EFFECTS OF THE PROCESSING AND MAGNESIUM CONTENTS ON THE COLOR OF ANODIZED AL-MN SHEETS

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ABSTRACT The effects of heat treatment and Magnesium content on the color of the anodic coatings of Al-Mn alloy sheets were investigated using both strip cast Al-2.0%Mn base alloy and laboratory cast Al-1.2%Mn base alloy. In the case of strip cast sheet, the L* value of anodic coating was the minimum of 36 when the alloy was heat treated at 698K. In the case of the more slowly cast Al-1.2%Mn with 3.5% Magnesium alloy, the color of the anodic coating becomes dark and colorless at a low homogenizing temperature and L* value is 35 at the homogenizing temperature of 723K. It is understood that Magnesium accelerates the precipitation of Mn_6Al in this alloy system.
Keywords: *Aluminum-Manganese alloy, color of anodic coatings, heat treatment, precipitation, sulfuric anodizing*

1. INTRODUCTION

Aluminum alloys containing manganese in solid solution are known to yield tan to brownish anodic coatings, whereas manganese imparts dark gray to black color to anodic coatings when it precipitates as fine Al_6Mn particles. Al_6Mn precipitates remain as metallic state in the anodic coatings and the incident light is scattered by these particles and absorbed , resulting in dark gray to black anodic coatings. These black anodic coatings are recognized to exhibit a excellent far-infrared emissivity therefore it is important to investigate more detailed relationships between the color of the anodic coatings and metallurgical conditions. In this study, the effects of heat treatment and Magnesium content on the color of the anodic coatings of Al-Mn alloy sheets were investigated using both strip cast Al-2.0%Mn alloy and laboratory cast Al-1.2%Mn alloy .

2. EXPERIMENT

The effects of heat treatment and Magnesium content on the color of the anodic coatings of Al-Mn alloy sheets were investigated on rapid cooled strip cast alloy and slowly cooled laboratory cast alloy . First, Al-2.04mass%Mn-0.51mass%Mg-0.13mass%Fe alloy was strip cast to 7mm thick 1000mm wide thin sheet by 3C process. The eutectic concentration of manganese is known as 1.9 %[1] according to the Al-Mn equilibrium diagram. In the case of strip cast sheet, the molten metal is rapidly solidified by a water cooled twin roll[2] . This enables to cast the hyper eutectic Al-Mn alloy without coarse primary crystals and forces manganese to be in solid solution beyond the equilibrium limit. The strip cast coil was cold rolled to 1.0mm thick and then subjected to the final annealing at 623K to 723K for 18ks.

Next, the experiments using the laboratory cast ingots in book mould were conducted. In this case, the cooling rate is slow compared with the strip cast sheets and there are possibilities of coarse primary crystals to form in hyper eutectic alloys. Therefore, the manganese contents of the experimental alloys were reduced to hypo-eutectic 1.2mass% with different magnesium contents from trace level to 3.5mass% as shown in Table 1. The alloys were cast in 25mm × 180mm × 180mm copper mould. The ingots were homogenized at 723K, 773K, 823K, 873K for 36ks then cold rolled to 1.2mm thick.

Both final sheets were 20 μ m etched in 5vol% caustic solution and anodized in sulfuric acid solution. Here, the concentration of sulfuric acid, current density and temperature was 15vol%, $1.5Adm^{-2}$ and 293K respectively. The color of the anodic coating was expressed by Hunter color system, L*, a*, b* . TEM and optical microstructure were observed. The etching condition was 5%NaOH at 293K for 40 seconds.

Next, an experiment was carried out to investigate the effect of magnesium content on the solute manganese concentration using Al-1% Mn high purity base alloy with 0, 0.5 and 3% Mg. The alloys listed in Table 2 were laboratory cast in a book mould and were subjected to cold rolling and heat treatment at 475K-723K for 18ks. Solute manganese concentration was analyzed directly by the phenol filtrate method[3].

Spectral emissivity was determined for some of the anodic coatings to certify the infrared property.

Table 1 Chemical compositions of specimens (mass%)

Mn	Mg	Fe	Si	Cr	Ti
1.19	tr	0.12	0.10	0.20	0.02
1.21	0.61	0.11	0.11	0.20	0.02
1.20	1.49	0.11	0.11	0.19	0.02
1.19	2.03	0.11	0.10	0.18	0.02
1.23	2.51	0.12	0.10	0.21	0.02
1.20	3.01	0.11	0.10	0.21	0.02
1.21	3.49	0.12	0.11	0.19	0.02

Table 2 Chemical compositions of specimen (mass%)

	Mn	Mg	Fe	Si	Cr	Ti
1Mn	1.06	tr	0.03	0.01	tr	tr
1Mn-0.5Mg	1.02	0.49	0.03	0.02	tr	tr
1Mn-3Mg	1.06	3.02	0.03	0.02	tr	tr

3. RESULT

3.1 The color of anodized sheets of strip cast Al-Mn alloy.

The effect of the annealing temperature on the color of anodic coatings on strip cast Al-Mn sheets is shown in Fig.1. It can be recognized that L* value decreases with increasing the annealing temperature till 698K then increases slightly at higher temperature. a* value which indicates reddish color and b* value which indicates yellowish color reduces respectively as the annealing temperature increases. Maximum black anodic coatings with mono color tone can be obtained at the annealing temperature of 698K in this alloy. Generally, the L* value under 40 is enough to feel black by naked eye.

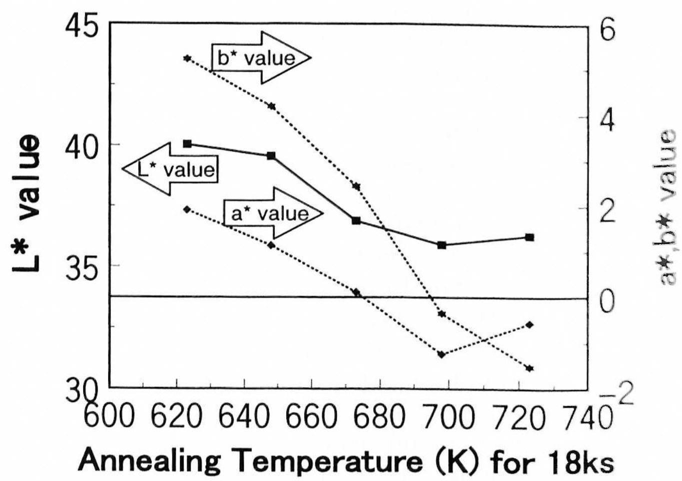


Fig.1 Effect of annealing temperature on the color of the anodic coatings of the strip cast Al-2.0%Mn-0.5%Mg alloy.

Fig.2 shows the effect of annealing temperature on the electric conductivity of annealed sheets. The electric conductivity increases as the annealing temperature increases. It indicates that the precipitation proceeds at higher annealing temperature. TEM microstructures of the specimen annealed at 623K and 723K for 18ks are shown in Fig.3. The sizes of precipitates annealed at 723K are about 0.4 to 0.5 μm whereas that of at 623K are smaller than 0.2 μm. These precipitates were identified as Al_6Mn by electron diffraction pattern. Supersaturated solute manganese dew to high cooling rate at the strip casting will precipitates as a large number of fine Al_6Mn particles. In the case of the alloy annealed at a low temperature, the slightly reddish and yellowish anodic coatings might due to the facts that the size of precipitation is very small or a considerable amount of solute manganese remains in matrix.

Optical microstructure of thin sulfuric anodic coating is shown in Fig.4. The thickness of the coating is about 1 to 2 μm.

Fine black particles can be recognized in the anodic coating. It is known that Al_6Mn phase is not oxidized during sulfuric anodizing[4,5]. Therefore, fine and dense Al_6Mn particles remain as metallic phase in the sulfuric anodic coatings. Black color can be obtained because the incident light is multiply reflected by these metallic particles and is absorbed in the anodic coatings

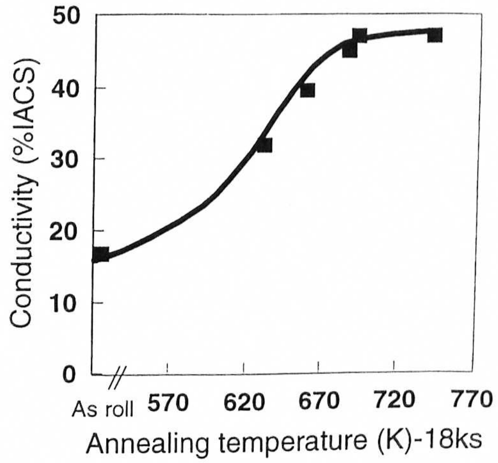
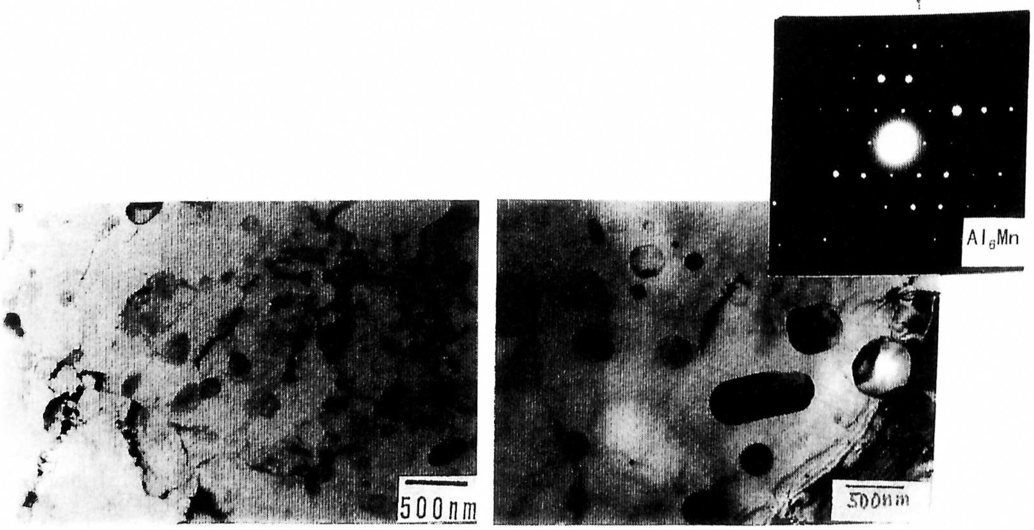


Fig.2 Effect of annealing temperature on the conductivity of the cold rolled sheet of strip cast Al-2.5%Mn-0.5%Mg alloy.



(a) 623K **(b) 723K**

Fig.3 TEM microphotographs of the strip cast Al-2.0%Mn-0.5%Mg alloy sheet showing fine Al_6Mn particles precipitated during annealing.

3.2 The color of anodized sheets of Al-Mn alloy cast in book mould.

The effects of homogenization conditions and magnesium contents on the color of anodized rolled sheets from the book mould ingot was next investigated. There are the possibilities of undesirable large primary Al_6Mn crystals to develop in high manganese alloy because the cooling rate of a book mould ingot is slow compared with that of a strip cast sheet. Therefore, manganese contents of the experimental alloys were reduced to 1.2%.

Fig.5 shows the effects of magnesium content and homogenizing temperature on L* value of the anodic coatings. It is found from this result that magnesium affects much on the color of anodic coating of the alloy. L* value of anodized sheets of the alloy containing 2.0%Mg or less are quite high regardless of the homogenizing temperature. When magnesium content exceed 2.0% , the influences of magnesium and homogenizing temperature on the color of anodic coatings become obvious. The color of anodic coatings becomes darker and colorless at lower homogenizing temperature. L* value of anodic coating on the alloy sheet containing 3.5%Mg is about 35 at the homogenizing temperature of 723K. This is almost similar to that of the blackest anodic coating on the strip cast rolled sheet containing 2.0% manganese. It is also noticed that the effect of homogenizing temperature becomes marked at higher magnesium content. L* value of the alloy containing 3.5%Mg changes very much from 35 to 75 with changing the homogenizing temperature. Optical microstructures indicating Al_6Mn precipitates are shown in Fig.6. It can be recognized that the fine precipitates of the alloy containing 3.5%Mg are much increased compared with that of the Mg free alloy. It is rather difficult to obtain the fine and dense Al_6Mn distribution enough for black color anodic coating on the laboratory cast Al-1.2%Mn base alloy sheets because the solute manganese concentration of the alloy is lower than that of strip cast Al-2%Mn alloy. However, it can be understood that in the case of the alloy containing more than 2%Mg, the precipitation of Al_6Mn is accelerated by magnesium and the desirable precipitate distribution for black anodic coatings are obtained.

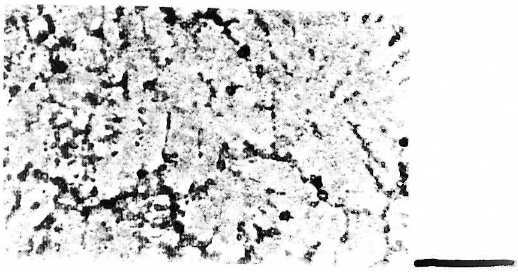


Fig.4 Optical microstructure of sulfuric anodic coating on the strip cast Al-2.0%Mn-0.5%Mg alloy sheet annealed at 723K for 36ks. Thickness of the anodized film is 1~2 μm.

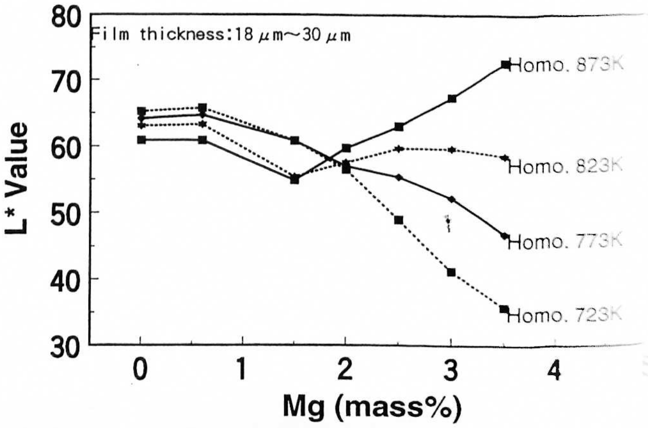


Fig. 5 Effects of Mg concentration and homogenizing temperature on L* value of anodized sheets of Al-1.2%Mn base alloys.

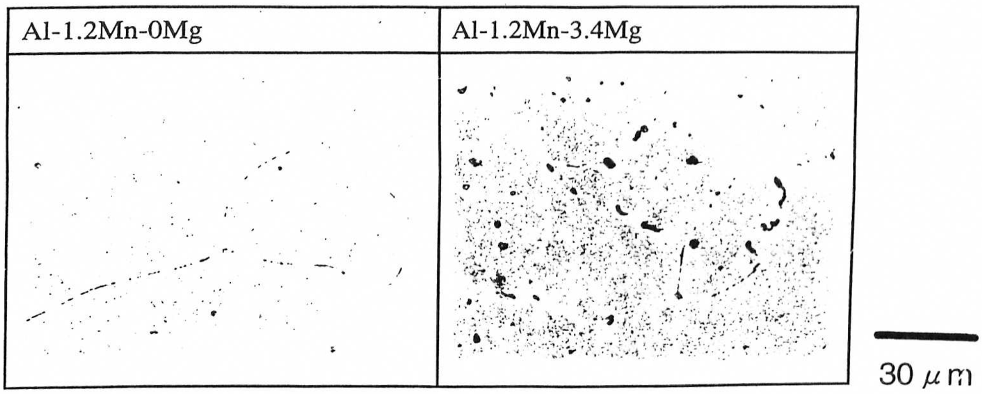


Fig.6 Microstructures of 1.2%Mn-0.19%Cr base alloys with different Mg contents after homogenizing at 773K for 36ks. (Etching condition: 1%NaOH, 293K-40s)

Fig.7 shows the effect of magnesium content on a solute manganese concentration change after annealing at different temperature. Solute manganese concentration of each alloy is about 1% before annealing indicating that manganese exists almost entirely in solid solution.

It is also found out that magnesium accelerates manganese precipitation especially in the case of the alloy containing 3%Mg. In the case of Al-1%Mn-3%Mg, solute manganese concentration decreases rapidly at higher annealing temperature. The solute manganese concentration after annealing at 673K is reduced to 0.18% which is about a half of that of Mg free Al-1%Mn alloy. It is reported that equilibrium solute manganese concentration decreases with increasing magnesium content[6] and this might be the reason for the acceleration of manganese precipitation. The phase of precipitates extracted by phenol residue method was identified as Al_6Mn by X-ray diffraction pattern.

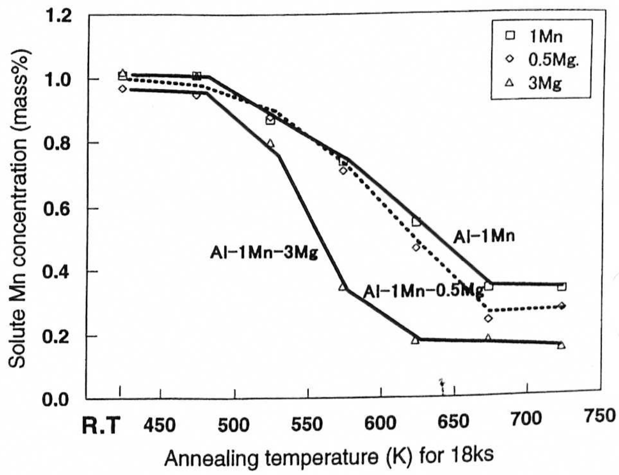


Fig.7 Effect of Mg content on solute Mn concentration change on annealing

3.3 Infrared property of black anodic coatings

Spectral emissivity of the anodic coating on the strip cast sheet annealed at 673K was shown in Fig.8. It can be seen that excellent far infrared

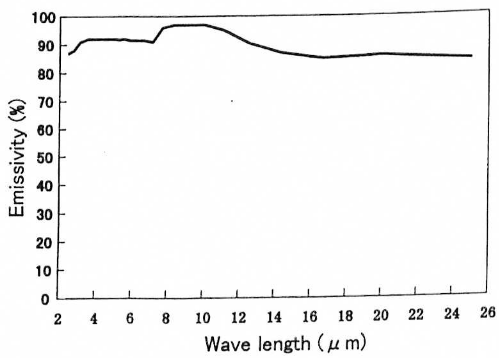


Fig.8 Spectral emissivity of the anodic coating on the Al-2.0%Mn-0.5%Mg sheet annealed at 673K. Measured temperature was 573K.

property was obtained.

4. CONCLUSION

The effects of heat-treatment and magnesium content on the color of anodic coatings on Al-Mn alloy sheets produced from strip cast sheet and laboratory cast ingot in book mould were investigated.

It concluded as follows.

1) In the case of the strip cast Al-2.0%Mn-0.5%Mg sheet, black anodic coating was obtained by annealing at 623K~723K.
2) Annealing condition for minimum L* value was 698K-18ks. In this case, the color of anodic coating seems black and colorless.
3) Fine and dense Al_6Mn precipitates from 0.1 to 0.5 μ m in size were recognized in annealed sheets. The size of Al_6Mn precipitates in the sheet annealed at 698K were larger than that of 623K.
4) Al_6Mn precipitates were found to remain as metallic phase in anodic coatings. It is concluded that the dark and black color of anodic coating is originated from these metallic particles in the coating.
5) In the case of laboratory book mould cast Al-1.2%Mn base sheets, dark and black anodic coatings can not be obtained from the alloy with 2%Mg or less.
6) The color of anodic coatings becomes dark and colorless with increasing magnesium content and with decreasing homogenizing temperature on the alloy of Al-1.2%Mn containing 2% Mg or more.
7) The color of anodic coating on Al-1.2%Mn-3.5%Mg sheets homogenized at 723K for 36ks was almost the same as the blackest anodic coating on strip cast Al-2.0Mn-0.5Mg sheets.
8) Solute manganese concentration after heat treatment was recognize to decrease with increasing magnesium content and it is understood that the color of anodic coating on the alloy containing magnesium becomes dark and black because the precipitation of Al_6Mn is accelerated by magnesium.
9) Good far infrared emissivity was recognized in some of the black anodic coatings on the investigated alloy sheets.

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