JOURNAL OF MATERIALS SCIENCE 21 (1986) 3348–3350

On the influence of silicon on the growth of the alloy layer during hot dip aluminizing

G. EGGELER*, W. AUER, H. KAESCHE
Lehrstuhl für Korrosion und Oberflächentechnik, Friedrich Alexander Universität Erlangen, Martensstrasse 7, D-8520 Erlangen, West Germany

The reactions between a low alloyed steel and a pure as well as a 2% silicon containing aluminium melt where studied at 780 and 792° C, respectively. The velocity of the iron enrichment was the same for both cases, whereas the alloy layer growth was much faster in the case of the pure aluminium melt. After hot dip aluminizing in the 2% silicon containing aluminium melt silicon was found to be incorporated in the alloy layer. From that it is clear that silicon acts on the solid state side, when reducing the alloy layer thickness during hot dip aluminizing.

1. Introduction

1.1. Coatings after hot dip aluminizing

It is well known [1–4], that after hot dip aluminizing of steel the coating obtained is of a duplex nature. It contains a brittle layer of intermetallic compounds adjacent to the steel substrate, which is called the alloy layer. On this a layer of the melt material is superimposed, which gives good corrosion resistance. As has been discussed in the literature [1, 3], thick alloy layers grow under normal operating conditions in pure and iron containing aluminium melts. These cannot withstand bending and forming operations without peeling and flaking. It was pointed out by Gittings *et al.* [1], that silicon as an addition to the aluminium melt reduces the thickness of the alloy layer. This can be seen in Fig. 1, for the low alloyed steel used in this work after hot dipping in a pure and a silicon-containing aluminium melt. Silicon-containing aluminium melts are often used in commercial hot dip aluminizing.

1.2. How silicon could reduce the alloy layer thickness during hot dip aluminizing

There are different explanations for the effect of silicon: Nicholls [5] assumes, that silicon atoms occupy the structural vacancies of the $\eta(Al_5Fe_2)$-phase, that has good diffusion possibilities for aluminium atoms in the pure (binary) state, as was discovered by Heumann and Dittrich [6]. Lainer and Kurakin [7] report, that in silicon-containing aluminium melts intermetallic phases $(Fe_xAl_ySi_z)$ are obtained, growing more slowly than the η-phase. In both instances, the presence of silicon results in a slower solid state growth.

Other authors [8, 9] take the view, that silicon accelerates the velocity of the iron enrichment in initially iron-free aluminium melts. If one assumes that the diffusion of iron atoms through a boundary layer of thickness δ is rate determining, then the velocity of this iron enrichment is given by

$$dc/dt = [(k_1S)/V](c_s - c) \qquad (1)$$

where dc/dt is the velocity of the iron enrichment, k_1 is the rate constant of the iron enrichment, S is the surface of the hot dipped specimen, V is the volume of the melt, c_s is the solubility of the iron in the melt, c is the actual concentration of the iron in the melt.

k_1 is given by

$$k_1 = D/\delta \qquad (2)$$

where k_1 is the rate constant of the iron enrichment, D is the diffusion coefficient of the iron atoms in the boundary layer, δ is the thickness of the boundary layer. It was argued [9], that silicon could accelerate the iron enrichment, because it increases the solubility c_s (Equation 1) of the melt, as follows from the Al–Fe–Si system reported by Rivlin and Raynor [10]. Moreover, since the viscosity of silicon-containing aluminium melts is smaller than the viscosity of pure aluminium melts, smaller δ-values (Equation 2) are obtained. Komatsu *et al.* [8] made weight loss studies and report that in the case of silicon-containing aluminium melts larger weight losses can be observed than in the case of silicon free aluminium melts. From this they concluded, that silicon acts by accelerating the iron dissolution.

1.3. Aim of this work

The present work concerns whether the silicon acts on the solid or the liquid side, when reducing the alloy layer thickness during hot dip aluminizing.

2. Experimental details

The low alloyed steel used in this work contained 0.16% C, 0.34% Si, 0.51% Mn, 0.97% Cr, 0.45% Mo and little phosphorus and sulphur. Specimens of size

---

*Present address: Laboratoire de Métallurgie Mécanique, Ecole Polytechnique Fédérale de Lausanne, Chemin de Bellerive 34, CH-1007 Lausanne, Switzerland.

0022–2461/86 $03.00 + .12

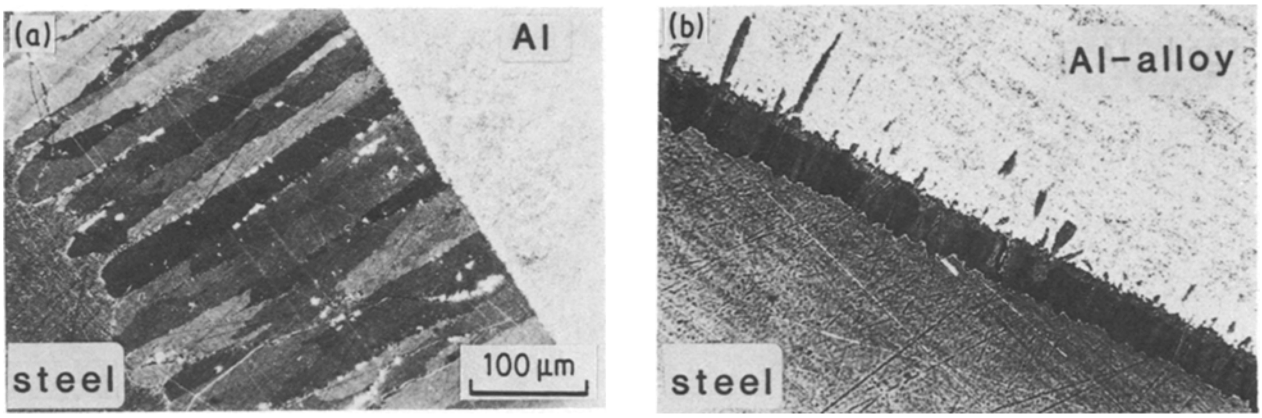

Figure 1 Alloy layers after hot dipping in pure and silicon-containing aluminium melts. (a) Melt: initially pure aluminium, 780° C, 900 sec. (b) Melt: Al + 2 wt % Si, 791° C, 900 sec.

15 mm × 20 mm × 3 mm were used for the investigation of the growth of the alloy layer and for the investigation of the iron enrichment in initially iron-free aluminium melts. The specimens were normalized, ground, polished, cleaned and fluxed [11]. The initial purity of the aluminium used in this work was 99.95 wt %. For the investigation in silicon-containing aluminium melts, 2 wt % silicon (purity: 99.999 wt %) were alloyed to the aluminium. The masses of the melts used were 200 g. Prior to immersion the specimens were above the melt and brought up to the reaction temperature.

The dip tests were carried out between 780 and 792° C. After dipping the specimens were water quenched within 1 sec. Metallographic cross-sections were prepared to study the growth of the alloy layer, the maximum thickness of which was measured. For the investigation of the iron enrichment in the initially iron-free aluminium melts, the iron content of the melts was analysed after solidification by means of a titration method [12].

3. Results

3.1. Alloy layer growth and iron enrichment

As can be seen from Fig. 2, the maximum thickness value $d_{\max}$, obtained during hot dipping of the low alloyed steel used in this work in an initially pure aluminium melt at 780° C grows much faster than the one obtained in an aluminium melt containing 2 wt % silicon at 791° C. Furthermore the iron concentration of the melt as a function of dipping time is incorporated in Fig. 2. The iron concentration is linearly related to the dipping time. This is, because c (Equation 1) is much smaller than c_s (Equation 1) for the dipping times used in this work. As can be seen from Fig. 2 no significant differences can be observed between the pure and the silicon-containing aluminium melt, as far as the iron enrichment is concerned.

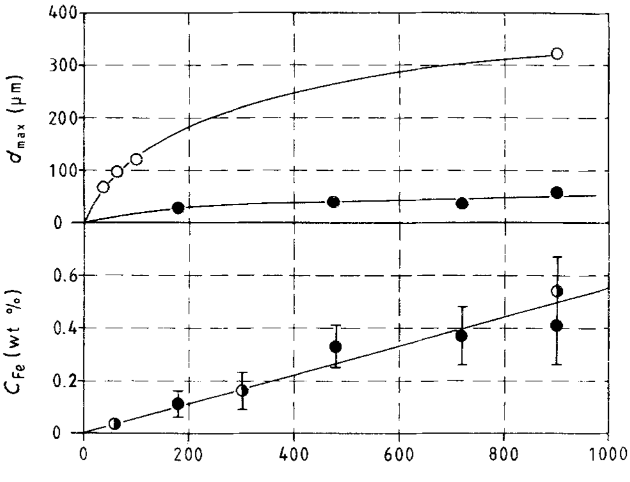

Figure 2 Alloy layer growth and iron enrichment in pure and silicon-containing aluminium melts. (◑, ○) pure Al, 792/780° C; (●) Al + 2 wt % Si, 791° C.

3.2. Build up of the alloy layers

After hot dipping in pure as well as silicon-containing aluminium melts for 900 sec at the temperatures mentioned in Fig. 2 for each case, both alloy layers consist of two phases. One of these adjacent to the steel substrate, is much thicker than the one adjacent to the melt material. The phases are called major and minor phase, respectively. In the case of the experiment in the pure aluminium melt, the alloy layer thickness is about 300 µm, 5 µm of which belong to the minor phase. For this case it is well known [2, 6, 12], that the major phase is the $\eta(\mathrm{Al_5Fe_2})$-phase. Recent investigations using a transmission electron microscope [13] pointed out, that in this case the minor phase is the $\theta(\mathrm{Al_3Fe})$-phase.

In the case of the aluminium melt containing two wt % silicon the alloy layer thickness is about 45 µm, 10 µm of which belong to the minor phase. In Fig. 3 one can see two spectra which were measured with a scanning electron microscope using energy dispersive analysis. These spectra where taken from the two major phases of the alloy layers which can be seen in Fig. 1. The spectra do not change very much in the major phase regions.

The composition of the major phases were calculated from the spectra, using the ZAF-correction. The results are incorporated in Fig. 3. The composition found for the major phase in the pure aluminium melt, corresponds with the composition of the $\eta(\mathrm{Al_5Fe_2})$-phase as given by Hansen and Anderko [14]. The compositions for the major and minor phases grown in an aluminium melt containing 2 wt % silicon correspond to the compositions of the η- and

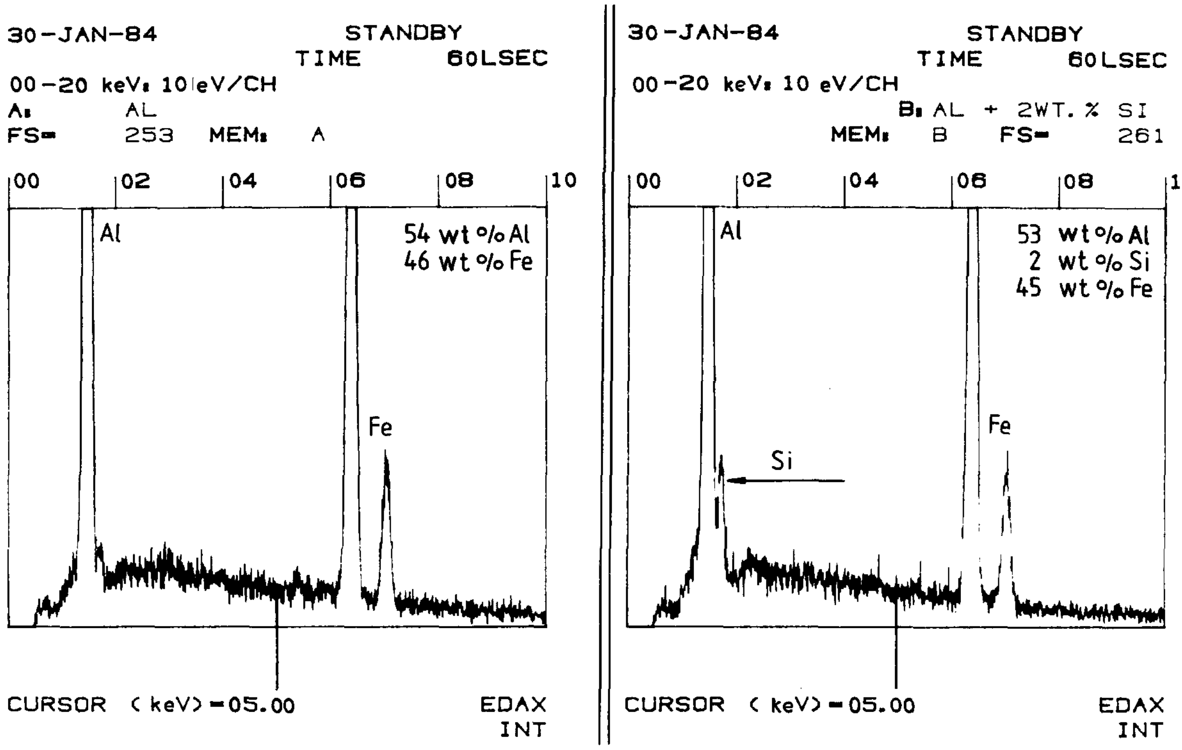

Figure 3 Composition of the major phases after hot dipping in pure and silicon-containing aluminium melts.

θ-phase from the ternary Al–Fe–Si system as given by Rivlin and Raynor [10]. The solubility limit for silicon in both phases is about 2 wt %.

4. Discussion

From the results reported in Section 3 it is clear that for the system investigated silicon acts in the solid state when reducing the alloy layer thickness. The experimental results confirm the assumption of Nicholls [5], who supposed, that the silicon changes the diffusion conditions in the η-phase. The assumption of Komatsu and co-workers [8], that silicon would accelerate the velocity of the iron enrichment does not hold. It was based on weight loss studies. In the case of hot dip aluminizing weight loss studies are difficult to interprate for two reasons: first, during dipping not only iron atoms leave the solid to get solved in the melt, but also aluminium atoms from the melt are incorporated in the solid, the amount of which being smaller in the case of the silicon-containing aluminium melt. Second, during withdrawal melt material sticks to the specimen the amount of which changes with the withdrawal rate [3].

5. Summary

When using aluminium melts containing 2 wt % silicon instead of pure aluminium melts for hot dip aluminizing, the thickness of the alloy layer growing is much smaller. The silicon is incorporated in the alloy layer, and thus slows its growth. It does not accelerate the process of iron dissolution in the aluminium melt, opposite to what has been previously assumed in the literature [8, 9].

References

1. D. O. GITTINGS, D. H. ROWLAND and J. O. MACK, *Trans. ASM* **43** (1951) 587.
2. E. GEBHARDT and W. OBROWSKI, *Z. Metallkde.* **44** (1953) 154.
3. A. KNAUSCHER, *Neue Hütte* **19** (1974) 398.
4. S. G. DENNER, R. D. JONES and R. J. THOMAS, *Iron Steel Int.* **48** (1975) 241.
5. J. E. NICHOLLS, *Corr. Technol.* **11** (1964) 16.
6. T. HEUMANN and S. DITTRICH, *Z. Metallkde.* **50** (1959) 617.
7. D. I. LAINER and A. K. KURAKIN, *Fiz. Met. Metallov.* **18** (1964) 145.
8. N. KOMATSU, M. NAKAMURA, H. FUJITA, *J. Jpn. Inst. Met.* **45** (1981) 416.
9. R. D. JONES and S. G. DENNER, in Proceedings of the 10th World Congress in Metal Finishing, (Metal Finishing Society of Japan, Kyoto, 1980).
10. V. G. RIVLIN and G. V. RAYNOR, *Int. Met. Rev.* **26** (1981) 133.
11. S. G. DENNER and R. D. JONES, *Met. Technol.* **4** (1977) 167.
12. G. EGGELER, Dr Ing thesis, Erlangen (1985).
13. G. EGGELER, H. VOGEL, J. FRIEDRICH and H. KAESCHE, *Prakt. Metallogr.* **22** (1985) 163.
14. M. HANSEN and K. ANDERKO, in "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) pp. 90–5.

Received 8 October
and accepted 15 November 1985