THERMAL CRACKING OF ANODIC COATINGS ON ALUMINUM ALLOYS

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ABSTRACT Factors influencing thermal cracking of sulfuric acid anodic coatings on aluminum alloys were investigated. The anodic coatings was prepared to be $20\,\mu$ m in thickness and sufficiently sealed by using nickel acetate type sealer. Susceptibility to thermal cracking of the anodic coatings was higher for 2014 and 7075 alloys containing copper than for copper free alloys. Anodic coatings containing hard particles, such as the coatings on 4104 alloy, showed low susceptibility to thermal cracking. The cracking occurred by heating at lower temperature for the coatings formed with higher anodizing temperature and lower current density. Possibility of application of a cracked anodic coating to undercoating for a fluorocarbon resin coating is also shown in this paper.

Keywords: sulfuric acid anodic coatings, 1XXX-7XXX alloys, thermal cracking, fluorocarbon resin coatings

1. INTRODUCTION

It is well known that heating causes cracking or crazing of anodic coatings on aluminum alloys¹⁾. For many uses, the cracks are considered harmful to soundness and durability of the anodic coatings. On the other hand, the anodic coatings with cracks can be useful for keeping implegnants such as lubricants, and for undercoatings for some resin coatings. It is important to improve understanding of the thermal cracking behavior of the anodic coatings from both standpoints of prevention and application of the cracking.

In this work, thermal cracking behaviors of sulfuric acid anodic coatings on aluminum alloys have been investigated fundamentally. Effects of alloy type, anodizing temperature and current density are discussed in this paper. And, as an example of application of the cracking, this paper also shows the possibility of usage of the cracked anodic coating as undercoating for a fluorocarbon resin coating.

2. FACTORS INFLUENCING THERMAL CRACKING BEHAVIOR

2.1 EXPERIMENTAL PROCEDURE

Sulfuric acid anodic coatings on various aluminum alloys in 1XXX - 7XXX series shown in Table 1 were evaluated for thermal cracking behavior. Sheet samples of these alloys used in this investigation were 1mm in thickness. T6 temper was employed for heat treatable 2014, 6061, 7075 and Al-5.5Zn-2.5Mg-1.6Mn alloys, and O temper was employed for the other alloys. Fig.1 shows a procedure of sulfuric acid anodizing treatment including pretreatment and sealing. Prior to anodization, the aluminum alloy sheets were etched in NaOH solution and desmuted in HNO₃ solution. They were anodized in a 15%H₂SO₄ solution at 10–30°C with current densities of 1.5 and 3 0A/dm², and the anodic coatings were produced to be 20 μ m in thickness. Then the coatings were

were investigated. Table2 shows the thermal cracking behavior of the coatings anodized at 20° C and 1.5A/dm^2 for the various alloys. In this table, the alloys are classified into (I)-(IV) classes according to susceptibility to thermal cracking of the anodic coatings.

The anodic coatings on 2014 and 7075 alloys in the class(I) containing copper showed high susceptibility to thermal cracking. For instance, cracks forming a fine network were seen on the anodized surface of 2014 alloy after sealing at 95°C, as can be seen in Photo.1(I). The coatings on these alloys were softer than the coatings on the other alloys. It is clear from comparison of the results of 7075 (Al-5.5%Zn-2.5%Mg-0.6%Cu) alloy and Al-5.5%Zn-2.5%Mg-1.6%Mn alloy that copper served to reduce hardness and to increase the susceptibility to thermal cracking.

In contrast, the coating on 4104 alloy in the class(IV) containing silicon particles had low susceptibility to thermal cracking. As can be seen in Photo.1(IV), no crack were found on the anodic coating on this alloy even after heating at 180°C. Susceptibility to thermal cracking was medium or a little high for the anodic coatings on 1100, 5052 and 5083 alloys in the class(II), and that is medium or a little low for the coatings on 3003, Al-1.6Mn, 6061 and Al-5.5Zn-2.5Mg-1.6Mn alloys in the class (III).

Effects of anodizing temperature and current density on thermal cracking behavior are shown in Table 3 and Photo.2. The higher anodizing temperature and the lower current density resulted in the higher susceptibility to thermal cracking of the anodic coatings. The coatings anodized at 30°C were soft and had cracks already after sealing at 95°C, while the coating anodized at 10°C had high hardness and much less susceptibility to thermal cracking.

In general, cracking problem occurs often for hard anodic coatings. However, from our results for the 20 μ m thick sulfuric anodic coatings sealed sufficiently, it can be said that soft coatings tend to be cracked easily even by heating at relatively low temperature. The soft and weak coatings are formed when chemical dissolution of the coatings and their constituents is active during anodizing, for example, when base metal is a copper-bearing alloy or anodizing temperature is high. The anodic coatings having high hardness shows low susceptibility to thermal cracking. In particular, the coatings with distribution of particles such as silicon particles in 4104 alloy or Al₆Mn particles in the Al-Mn alloys are low in thermal cracking susceptibility. The reduction in susceptibility is explained that those hard particles depress stress concentration and crack initiation.

The thermal cracks on the soft coatings formed a fine network. When the harder coatings were cracked by heating, the cracks formed the coarser network or straight line shape. It should be noted that the cracks with a coarser network or straight-line shape might be harmful from an appearance standpoint.

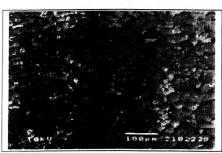
Generally, avoiding heating at 110°C or more high temperature is recommended in order to prevent thermal cracking of anodic coatings²⁾. However, we believe from our experimental results that it is possible to obtain crack free anodic coatings even after heating at 140-180°C by employing proper alloys and anodizing conditions. Relatively low anodizing temperature and high current density are desirable for preventing thermal cracking.

As for application of cracking of anodic coatings to pretreatment of fluorocarbon resin coatings, a fine crack network is required. An example of this application will be given next.

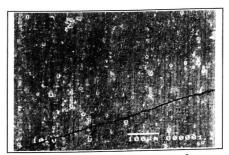
Table 3 Effects of Anodizing temp, and current density on thermal cracking behavior of the coatings on 7075,5052 and Al-1.6Mn alloys.

| of the coatings of 7070,0002 and 71 1.00m alloys. | | | | | | | | | | |
|---|-----------|---------|-----------------|------------------------|-------------------------|------------------------|------------------------|------------------------|--|--|
| Alloy | Anodizing | | Microhardness | Cracks | | | | | | |
| | temp. | current | of the coatings | as sealed | after heating for 30min | | | | | |
| | | density | | | | | | | | |
| | °C | A/dm² | HM∨ | at 95°C | at 100°C | at 140°C | at 180°C | at 220°C | | |
| 7075 | 30 | 1.5 | * | × (40 μ m) | \times (40 μ m) | × (30 μ m) | \times (20 μ m) | × (20 μ m) | | |
| | 20 | 1.5 | 230 | \times (100 μ m) | \times (100 μ m) | × (80 μ m) | \times (70 μ m) | \times (70 μ m) | | |
| | | 3 | 297 | 0 | 0 | × (500 μ m) | \times (300 μ m) | \times (250 μ m) | | |
| | 10 | 1.5 | 317 | 0 | 0 | × (>1mm) | \times (600 μ m) | \times (400 μ m) | | |
| 5052 | 30 | 1.5 | 244 | \times (50 μ m) | \times (50 μ m) | \times (50 μ m) | \times (50 μ m) | \times (30 μ m) | | |
| | 20 | 1.5 | 390 | 0 | × (>1mm) | \times (700 μ m) | \times (400 μ m) | \times (300 μ m) | | |
| | | 3 | 387 | 0 | 0 | × (>1mm) | × (>1mm) | \times (400 μ m) | | |
| | 10 | 1.5 | 416 | 0 | 0 | × (>1mm) | × (>1mm) | \times (500 μ m) | | |
| 1.6Mn | 30 | 1.5 | 305 | \times (50 μ m) | \times (50 μ m) | \times (50 μ m) | \times (30 μ m) | \times (30 μ m) | | |
| | 20 | 1.5 | 416 | 0 | 0 | × s | x s | × s | | |
| | | 3 | 416 | 0 | 0 | O s | x s | × s | | |
| | 10 | 1.5 | 446 | 0 | 0 | 0 | 0 | × s | | |

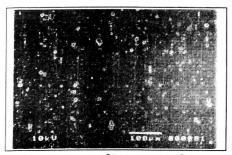
- X: Cracks exist, O: No crack exists.
-): Estimated average size of a unit of crack network.
- S : straight line type cracks
- * too soft to measure microhardness.



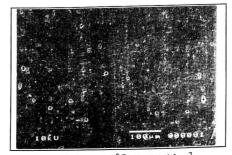
Anodizing:30°C,1.5A/dm²



Anodizing:20°C,1.5A/dm²



Anodizing:20°C,3.0A/dm²



Anodizing:10°C,1.5A/dm²

Photo.2 Scanning electron micrographs of surfaces of the anodic coatings on 5052 alloy after heating at 100° C at 30min.

were investigated. Table2 shows the thermal cracking behavior of the coatings anodized at 20° C and 1.5A/dm^2 for the various alloys. In this table, the alloys are classified into (I)-(IV) classes according to susceptibility to thermal cracking of the anodic coatings.

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Effects of anodizing temperature and current density on thermal cracking behavior are shown in Table 3 and Photo.2. The higher anodizing temperature and the lower current density resulted in the higher susceptibility to thermal cracking of the anodic coatings. The coatings anodized at 30°C were soft and had cracks already after sealing at 95°C, while the coating anodized at 10°C had high hardness and much less susceptibility to thermal cracking.

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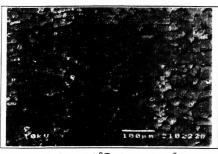
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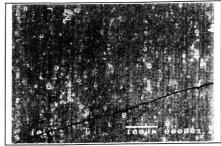
Table 3 Effects of Anodizing temp. and current density on thermal cracking behavior of the coatings on 7075,5052 and Al-1.6Mn alloys.

| Alloy | Anodizing | | Microhardness | Cracks | | | | | |
|-------|-----------|---------|-----------------|------------------------|-------------------------|------------------------|------------------------|------------------------|--|
| | temp. | current | of the coatings | as sealed | after heating for 30min | | | | |
| | | density | Esperador de | | | | | | |
| | °C | A/dm² | HM∨ | at 95°C | at 100°C | at 140°C | at 180°C | at 220°C | |
| 7075 | 30 | 1.5 | * | \times (40 μ m) | \times (40 μ m) | × (30 μ m) | × (20 μ m) | \times (20 μ m) | |
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| | | 3 | 297 | 0 | 0 | × (500 μ m) | \times (300 μ m) | \times (250 μ m) | |
| | 10 | 1.5 | 317 | 0 | 0 | × (>1mm) | \times (600 μ m) | \times (400 μ m) | |
| 5052 | 30 | 1.5 | 244 | \times (50 μ m) | × (50 μ m) | \times (50 μ m) | \times (50 μ m) | \times (30 μ m) | |
| | 20 | 1.5 | 390 | 0 | × (>1mm) | \times (700 μ m) | \times (400 μ m) | \times (300 μ m) | |
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| 1.6Mn | 30 | 1.5 | 305 | \times (50 μ m) | \times (50 μ m) | × (50 μ m) | \times (30 μ m) | \times (30 μ m) | |
| | 20 | 1.5 | 416 | 0 | 0 | × s | × s | × s | |
| | | 3 | 416 | 0 | 0 | O s | × s | × s | |
| | 10 | 1.5 | 446 | 0 | 0 | 0 | 0 | × s | |

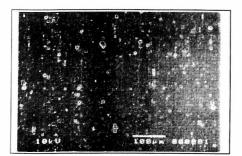
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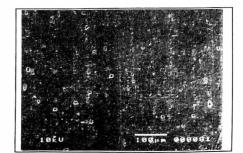
Anodizing:30°C,1.5A/dm²



Anodizing:20°C,1.5A/dm2



Anodizing:20°C,3.0A/dm²



Anodizing:10°C,1.5A/dm²

Photo.2 Scanning electron micrographs of surfaces of the anodic coatings on 5052 alloy after heating at 100°C at 30min.

3. Application of anodized coatings with cracks

Parts made of an Al-Mg alloy containing 3mass%Mg were anodized at 25°C and sealed with commercial scale equipment. Then the $20\,\mu$ m thick anodic coatings on the parts were finely cracked by heating. Fluorocarbon (PFA) resin was coated on the parts by electrostatic spraying and cured.

SEM observation of the PFA coating separated from the base metal reveals that the PFA resument into the network of cracks of the anodic coating sufficiently. This anodic coating cracked properly was recognized to improve adhesion of the fluorocarbon resin coating.

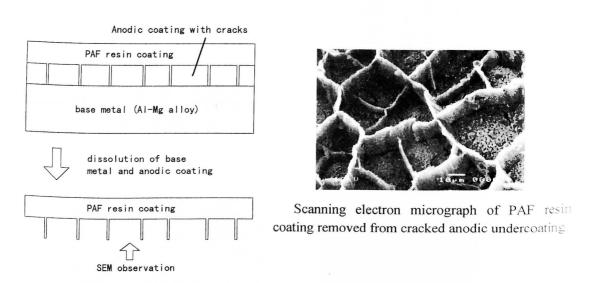


Fig.3 SEM observation of PAF resin coating separated from cracked anodic undercoating

4. CONCLUSION

The sulfuric acid anodic coatings on 2104 and 7075 alloys containing copper showed low hardness and high susceptibility to thermal cracking. The coating on 4104 alloy containing silicon particles had low susceptibility to thermal cracking. The susceptibility increased with increasing anodizing temperature and decreasing current density. Fine network of cracks was formed on the coating with low hardness and high cracking susceptibility.

The anodic coating with fine network of cracks could be applied to undercoating for PAF result coating.

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