

S. SUNADA\*, N. NUNOMURA\*\*

**ELECTROCHEMICAL IMPEDANCE CHARACTERISTICS OF SINTERED 7075 ALUMINUM ALLOY UNDER SSRT CONDITION**

**CHARAKTERYSTYKA SPIEKU STOPU ALUMINIUM 7075 METODĄ ELEKTROCHEMICZNEJ SPEKTROSKOPII IMPEDANCYJNEJ (EIS) W WARUNKACH PRÓBY ROZCIĄGANIA Z MAŁĄ PRĘDKOŚCIĄ ODKSZTAŁCENIA (SSRT)**

Powder metallurgy (P/M) process has the advantage of better formability to fabricate complex shape products without machining and welding. And recently this P/M process has been applied to the production of aluminum alloys. The P/M aluminum alloys thus produced also have received considerable interest because of their fine and homogeneous structure. Many papers have been published on the mechanical properties of the aluminum alloys produced by P/M process while there have been few on their corrosion properties from the view point of electrochemistry. In this experiment, therefore, two kinds of 7075 aluminum alloys prepared by the conventional ingot metallurgy (I/M) process and P/M process were used, I/M material is commercially available, and their corrosion behavior were investigated through the electrochemical tests such as potentiodynamic polarization test, slow rate strain tensile (SSRT) test and electrochemical impedance spectroscopy (EIS) measurement under SSRT test in the corrosion solution and the deionized water.

*Keywords:* sintered material, pitting corrosion, electrochemical impedance spectroscopy

Zaletą procesu metalurgii proszków (P/M) jest lepsza formowalność podczas wytwarzania produktów o złożonym kształcie nie wymagająca późniejszej obróbki mechanicznej i spawania. Ostatnio ten proces stosowano do wytwarzania stopów aluminium. Tak wytworzone stopy aluminium spotkały się z dużym zainteresowaniem ze względu na ich rozdrobnioną i jednorodną strukturę. Opublikowano wiele prac na temat właściwości mechanicznych stopów aluminium wytworzonych metodą metalurgii proszków, ale niewiele jest prac poświęconych ich korozji z punktu widzenia elektrochemii. W przedstawionej pracy badano korozję dwóch rodzajów stopu 7075, przygotowanych poprzez konwencjonalne odlewanie oraz metodą metalurgii proszków. Badania korozyjne wykonano z wykorzystaniem technik elektrochemicznych takich jak: metoda polaryzacji potencjodynamicznej, próby rozciągania z małą prędkością odkształcenia (SSRT), pomiarów elektrochemicznej spektroskopii impedancyjnej (EIS) podczas próby rozciągania z małą prędkością odkształcenia w roztworze korozyjnym oraz w wodzie dejonizowanej.

**1. Introduction**

It is well known that the aluminum alloys are widely used in the aerospace industry due to their high strength and low density, and, recently, the P/M aluminum alloys have received considerable attention because of their fine and homogeneous structure. Though several papers have been published on the mechanical properties of the aluminum products fabricated by the P/M process, very few studies have been reported regarding their corrosion behavior. In this study, the electrochemical impedance spectroscopy (EIS) measurement [1-6] under slow strain rate tensile (SSRT) test was carried out in order to clarify the corrosion behavior under stress for the P/M specimen process compared with the I/M process and the 0.6 M NaCl + 0.1 mM HCl was used for the corrosion test solution. The impedance spectroscopy test was performed in the frequency range from 100 kHz to 1.0 mHz. This corrosion type is the active pass corrosion stress corrosion cracking (APC-SCC) originated the pitting corrosion.

**2. Experimental**

Two kinds of specimens fabricated by I/M and P/M process were used in this experiment, and their shape and dimensions were indicated in Fig. 1, where the gage length is 10 mm as shown by GL in the figure.

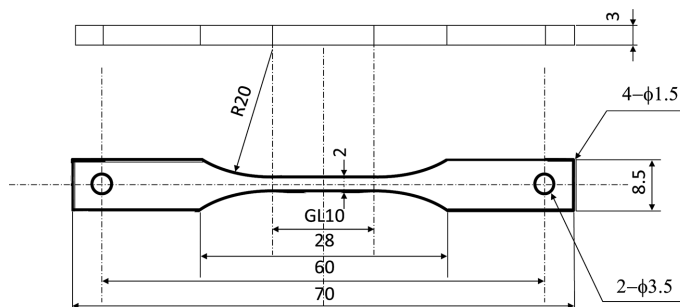


Fig. 1. Shape of specimen for SSRT test

\* GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR RESEARCH, UNIVERSITY OF TOYAMA, JAPAN

\*\* INFORMATION TECHNOLOGY CENTER, UNIVERSITY OF TOYAMA, JAPAN

The specimen surface was wet-polished with a series of water-proof Emery papers up to No.2000 followed by washing in alcohol and ultrasonic rinsing in acetone. The specimen electrode was coated with silicon rubber leaving an uncoated area of  $1 \times 10^{-4} \text{ m}^2$ . The specimens thus obtained were subjected to SSRT test in the deionized water and NaCl + HCl solution at 303K, where the strain rate of SSRT was kept at  $2.5 \times 10^{-6} \text{ /s}$ . The schematic illustration of the SSRT test apparatus was shown in Fig. 2.

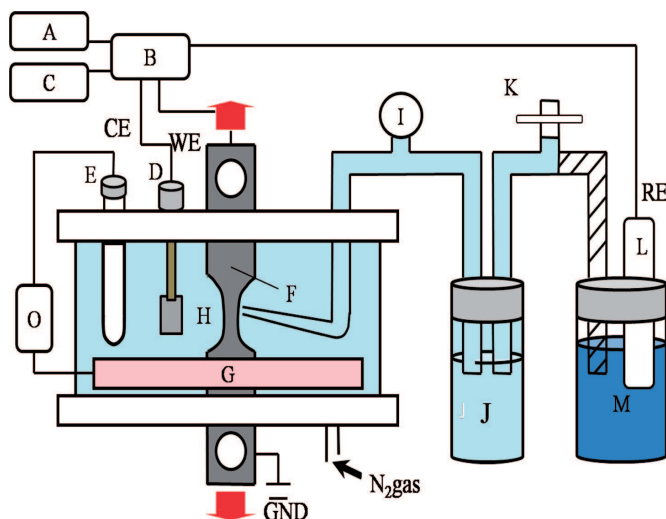


Fig. 2. Experimental apparatus for SSRT test equipped with computer controlled impedance measuring system. A: Computer B: Potentiostat C: FRA D: Counter electrode(Pt) E: Thermo couple F: Specimen G: Heater H: Electrochemical cell I: Bridge J: Intermediate beaker K: Salt Bridge L: Reference electrode M: Saturated potassium chloride solution O: Thermo controller

The test solution in the electrochemical cell shown by H was deoxidized through  $\text{N}_2$  gas flowing and kept at 303 K. All of the potential values were shown based on Ag/AgCl reference electrode. The electrochemical impedance spectroscopy (EIS) measurement was conducted through frequency analyzer (FRA) indicated by C controlling electrochemical potential by B of potentiostat as shown in Fig. 2. The apparatus for impedance measurement consists of thermostatic bath, H-shape electrolytic cell with anodic and cathodic chambers of  $2 \times 10^{-4} \text{ m}^3$  in volume, intermediate cell Ag/AgCl ( $3.33 \text{ kmol/m}^3$  KCl) as a reference electrode, potentiostat, AC impedance meter and a personal computer for the measurement control. The reference electrode was placed outside the cell and connected to the specimen surface by Luggin capillary and a salt bridge. A natural electrode potential with perturbation AC potential, amplitude of which was 10 mV, was applied to the specimen in AC impedance measurements. Analyzing frequency range was from 100 kHz to 1.0 mHz. All of the potential values were indicated based on the Ag/AgCl reference electrode.

### 3. Results and discussion

Two kinds of 7075 aluminum alloys prepared by P/M process and the conventional ingot metallurgy (I/M) process were subjected to SSRT test in order to investigate mechanical properties in deionized water and corrosive solution. The  $\sigma$ - $\epsilon$

curves of P/M specimens and I/M specimens in each circumstance are shown in Fig. 3.

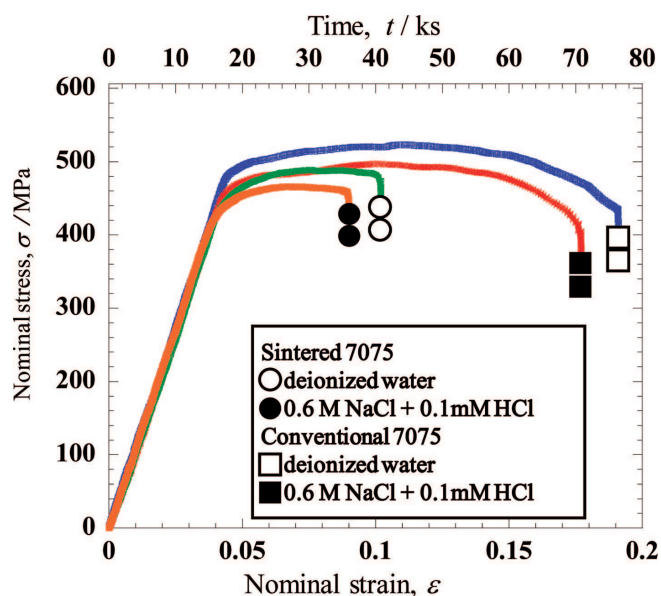


Fig. 3. Stress-strain curves measured at various environments at 303K. Green and orange are sintered 7075. Blue and red are conventional 7075

The P/M specimen showed the maximum stress of 489MPa and the maximum strain of 0.102 and the I/M specimen showed the maximum stress of 523MPa and the maximum strain of 0.191 in the deionized water.

The maximum elongation of P/M is much smaller, 53% of I/M, than that of I/M, while the maximum stress of P/M is almost as same as I/M, 94% of I/M. This result is possibly due to the effect of oxides on powder surface, which are formed during pelletization of aluminum powders in P/M process.

On the other hand, in corrosive solution, the P/M specimen showed the maximum stress of 465MPa and the maximum strain of 0.090 and the I/M specimen showed the maximum stress of 487MPa and the maximum strain of 0.177. Mechanical properties of P/M and I/M specimens in corrosive solution were slightly lower than those in deionized water.

These results imply that some kind of strength deterioration due to corrosion happened in P/M and I/M specimens. However, decrement ratio of mechanical properties in corrosive solution is almost same between both specimens.

Therefore, in order to discuss fracture behavior of 7075 aluminum alloys, produced by P/M and I/M process, in each circumstance, side surfaces of specimens after SSRT test were observed by SEM.

Fig. 4 indicates side surfaces of P/M and I/M specimens after SSRT test in each circumstance. As shown in (b) and (d) of P/M specimen, pit corrosion originated from grain boundary and pseudo grain boundary and connected each other in corrosive solution, while pit corrosion is hardly observed in deionized water.

On the other hand, in I/M specimens as shown in (a) and (c), pit corrosion happens near fracture surface and resulted in grain boundary crack in corrosive solution, while tiny crack is only observed in deionized water. In corrosive solution, plastic deformation, which connects each pit corrosion, is large in I/M specimen and resulted in grain boundary crack. In comparison,

in P/M specimen, pit corrosion occurred along pseudo grain boundary followed by generating cracks.

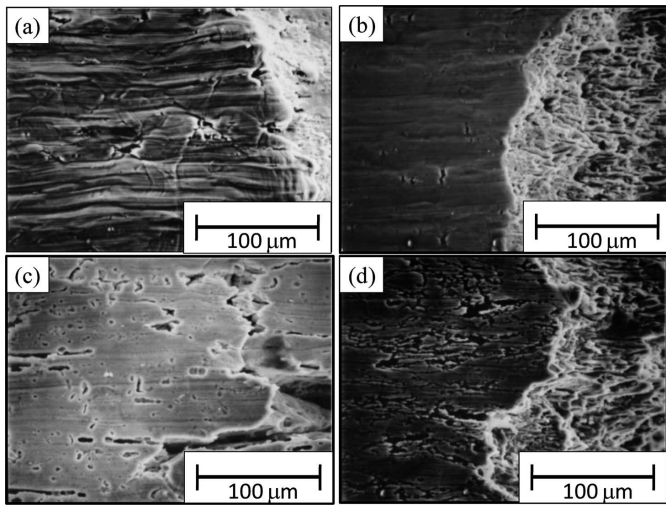


Fig. 4. GL surface of Al alloys after measured SSRT test under various environments. (a) Conventional 7075 and (b) Sintered 7075 at deionized water, (c) Conventional 7075 and (d) Sintered 7075 in 0.6M NaCl + 0.1mM HCl solutions

Consequently, configuration of grain boundary cracks between I/M and P/M are obviously different and larger pit corrosion is observed in I/M specimen because maximum strain of I/M is bigger than that of P/M due to extensive emersion in corrosive solution. That is, it is presumed that SCC originated from pit corrosion and it leads to deterioration of mechanical properties.

Subsequently, the electrochemical impedance spectroscopy (EIS) measurement of P/M and I/M specimens was carried out in order to clarify the effects of applied stress on charge transfer resistance ( $R_{ct}$ ) at specimen boundary.

In EIS test w/o applied stress, under the shutoff of SSRT, measurement was performed at the same elapse time as the measurement point of EIS. Fig. 5 shows the pattern diagrams of obtained impedance trajectory, and those are divided into two major patterns.

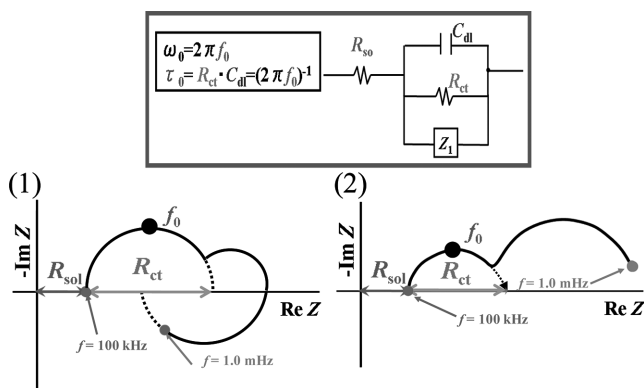


Fig. 5. Schematic Nyquist diagrams of Al alloys measured under SSRT test

When the frequency  $f$  is 100kHz or lower, two capacitive semicircles emerged followed by inductive semicircle as shown in (1), and only two capacitive semicircles were obtained as shown in (2).

Although it is presumed that the difference among these circles is caused by the generation and breaking of passivation film at specimen boundary, generation and breaking of passivation film are assumed to be repeated regardless of with or without stress in P/M and I/M specimens because no regularity related to applied stress and elapse time is observed.

Therefore, temporal change of charge transfer resistance ( $R_{ct}$ ) with and w/o applied stress was investigated by calculating semicircle diameter including that at 100kHz shown in Fig. 5 (1) and (2).

Fig. 6 shows the temporal change of charge transfer resistance ( $R_{ct}$ ) of P/M specimen at each elapsed time in the cases with and w/o applied stress respectively. Initial resistance is  $250\text{--}300 \times 10^{-4} \Omega \cdot \text{m}^2$  in both cases with and w/o stress, and it is inclined to increase to  $500 \times 10^{-4} \Omega \cdot \text{m}^2$  with time. The effect of  $R_{ct}$  on the temporal change is hardly recognized, which is presumably caused by the tiny difference between two cases with and w/o stress due to defects in passivation film including voids and oxides in P/M specimen.

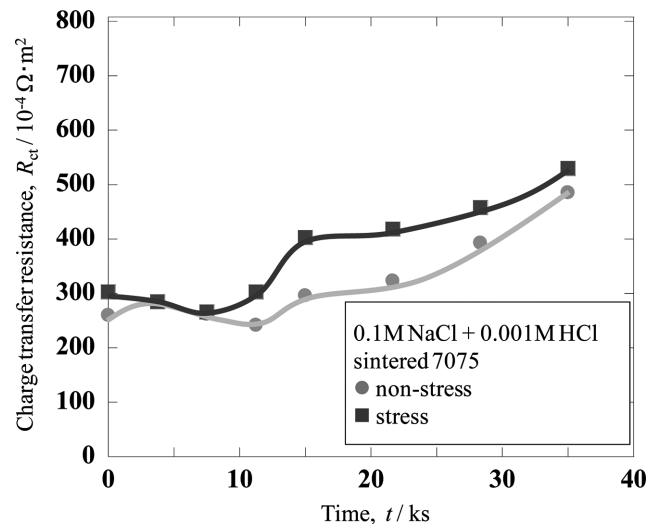


Fig. 6. Influence of time on charge transfer resistance ( $R_{ct}$ ) of sintered 7075 Al alloy

Next, the temporal change of charge transfer resistance ( $R_{ct}$ ) of I/M specimen at each elapsed time in the cases with and w/o applied stress is indicated respectively in Fig. 7. Although initial resistance without stress is  $800 \times 10^{-4} \Omega \cdot \text{m}^2$ , more rapidly decrease of charge transfer resistance ( $R_{ct}$ ) was observed in the condition with stress compared to the case w/o stress. The charge transfer resistance ( $R_{ct}$ ) in the case with stress is inclined to be lower than that of the case w/o stress during elapsed time ranging from 0 to 18ks.

This 18ks corresponds to the elastic area of I/M specimen, and charge transfer resistance ( $R_{ct}$ ) is supposed to decrease more than the case w/o stress, because newly formed surface generated by the breakdown of passivation film accompanied by deformation is exposed. This implies that pit corrosion which isn't effected by the existence or non-existence of stress occurred and the difference between with and w/o stress was reduced.

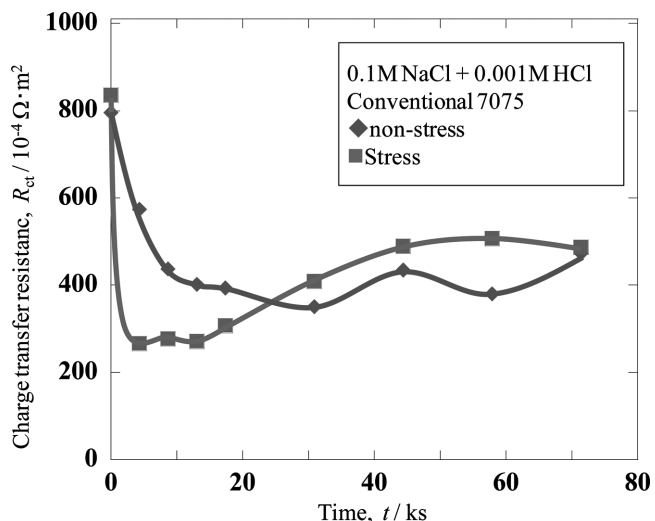


Fig. 7. Influence of time on charge transfer resistance ( $R_{ct}$ ) of conventional 7075 Al alloy

#### 4. Conclusions

The results obtained in this study are summarized as follows. The maximum strain of P/M specimen is approximately half in comparison with that of I/M specimen, although the maximum stresses are almost same between P/M and I/M

specimens. Mechanical properties of P/M and I/M specimens in corrosive solutions deteriorated more than the case in deionized water, which is caused by SCC originated from pit corrosion. The effect of corrosion in corrosive solutions is almost the same between P/M and I/M specimens. The significant temporal change of charge transfer resistance ( $R_{ct}$ ) isn't observed between the cases with and w/o applied stress. In I/M specimen with applied stress, charge transfer resistance ( $R_{ct}$ ) is lower than that of specimen w/o stress in the elastic area.

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