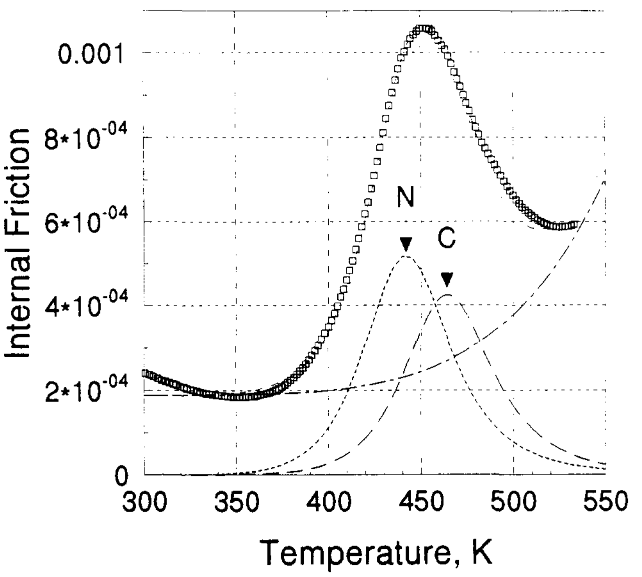


Fig. 3. Typical internal friction *vs.* temperature data for aluminized steel sheet. The data can be deconvoluted into an exponential background and two overlapping Debye peaks due to interstitial N and C.

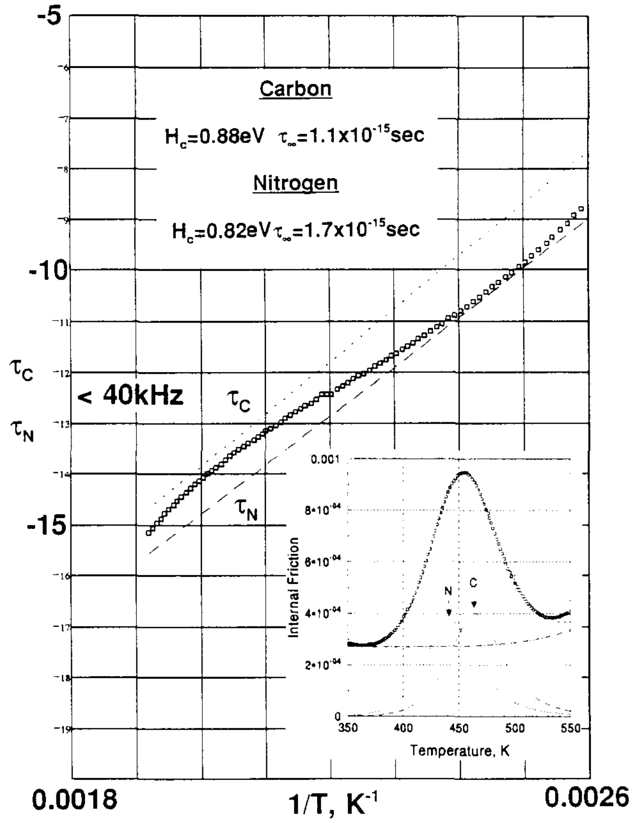
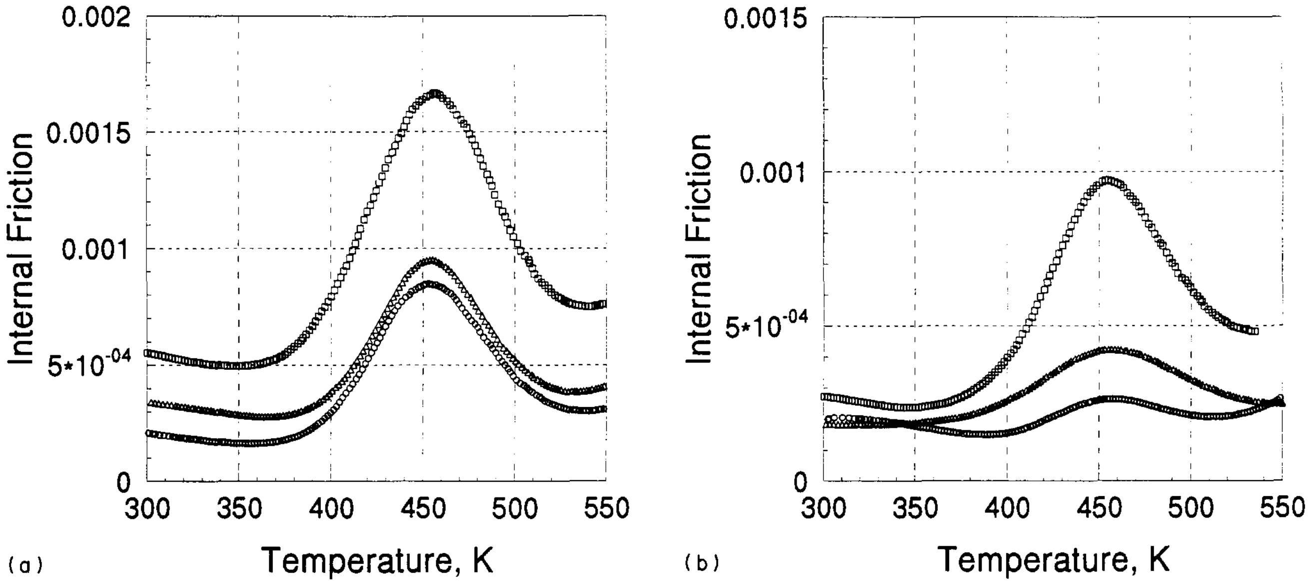


Fig. 4. Ln τ–$1/T$ plot based on data obtained after background substraction and ln τ–$1/T$ values for a single C and a single N peak. The inset shows the original internal friction data for an aluminized sheet with 7.6 p.p.m. interstitial N and 6.6. p.p.m. interstitial C.

data were recorded in the as-received state, after 4 and 8 h at 450 °C. Four types of evolution in the internal friction plots were observed. In the first type of behaviour (Fig. 5(a)), which was found for materials 1 and 2, the amplitude of the internal friction peak near 450 K remains constant after 4 h of annealing. The second type of internal friction peak evolution was found for material 3 (Fig. 5(b)). It is characterized by a gradual decrease in peak amplitude as the annealing time increases. The third type of internal friction peak evolution is shown in Fig. 5(c). It is characterized by the total disappearance of the internal friction peak originally present in the internal friction data of the as-received material. It is characteristic of materials 4 and 5. Finally no internal friction peak was observed in the as-received state and none resulted from the thermal treatment of the interstitial-free steel (material 6). Figure 6 shows the results of the deconvolution of the measured internal friction peaks. The data are ranked according to the N/Al (or N/(Al+Ti) atomic ratio for each material. Clearly, materials with a high N/Al ratio have a correspondingly high concentration of residual interstitial N after the thermal treatment of 8 h at 450 °C.

The materials were tested in air at 450 °C to determine the time needed for them to discolour from bright metallic to dull grey owing to the alloying of the coating (Fig. 7). The three materials which contained residual interstitial N after 8 h at 450 °C could all be tested for times in excess of 2000 h before any discoloration occurred. The full surface of the materials without residual interstitial N turned dull grey in less than 800 h. The discoloration tests on the materials with the three highest N/Al ratios were interrupted before the material had started to discolour. Hence their resistance to alloying is superior to that indicated in Fig. 7.

Secondary-ion mass spectroscopy (SIMS) depth profiling of the aluminized materials was carried out on a Cameca type 5F secondary-ion mass spectroscope. Figure 8 shows a semiquantitative SIMS depth profile



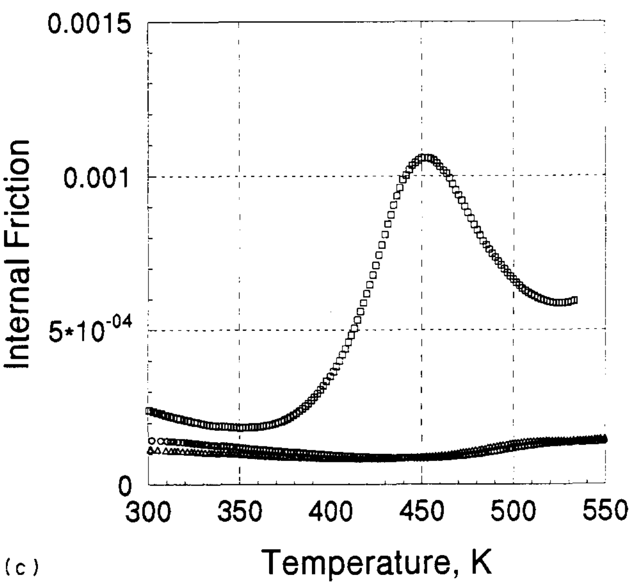


Fig. 5. Successive internal friction data for hot-dipped aluminized sheet in the as-produced state (□), after 4 h at 450 °C (△) and after 8 h at 450 °C (○). Three types of behaviour are observed: (a) an initial decrease followed by the stabilization of the amplitude of the internal friction peak near 450 K (materials 1 and 2; data shown are for material 1); (b) a gradual decrease in the amplitude of the internal friction peak near 450 K (the data shown are for material 3); (c) an initial internal friction peak disappearing entirely after the first heat treatment (materials 4 and 5; the data shown are for material 4).

obtained by Cs^+ sputtering on material 1 after an 8 h anneal at 450 °C. Three regions can easily be identified: the substrate, the intermediate intermetallic layer and the Al–Si coating layer. A clear N concentration profile was obtained showing that there is a strong N segregation at the interface between the steel and the intermetallic layer. Hence this interface acts as an effective trap for the N interstitials. In view of the stability of AlN, this strongly suggests that a thin AlN diffusion barrier is formed during the high temperature annealing of the material. This is also confirmed by the AlN profile shown in Fig. 8.

4. Discussion and conclusion

All the materials, studied with the exception of material 6, contain interstitial N that can be trapped in a variety of traps in the bulk and at the steel–coating interface. The bulk traps are: substitutional atoms (Al and Mn), dislocations and grain boundaries. The steel–coating interface can also act as a trap for interstitial N by interfacial AlN formation. In contrast to the bulk traps the steel–coating interface creates a well-defined diffusion profile that will bias the drift of the N atoms towards it, favouring the formation of a stable AlN diffusion barrier. The AlN formation occurs at the interface in the materials with both low and high N/Al ratios. The barrier needs to be continuous to prevent effectively the Fe_2Al_5 formation. The continuous diffusion barrier is only formed in materials with a higher N/Al ratio. This is supported by the fact that in those materials the AlN barrier prevents the further diffusion of both Al and N once a continuous diffusion barrier is formed. A stable residual interstitial

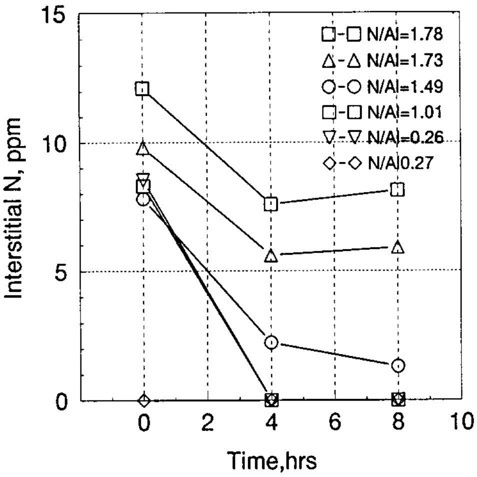


Fig. 6. N ageing kinetics at 450 °C as a function of the substrate N/Al atomic ratio for the six aluminized materials used. The results are based on the internal friction data of Fig. 5.

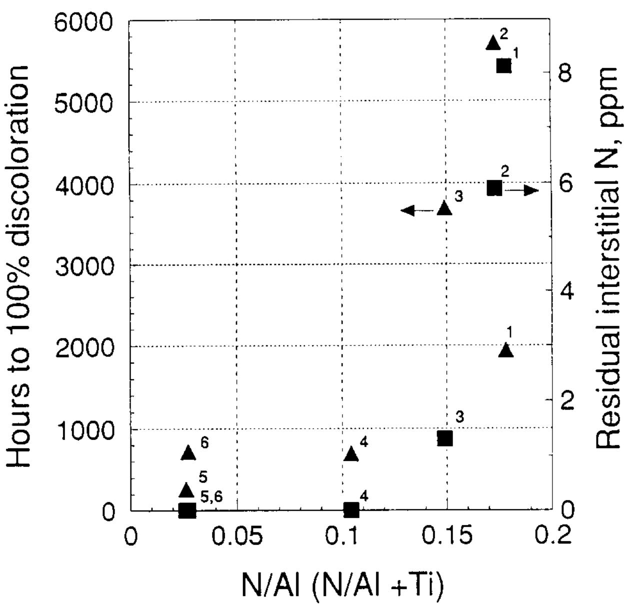


Fig. 7. Diagram of the material performance (▲) and the concentration of residual interstitial N after an 8 h anneal at 450 °C (■), as a function of the atomic ratio N/Al (or N/(Al + Ti)). The numbers next to the data points are the material numbers as given in Table 1.

N concentration is therefore obtained after the formation of the diffusion barrier. Even though bulk traps for these N atoms remain, in particular the substitutional atoms, the fact that the interstitial N concentration remains constant proves that the main trap for the N atoms is the steel–coating interface.

Consequently, a particularly novel and cost-effective improvement in the high-temperature resistance to Fe–Al alloy formation on standard commercial hot-

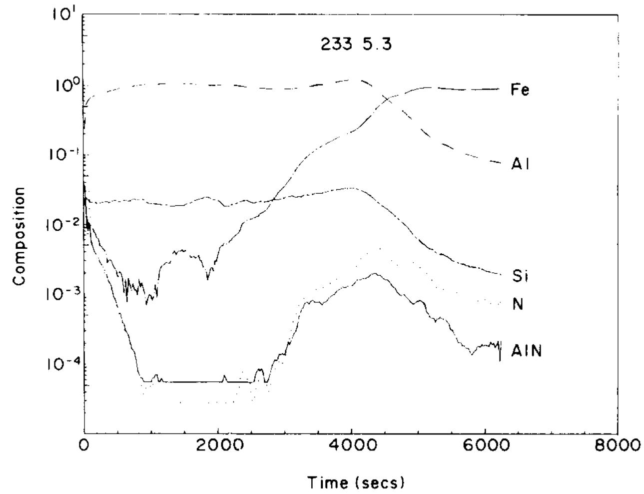


Fig. 8. SIMS depth profile for aluminized material 1 showing clearly the presence of a higher N concentration at the interface between the steel and the intermetallic layer. The ionized molecular species AlN^- has a similar depth profile.

dipped aluminized grades can now be achieved. The improvement is based entirely on the formation of an effective AlN diffusion barrier between the coating and the substrate during the high temperature use of parts made from the material.

Acknowledgments

The authors gratefully acknowledge the technical assistance of Dr. Z. Pan and Mr. H. Schmidt, both at the AECL Laboratories in Pinawa, Canada.

The SIMS experiments were carried out at the Centre de Recherche Publique (Centre Universitaire, Luxembourg) and analysed in collaboration with Dr. H.-N. Migeon and Dr. Y. Gao.

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