4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

ALUMINUM ALLOY ELECTROPLATING ON STEEL SHEET FROM MOLTEN SALT BATH

Seiji Nakajima, Shuji Gomi, Hisatada Nakakoji and Nobuyuki Morito

Technical Research Division, Kawasaki Steel Corporation, Japan

Synopsis: Al-Nb and Al-Nb-Mn alloy coatings were electroplated from a molten $AlCl_3$-NaCl-KCl bath containing $NbCl_5$ and $MnCl_2$. The influence of Nb^{5+} concentration in the bath, current density and bath temperature on the niobium content in the coating was investigated. The Al-5%Nb and Al-Nb-Mn alloy coatings exhibited an extremely smooth surface. The Al-Nb alloy coating consisted of a single aluminum phase supersaturated with niobium. It was presumed that the niobium at the interface between the coating layer and the steel substrate interrupted the formation of an Al-Fe intermetallic compound layer during heat treatment. The Al-Nb-Mn alloy coating was amorphous. The corrosion resistance of each coating was examined by a salt spray test; the red rust onset times for 20 g/m^2 of the Al-5%Nb and Al-4%Nb-26%Mn alloy coated steel sheets were longer than 100 days and 300 days, respectively.

Key words: aluminum alloy, niobium, manganese, molten salt, electroplating, metal surface treatment, corrosion resistance

1. Introduction

The application of molten salt to metal surface treatment has received much attention, and electroplating of aluminum from a molten salt bath has been studied by many investigators. Aluminum can not be electrodeposited from an aqueous solution, and coating by the hot-dip process requires a high temperature above 660° C which results in the formation of a brittle Al-Fe intermetalic compound layer. However, it is known that the aluminum deposits obtained from a molten salt bath tend to have a dendritic or powderlike appearance[1]. In order to form a smooth deposit, codeposition of a second element with Al has been studied; among such elements, Pb[2] and Mn[3] have been found to be effective. In the present work, we will show that codeposition of niobium with aluminum or Al-Mn alloy is extremely effective to form a smooth deposit and to improve the corrosion resistance of the coating. The structures of the Al-Nb and Al-Nb-Mn alloy coatings will also be studied.

2. Experimental

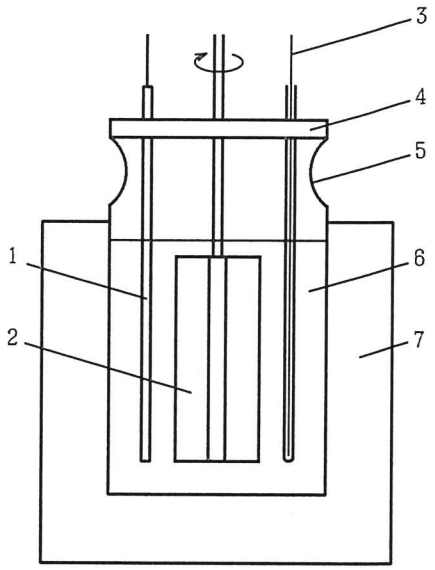
The apparatus for electroplating is shown in Fig. 1. The electroplating cell was a one-liter Pyrex glass beaker with a Teflon cover. Cold rolled steel sheets were used as the electroplating substrate. Two pure aluminum plates were joined together crosswise, and it is used both as the anode and the impeller. The electrolyte used in this study was a molten $AlCl_3$ (75.7 mass%)-NaCl (14.4 mass%)-KCl (9.9 mass%) mixture. $NbCl_5$ and $MnCl_2$ were added to this electrolyte to electrodeposit Al-Nb and Al-Nb-Mn alloys. The concentrations of Nb^{5+} and Mn^{2+} were 0-1.9 mass% and 0-0.5 mass%, respectively. The temperature of the electrolyte was held at 200° C in most cases, and varied in the 180-220° C range to study the influence of temperature. In order to remove impurities from the molten salt bath, it was subjected to pre-electrolyses at a current density of 20 A/dm^2 for 10 min. The current density for electroplating was 5-20 A/dm^2, and the coating amount was varied in the 10-30 g/m^2 range by changing the electroplating time period. All electroplating procedures were carried out

under a dry nitrogen atmosphere.

The amounts of aluminum, niobium and manganese in the coatings were evaluated by inductively coupled plasma atomic emission spectrometry, and by X-ray fluorescence spectrometry. The surface and cross section of each coating were observed with a scanning electron microscope and an optical microscope, respectively. The distribution of aluminum, niobium and manganese in each coating was examined with an electron probe micro analyzer and a glow discharge spectroscope.

The coating structures were studied by X-ray diffractometry, and the coatings after heat treatment at 400° C for 30 min were also measured.

The corrosion resistance of each coating was examined by a salt spray test, and compared with that of Al-9%Si alloy coated steel sheet prepared by the hot-dip process.



1: Steel substrate 2: Aluminum anode
3: Thermocouple 4: Teflon cover
5: Pyrex glass beaker 6: Electrolyte
7: Heater

Fig. 1 Apparatus for electroplating

3. Results and discussion

3.1 Niobium content in the coating

Fig. 2 shows the relationship between the niobium and manganese content in the coating and Nb^{5+} concentration in the bath. The niobium content in the coating increased with increasing Nb^{5+} concentration in the bath irrespective of the addition of Mn^{2+}. On the other hand, the manganese content in the coating decreased with increasing Nb^{5+} concentration in the bath when 0.5 mass% of Mn^{2+} was added. These results indicate that niobium, which is noble to both aluminum and manganese, was preferentially electrodeposited.

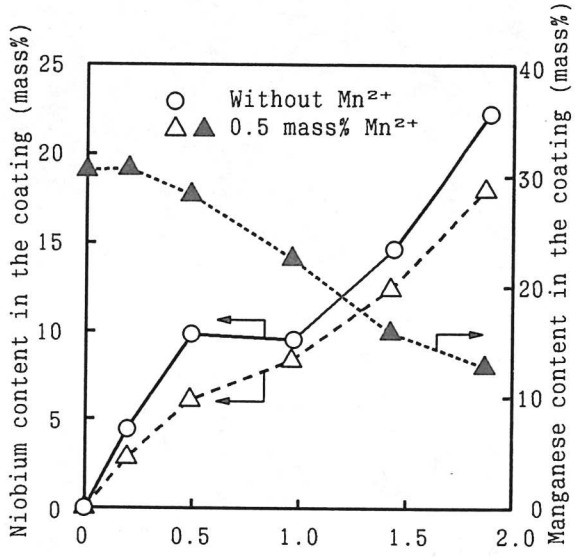


Fig. 2 Relationship between the niobium and manganese content in the coating and Nb^{5+} concentration in the bath

Fig. 3 shows the relationship between the niobium content in the Al-Nb alloy coating and current density. The niobium content at current densities of 10 A/dm² and 20 A/dm² was almost the same although its content at a current density of 5 A/dm² was a little higher.

The relationship between the niobium content in the Al-Nb alloy coating and bath temperature is shown in Fig. 4, the niobium content in the coating being independent of bath temperature. The results shown in Fig. 3 and Fig. 4 suggest that the niobium content in the coating was not only controlled by the diffusion of Nb^{5+}.

3.2 Appearance of the coating

The surfaces of the Al-Nb and Al-Nb-Mn alloy coatings were observed by a scanning electron microscope, the micrographs being shown in Fig. 5. Compared with the coarse surface of a pure aluminum coating, the Al-1%Nb alloy coating had a fairly smooth surface. In the case of the Al-5%Nb alloy coating, an extremely smooth surface was observed. However, the coating surface became coarser when the niobium content was increased to more than 10 mass%. Codeposition of manganese with aluminum and niobium was most effective for a smooth coating surface.

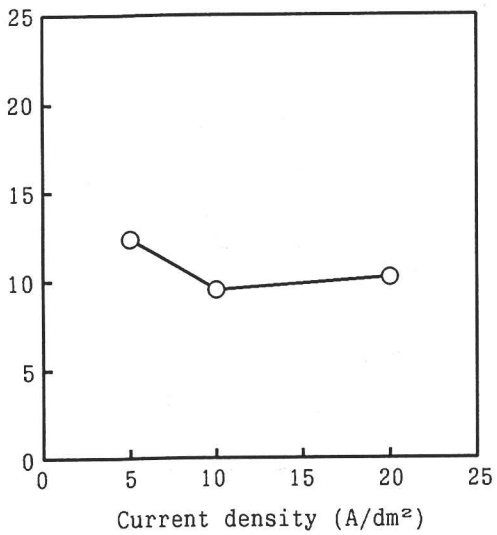


Fig. 3 Relationship between the niobium content in the coating and current density

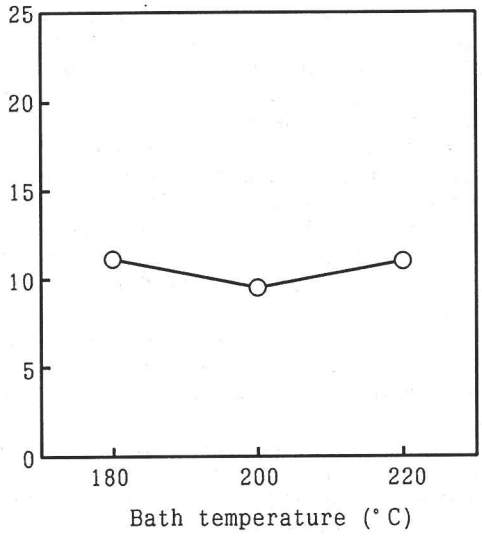


Fig. 4 Relationship between the niobium content in the coating and bath temperature

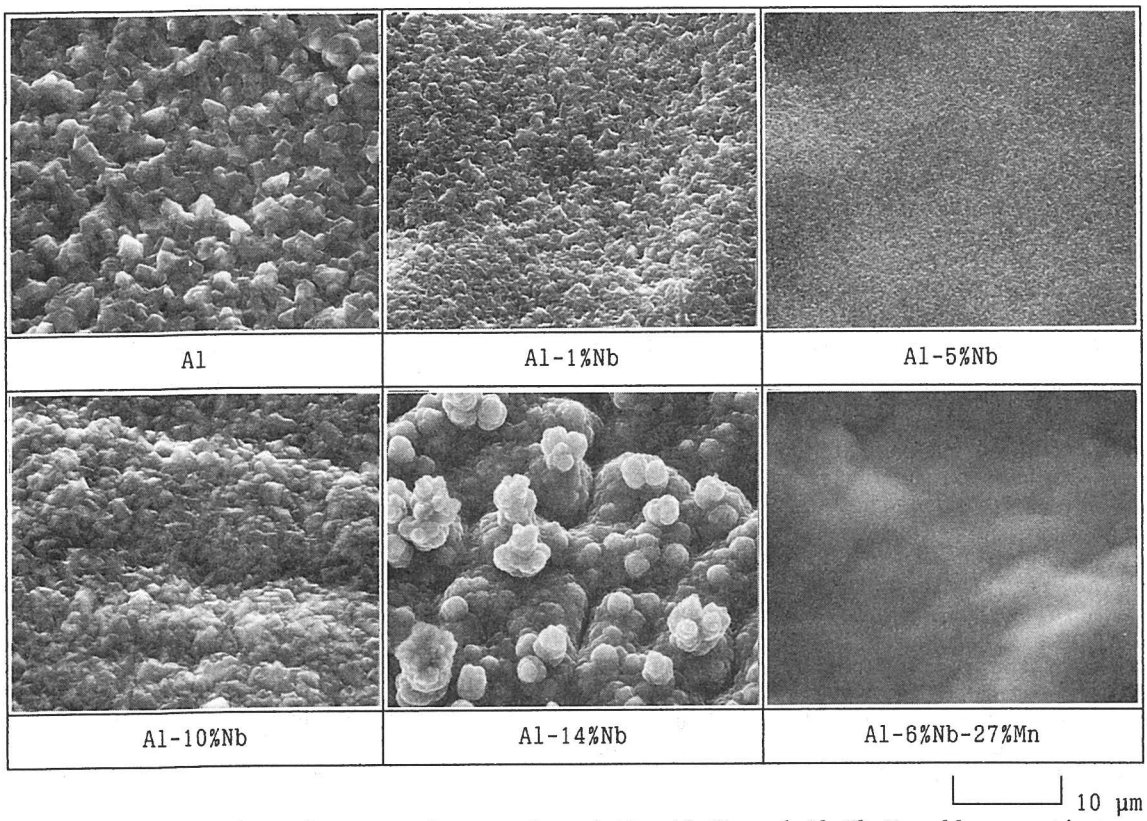


Fig. 5 Scanning electron micrographs of the Al-Nb and Al-Nb-Mn alloy coatings

Cross sections of the Al-Nb and Al-Nb-Mn alloy coated steel sheets were observed with an optical microscope, and the resulting micrographs are shown in Fig. 6. In all the coatings, no Al-Fe intermetallic compound layer between the coating and the steel substrate was apparent, since the electroplating was performed at a low temperature of 200°C. The appearance of the Al-Nb alloy coating layer was similar to that of the aluminum coating layer, while the Al-Nb-Mn alloy coating layer had a different appearance.

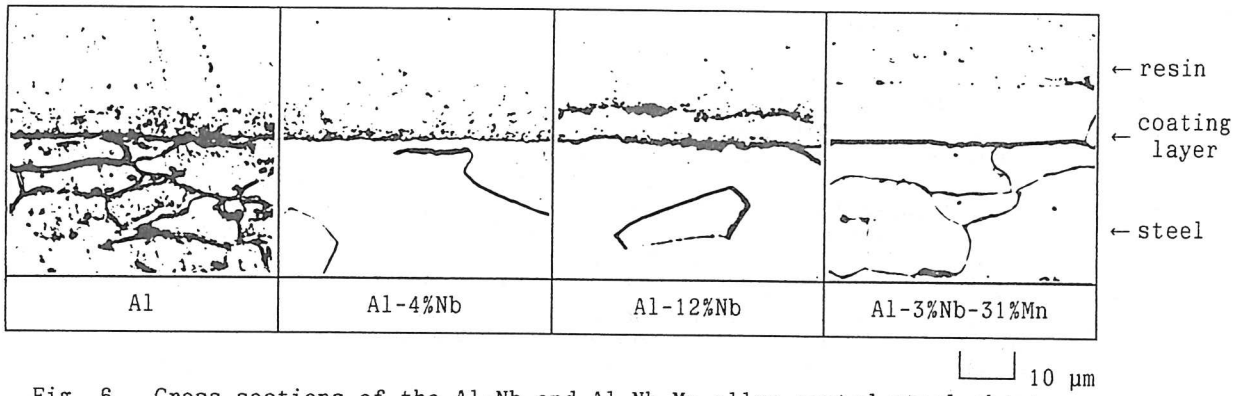


Fig. 6 Cross sections of the Al-Nb and Al-Nb-Mn alloy coated steel sheets

3.3 Distribution of aluminum, niobium and manganese in the coating

The distribution of aluminum and niobium in the Al-5%Nb alloy coating was analyzed with an electron probe micro analyzer, the results being shown in Fig. 7. It was found that aluminum and niobium were distributed uniformly without aggregation.

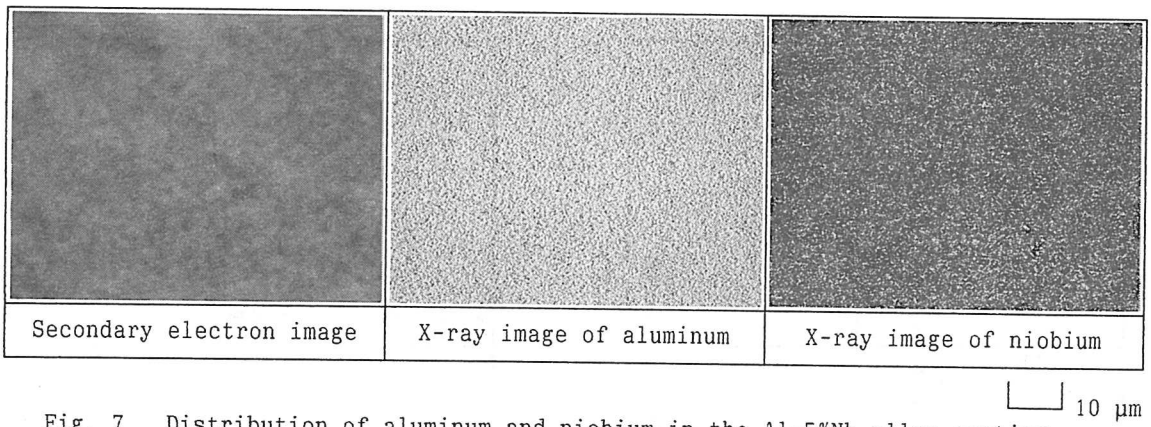


Fig. 7 Distribution of aluminum and niobium in the Al-5%Nb alloy coating analyzed with an electron probe micro analyzer

The depth profiles of the Al-Nb and Al-Nb-Mn alloy coated steel sheets were analyzed by glow discharge spectroscopy, with the results being shown in Fig. 8. In the case of the Al-4%Nb alloy coating, the concentration of niobium increased at the interface between the coating layer and the steel substrate. With the Al-Nb-Mn alloy coating, each element was uniformly distributed through out the coating layer.

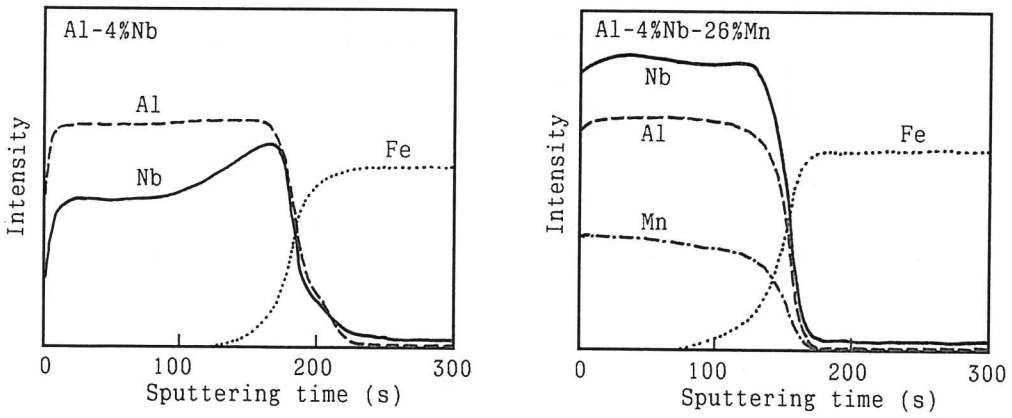


Fig. 8 Depth profiles of the Al-Nb and Al-Nb-Mn alloy coated steel sheets analyzed by glow discharge spectroscopy

3.4 Structure of the coating

The structures of the Al-Nb and Al-Nb-Mn alloy coatings were studied by X-ray diffractometry, Fig. 9 showing the diffraction patterns. In the case of the Al-Nb alloy coating, only the reflection for aluminum appeared in addition to that of the steel substrate, and the lattice parameters were the same as those of the aluminum coating. These results suggest that the Al-Nb alloy coating consisted of a single aluminum phase supersaturated with niobium. It is assumed that the constant lattice parameters regardless of the substitution of niobium for aluminum were due to the closely similar atomic diameters of aluminum and niobium, which are 2.86 Å and 2.68 Å, respectively. The Al-Nb-Mn alloy coating was amorphous, and had a similar structure to that of an Al-25%Mn alloy coating[4]. This can also be explained by the substitution of niobium for aluminum.

Fig. 10 shows X-ray diffraction patterns of the Al-Nb and Al-Nb-Mn alloy coated steel sheets heat treated at 400° C for 30 min. The reflections of Al_3Nb appeared for the Al-Nb alloy coating, and the formation of Al_5Fe_2 decreased with increasing niobium content. This can be explained by the assumption that a sufficient amount of niobium at the interface between the coating layer and the steel substrate shown in Fig. 8 interrupted the diffusion of aluminum and iron. On the other hand, the Al-Nb-Mn alloy coating maintained an amorphous structure. It has been reported that an Al-25%Mn alloy coating crystallized to Al_6Mn after heat treating at 400° C for 10 min[4]. It is presumed that niobium substituting for aluminum would interrupt the arrangement of aluminum and manganese.

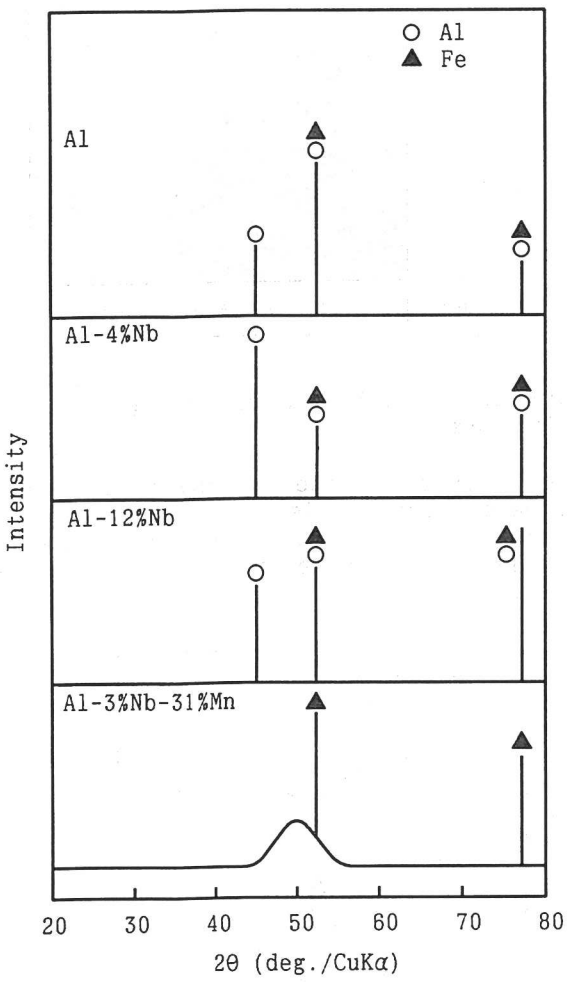


Fig. 9 X-ray diffraction patterns of the Al-Nb and Al-Nb-Mn alloy coated steel sheets

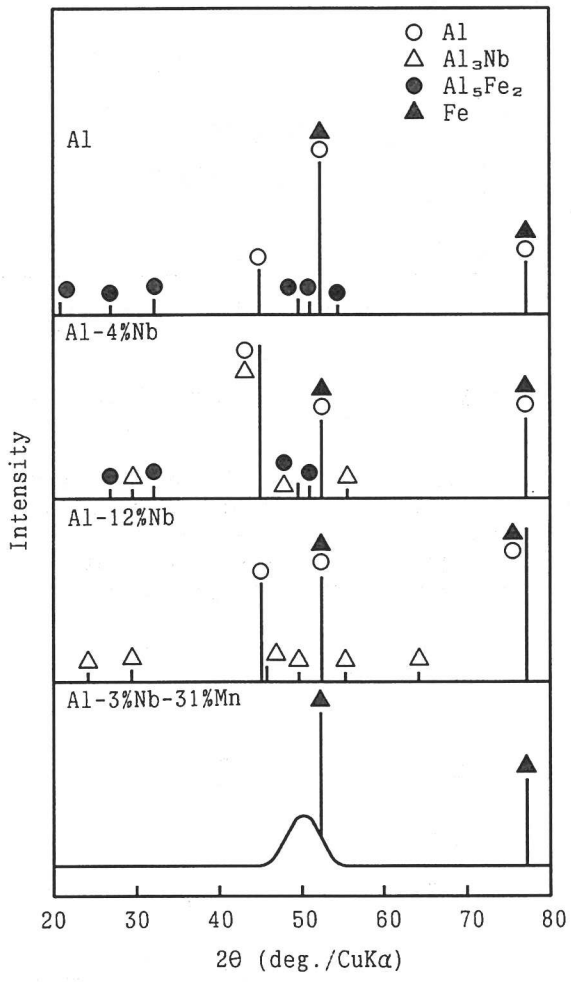


Fig. 10 X-ray diffraction patterns of the Al-Nb and Al-Nb-Mn alloy coated steel sheets heat treated at 400° C for 30 min

3.5 Corrosion resistance of the coating

The corrosion resistance of the Al-Nb and Al-Nb-Mn alloy coated steel sheets was examined by a salt spray test, and compared with that of an Al-9%Si alloy coated steel sheet prepared by the hot-dip process. The results are shown in Fig. 11. Red rust appeared within one day with the pure aluminum coated steel sheet because of the coarse surface shown in Fig. 5. The Al-Nb alloy coated steel sheet showed greater corrosion resistance, the red rust onset time being longer than 100 days for 20 g/m² of the Al-5%Nb coated steel sheet, while red rust appeared within 30 days for 30 g/m² of the Al-9%Si alloy coated steel sheet. With the Al-Nb-Mn alloy coated steel sheet, there was outstanding corrosion resistance; the red rust onset time for 20 g/m² of the Al-4%Nb-26%Mn alloy coated steel sheet being longer than 300 days. These results correspond well to the observations of the coating surface shown in Fig. 5, that is to say, the corrosion resistance was improved when the coating surface was smooth.

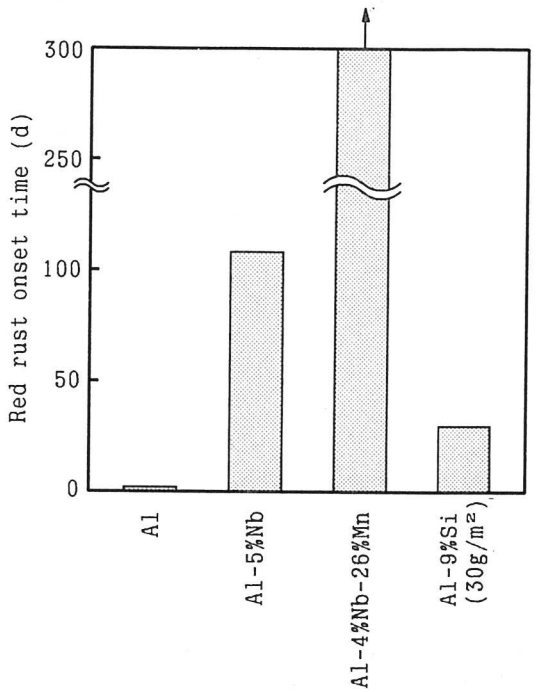


Fig. 11 Red rust onset times for 20 g/m² of the Al-Nb and Al-Nb-Mn alloy coated steel sheets by a salt spray test

4. Conclusion

Al-Nb and Al-Nb-Mn alloy coatings were electroplated from a molten $AlCl_3$-NaCl-KCl bath containing $NbCl_5$ and $MnCl_2$. The niobium content in the coating increased with increasing Nb^{5+} concentration in the bath; however, it seems that the niobium content in the coating was not only controlled by the diffusion of Nb^{5+}. The Al-5%Nb and Al-Nb-Mn alloy coatings exhibited an extremely smooth surface. The Al-Nb alloy coating consisted of a single aluminum phase supersaturated with niobium. It was presumed that the niobium at the interface between the coating layer and the steel substrate interrupted the formation of an Al-Fe intermetallic compound layer during heat treatment at 400° C for 30 min. The Al-Nb-Mn alloy coating was amorphous, and this structure was unchanged by heat treatment. The corrosion resistance of each coating was examined by a salt spray test; the red rust onset times for 20 g/m² of the Al-5%Nb and Al-4%Nb-26%Mn alloy coated steel sheets were longer than 100 days and 300 days, respectively.

References

1) R. Midorikawa: Denki Kagaku, 24 (1956), 366.
2) R. Midorikawa: Denki Kagaku, 24 (1956), 562.
3) L.W. Austin, M.G. Vucich and E.J. Smith: Electrochemical Technology, 1 (1963), 267.
4) T. Tsuda, H. Seto, J. Uchida, Y. Yamamoto, N. Usuki, T. Shiota, A. Shibuya and R. Nomi: Technical Paper Series of Society of Automotive Engineers, Detroit, 1990, 900719.