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

DEVELOPMENT OF AL-MN ALLOY PLATING PROCESS FROM MOLTEN SALT

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Synopsis: Electroplating process from molten salt has been studied as a new metal coating process to develop Al or Al alloy electroplated steel sheet. There have been few examples for practical use of this process because of dendritic and powdery electrodeposition. So it is necessary for application to metal coating process to get flat and smooth electrodeposited film on steel sheet at high current density. High masstransfer and alloy deposition of Mn were found to be most effective to get flat and smooth electroplated surface of Al alloy even at high current density. Smooth and lustrous Al-25%Mn alloy coatings with an amorphous structure and good performances as a pre-coated steel sheet, were electroplated at current density as high as 800 mA/cm² in a continuous bench-scaled electroplating equipment.

Key words: molten salt, electroplating, Al-Mn alloy, amorphous structure, steel sheet, $AlCl_3$-KCl-NaCl eutectic composition, flow rate, high current density, continuous bench-scaled plating equipment.

1. Introduction

Many pre-coated steel sheets are utilized in a variety of markets such as automobile, household appliances, building and construction, and containers. These pre-coated steel sheet are manufactured by electroplating from aqueous solution, hot-dip galvanizing, and painting process. Recently, there has been increased demands for superior performance of these materials. Aim of this study is to develop a new electroplating process using the molten salt as a new surface finishing technology.

In comparison with the method using aqueous solution, almost all metallic elements can be electrodeposited by the molten salt electroplating process. However, there have been few examples for practical use owing to several operational difficulties, such as high operating temperature and avoidance of moisture in the molten salt, as well as dendritic and powdery deposition. R & D efforts were focused on Al coating, since Al is relatively inexpensive metal, nevertheless impossible to electrodeposit from aqueous solution. It is known that Al-Mn alloy elecroplated film from molten salt has a lustrous surface and a good corrosion resistance[1], and its structure is amorphous[2]. In this paper, process parameters for smooth deposition of Al-Mn alloy at high current density which has good performances as a pre-coated steel sheet[3-4], and some results of continuous plating tests to steel strip by bench-scaled equipment which has been developed in cooperation with Mitsubishi Heavy Industries, Ltd., are described.

2. Experimental Procedure

2-1 Plating cell for electrodeposition from molten salt

The Al-Mn alloy was electroplated galvanostatically onto mild steel sheet from the molten salt with eutectic composition with addition of $MnCl_2$, which is composed of reagent grade $AlCl_3$, KCl and NaCl. Impurities were purified by Al powder treatment prior to plating runs. The bath was kept in N_2 atmosphere to avoid moisture contamination and held at 150℃

~200℃. As shown in Fig.1, a rectangular flow-channel cell was constructed, which provided high and uniform fluid flow of molten salt electrolyte on electrode surfaces. This flow-cell was made of SUS316, and fluid flow was induced by rotation of propelling blades in molten salt. A mild steel sheet which was degreased, pickled and dried, was placed parallel to Al counter electrode. The plated area was 100mm×100mm. The surface of steel substrate was dissolved anodically in the same molten salt bath before plating, to get good adhesive deposits. The oxide ion concentration in molten salt which was generated by water and moisture, was determined by Karl Fischer titration method[5]. The concentration just before plating was about 0.2%.

2-2 Reel to reel continuous strip-plating bench-scaled equipment

The outline of the bench-scaled test equipment is shown in Fig.2 with its main specification. This prototype equipment is a miniature line to develop almost all of this plating process. The large difference from plating in aqueous solution is that a drying and pre-heating process is needed prior to plating. Anodic activation treatment is conducted in molten salt for improving adhesion of the coatings to a steel substrate. Careful engineering consideration should be taken to maintain precisely plating cell temperature and also to avoid introduction of moisture into the system. The alloy was coated on only one side of steel strip.

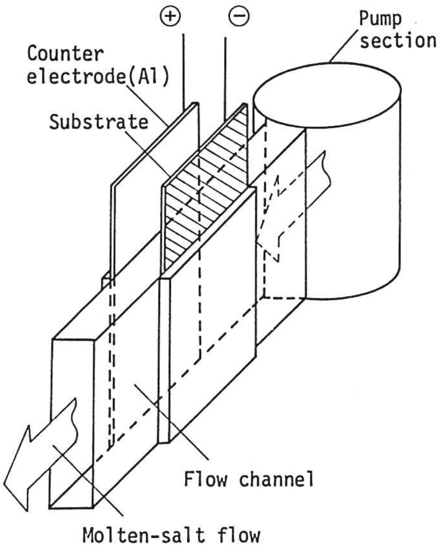


Fig.1 Flow-channel cell

Line speed	1.0m/min
Strip size	$120^{W} \times 0.5^{t}$
Current density	max 8000 A/m^2
Cell	One vertical cell
Anode	Soluble Al-Mn pellet

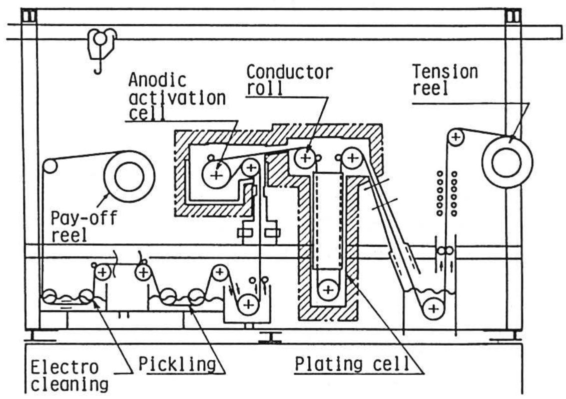


Fig.2 Bench-scaled equipment for continuous strip plating

3. Results and discussions

3-1 Electrodeposition from molten salt of aluminum chloride

The aluminum ion in an aluminum chloride-alkali molten salt is assumed to be in equlibrium as follows and it is supposed that cation Al^{3+} does not exist[6].

$$AlCl_3 + XCl \quad X^+ + AlCl_4^- \quad (X: Na, K) \quad \cdots (1)$$

$$AlCl_4^- + AlCl_3 \quad Al_2Cl_7^- \quad \cdots (2)$$

The following can be expected as the depositing reactions of aluminum:

$$4Al_2Cl_7^- + 3e^- \rightarrow Al + 7Al_2Cl_4^- \quad \cdots (3)$$

$$AlCl_4^- + 3e^- \rightarrow Al + 4Cl^- \quad \cdots (4)$$

In order to obtain favorable electrodeposited production, it is important that the reaction(3) should occur preferentially. Therefore, masstransfer of the $Al_2Cl_7^-$ ion needs to be taken into consideration. In Photo.1, it is shown that electrodeposited Al surfaces from $AlCl_3$-NaCl-KCl eutectic molten salt without $MnCl_2$ were improved in the case where flow

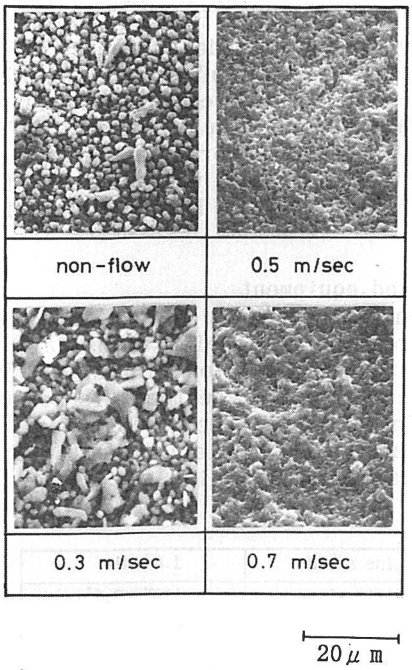


Photo.1 SEM images of electro-deposited Al at various flow-rate at 200 mA/cm²

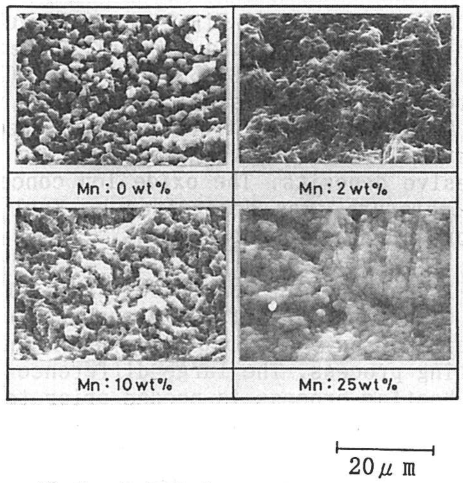


Photo.2 SEM images of electro-deposited Al-Mn alloy with various Mn content at 300mA/cm2 and 1m/sec. of flow-rate

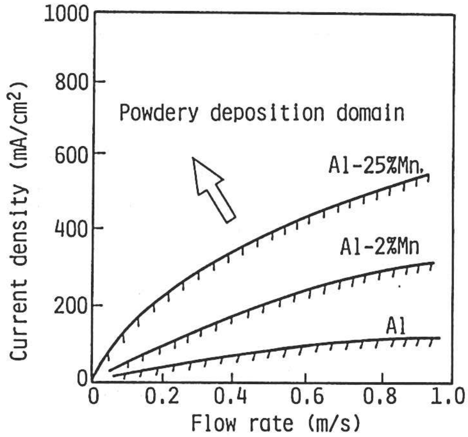


Fig.3 Effects of flow rate and Mn content on current density for smooth deposits

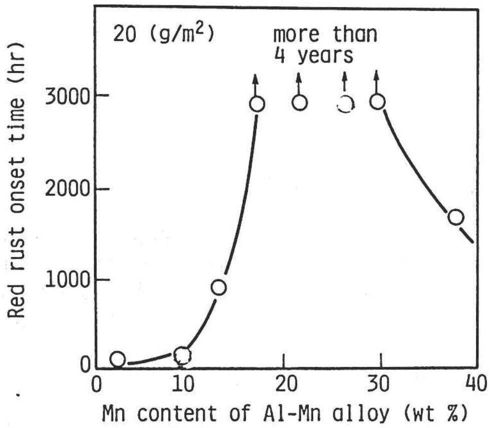


Fig.4 Corrosion resistance of Al-Mn alloy plated steel sheet by salt spray test

rate was raised in flow cell. The control of masstransfer is a mandatory factor in order to obtain favorable coatings. But it is still inadequate from the view point of practical high current density for steel strip coating. On account of this, alloy deposition by addition of $MnCl_2$ was examined in order to improve smoothness. Photo.2 shows the effects of alloying by SEM images of Al-Mn alloy platings. Mn as an alloy element effected the refining of a microtopography, and in the case of 2wt% Mn content in deposit, the smoothness of film was improved. As Mn content increased, brighter and smoother surfaces were obtained in the area of 15~45wt% Mn content. Fig.3 shows the effects of electrolyte flow rate and Mn content by the critical current density line of good deposition. In the case of Al-Mn alloy plating at a high flow rates, it was clarified that smooth deposits of 25wt% Mn content were obtained even at high current density exceeding 600mA/cm².

This electrodeposited Al-25wt%Mn alloy film had the best corrosion resistance as shown in Fig.4, and was the amorphous structure as shown in Photo.3. Moreover, Photo.4 shows that deposition of this film was macroscopically uniform and smooth. In this paper, properties of this coated steel sheet are not mentioned, since it was described elsewhere that Al-25wt%Mn alloy coated steel sheet revealed excellent performances as a new pre-coated steel, in terms of corrosion resistance, heat-resistance, formability, weldability, and so on[3].

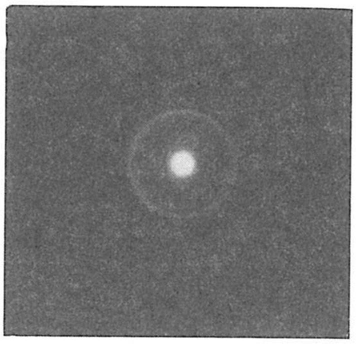


Photo.3 Electron diffraction pattern of electro-deposited Al-Mn alloy with 25wt% Mn

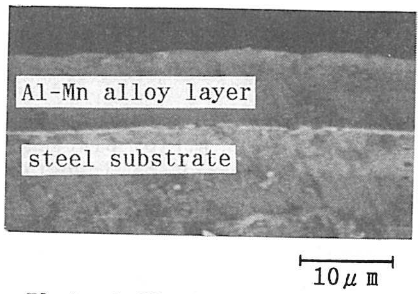


Photo.4 SEM images of cross-section of electro-deposited Al-Mn alloy with 25wt% Mn

3-2 Behavior of Al-Mn alloy electrodeposition

It was understood that powdery deposits could be inhibited by the addition of $MnCl_2$ even at high current density. Process variables affecting the Mn content was studied. Relations between Mn^{2+} concentration in molten salt and Mn content in deposited films is shown in Fig.5. Mn content was determined by ICP analysis of the solution, which was obtained by dissolution of Al-Mn alloy deposits in hydrochloric acid. As Mn^{2+} concentration increased, Mn content in film increased linearly. As Al^{3+} concentration in 61mol% $AlCl_3$ molten salt was about 15wt%, it is understood that Mn deposited preferentially and condensed in deposited films. In Fig.6 (a),(b),(c) effects of current density, flow rate, $AlCl_3$ composition on Mn content in films are shown respectively. As $AlCl_3$ in molten salt reached to eutectic composition, smooth and bright film was deposited. But in lower $AlCl_3$ composition, deposits were powdery at high current density. In the eutectic composition, Mn content in film was virtually independent on plating conditions such as flow rate and current density. This alloy deposition seems to be like reaction rate determining. The behavior of Al-Mn alloy electrodeposition is similar

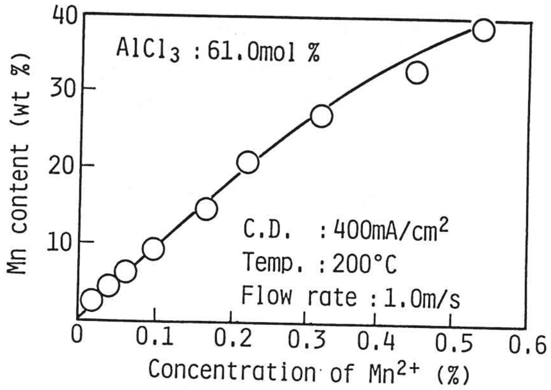
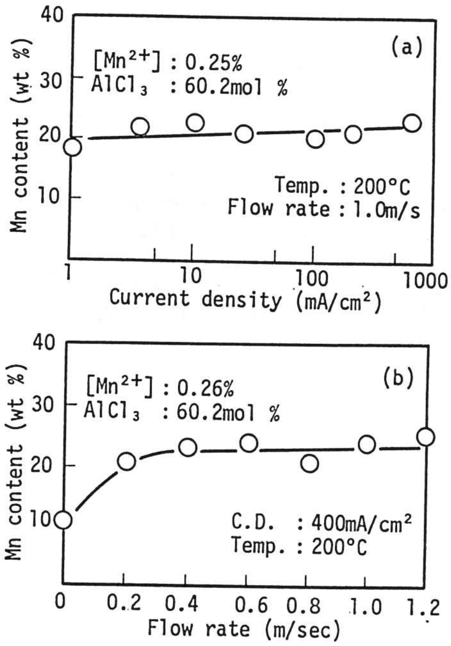


Fig.5 Relationships between Mn^{2+} concentration and Mn content in film



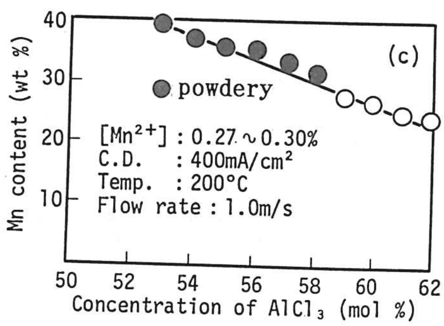


Fig.6 Influence of electroplating conditions on Mn content
(a) influence of current density
(b) influence of flow-rate
(c) influence of bath composition

to anomalous codeposition of tow element from aqueous solution. Further mechanistic studies are essential to fully explain this complex electrodeposition behavior in future.

Consequently, from point of view of manufacturing pre-coated steel sheet, this results are considered to be a great advantage to the stability of alloy plating.

3-3 Continuous bench-scaled test

Reel to reel strip plating tests were conducted in a miniature bench-scaled electroplating equipment to investigate key design factors for continuous electroplating from molten salt which cannot be confirmed by batchwise laboratory experiments, such as plating parameter, molten salt bath control, pre-treatment process and so on. Table 1 shows the test conditions of the bench test. The molten salt for plating was used for a period of approximately 7 months without significant deterioration. Most attentions were paid to the moisture from atmosphere and Fe ion from anode activation section as impurities. The moisture reacts with molten salt and reduced effective $AlCl_3$ concentration by the following reaction:

$$H_2O + AlCl_4^- \rightarrow AlOCl_2^- + 2HCl \quad (5)$$

And the appearance of plated surface became worse by accumulation of Fe ion. The moisture could be eliminated by use of N_2 atmosphere and Fe ion was effectively removed by replacement reaction of granular Al. As the soluble anode, which was made of Al-Mn alloy pellet, was used, film content and salt composition could be controlled within the limit of aimed values. It was also confirmed that anodic activation in fused salt after drying and pre-heating step gave the good adhesion at a suitable condition, by removing oxide film on steel substrate. As shown in Fig.7, the film with a smooth surface covered the steel strip even at 800 mA/cm^2 which was maximum current density of the bench-scaled equipment. This was attributed to the provision with high and uniform flow rate of fused salt fluid. Photo.5 shows a Al-Mn alloy electroplated steel strip coil which were produced experimentally by the bench-scaled equipment.

Table 1 Overall testing conditions of Al-Mn alloy continuous plating

Test period	212 days
Total quantity of electricity	105 x10^{6}C
Total quantity of electrodeposition	12.0kg
Total time of electrodeposition	90h
Number of coils	50 coils

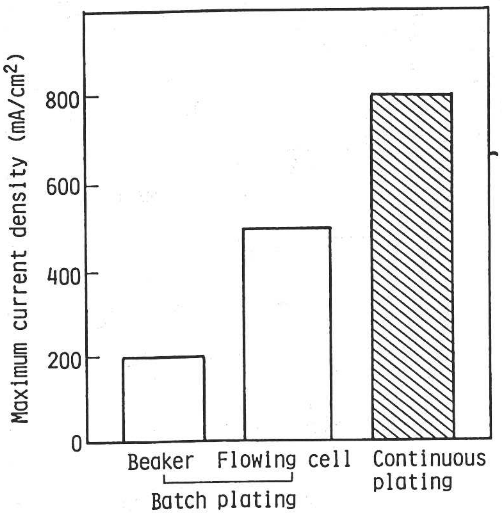


Fig.7 Maximum current density reached for smooth faced electroplating coatings

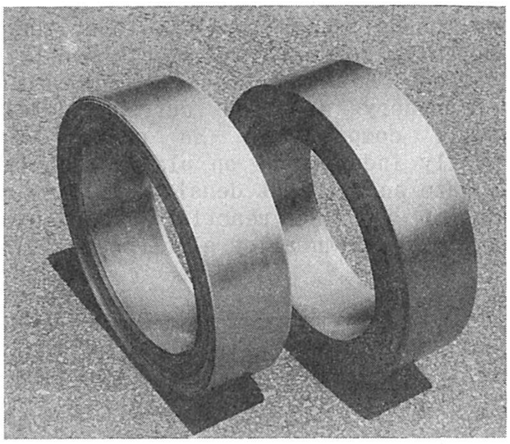


Photo.5 Al-Mn alloy coated steel coils

4. Conclusions

With the purpose to develop a new pre-coated steel, research and development of Al-Mn alloy electroplating process were conducted using a molten salt electrolysis method. Extensive investigations were performed with the goal to develop the technology for practical uses, in particular, to get a smooth faced coating at high current density. As a result, a smooth faced and also amorphous coatings were obtained at high current density of 800mA/cm^2 . The composition of Al-Mn alloy was independent on current density and flow rate of molten salt fluid. And continuous steel strip coil plating process was examined by the bench test for approximately 7 months for the purpose of industrial application.

5. References

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