

Structure and Corrosion Behavior of Rapidly Solidified Al-7Mn Alloys

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Abstract

Aluminum alloys are used in manufacturing of some components for nuclear reactors research application. The formed alloy using rapid solidification technique, contains high volume fraction of ultra fine dispersoids which improve the properties of the alloy. Microstructure and thermal stability of rapidly solidified Al-7Mn-2Ni was investigated. The electrochemical behavior of as-rapidly solidified and annealed Al-7% Mn, Al-7% Mn-2% Cr, Al-7% Mn-2% Ni and Al-7% Mn-2%Ti alloys ribbons produced by melt spinning technique were investigated. The rapidly solidified Al-base alloys with addition of small quantities of Cr, Ni and Ti precipitates small dispersoids. These dispersoids retain good properties at elevated temperatures. The effect of alloying and annealing temperature on the electrochemical behavior of the alloy were the aim. The as-rapidly solidified alloys were annealed in reducing atmosphere at 300°C and 500°C for one hour.

The electrochemical behavior of the as-rapidly solidified and annealed ribbons was tested in 0.1 N NaCl aqueous solution using cyclic potentiodynamic polarization technique. The results of cyclic polarization runs show that the specimens annealed at 300°C for one hour exhibited the most noble corrosion potentials, while specimens annealed at 500°C for one hour exhibited the most less noble corrosion potentials. Thermal analysis indicated that such alloys are stable up to 540 °C. The microstructure of the corroded surface was examined using optical microscopy and scanning electron microscopy (SEM).

1. Introduction

Aluminum alloys are used in many industrial and research applications because of its acceptable corrosion resistance and low density[1]. In marine applications aluminum alloys are used in ventilation equipment, also welded aluminum alloy plates are used in large tanks used for transportation of liquefied gases[2]. In nuclear applications, aluminum alloys are used in manufacturing of some components in research reactors as irradiation grid and guide box for control rods.

Rapid solidification processing of metallic materials gives expanding ranges of possible microstructures and alloy compositions beyond those achieved through conventional technology. By rapid solidification processing alloy systems incorporating high volume fraction of ultra fine dispersed phases can be produced yielding corrosion and oxidation resistances and combinations of toughness and elevated temperature strength[2].

Rapid solidification processing has been used to develop improved aluminum alloys for ambient service. The leading work in this area was in Al-Zn-Mg alloy subsystem, where more highly alloyed variants with dispersed transition-metal intermetallic phases were investigated. Rapid solidification processing leads to enhanced mechanical properties, which can be rationalized in terms of extended solubility limits, refined microstructures and minimal coarsening of the second phase particles [3]. The fine microstructure obtained in rapid solidification exhibit excellent corrosion resistance.

In case of aluminum alloys exposed to a salt spray environment weight loss is 9 times less for the powder metallurgy fabricated alloys such as 7090 and 7091[4]. Strengthening of the rapidly solidified alloys is achieved by adding small amounts of transition elements. Alloy 7064 is one of the alloys strengthened by zirconium-, chromium- and cobalt- containing dispersoids, this alloy displays a combination of strength and SCC resistance[5]. The alloy Al-Ni-Co is one of the rapidly solidified aluminum alloys, which is a candidate for high temperature applications, the main dispersoids after fabrication or during annealing are Al_3Ni and $Al_3(Co,Ni)_2$. By rapid solidification processing it is possible to obtain products with high volume fractions of finely-dispersed intermetallics[6].

In some applications of the aluminium alloys, a specified level of corrosion resistance is required. For aluminium alloys corrosion performance regularly tested are durability of coating applied to aluminium substrates, resistance to exfoliation corrosion, resistance to SCC and resistance to intergranular corrosion[7]. It was found[8] that after heat treatment of Al-5%Mn at 450°C, the morphology of the second phase changed and it precipitated at grain boundaries.

The aim of this work is to get better understanding of the effect of Cr, Ni and Ti elements on the corrosion characteristics of the rapidly solidified Al-Mn alloy. Also, the effect of annealing on the corrosion behavior has been investigated.

2. Experimental

The rapidly solidified alloys were prepared by arc melting of pure elements on a water cooled copper hearth with a tungsten electrodes in argon atmosphere. Rapid quenching from melt was performed by ejecting the melt with pressurized helium onto a water cooled single copper roller of 145mm diameter and rotating at 2200 rpm. The produced rapidly solidified ribbons were of 5.8mm width and 0.02-0.08mm thickness. The melt was rapidly solidified from 950 °C to 20 °C.

The microstructure was studied by optical and using scanning electron microscope. Standard polishing and etching techniques was used to prepare sections for optical and hardness measurements. For optical metallography the samples were etched using 50% keller's reagent in water at room temperature.

X-ray diffraction with Cu-K α radiation was used to identify the present phases. DSC measurements were performed using Perkin-Elmer thermal analysis system in a high purity argon. Samples from room temperature were heated up to 600 °C. at the rate of 10,20,and 30 deg./min..

The produced Al- 7%Mn , Al-7%Mn-2%Ti , Al-7%Mn-2%Cr and Al-7%Mn-2%Ni ribbons were heat treated at two temperatures , namely, 300°C and 500°C for one hour. The electrochemical behavior of produced ribbons was tested in 0.1N NaCl using cyclic potentiodynamic polarization. The low concentration of (Cl) ions was chosen because of the metastable structure of the as-rapidly solidified (as received) specimens. The initial potential was -100mv relative to open circuit potential, vertex potential was 100mv and final potential was -600mv. The scanning rate was 0.5 mv/sec and reference electrode was Saturated Calomel Electrode (SCE). The device used in electrochemical runs was Electrochemical Impedance Analyzer model 6310.

3.Results

The microstructure of the as rapidly solidified Al7Mn2Ni alloy is shown in Figure(1).The whole cross section of the ribbon is shown in Fig.(1a) where some very fine primary intermetallics shows up in the middle where the rate of cooling is the lowest. The microstructure of the middle part, air side, wheel side, and are shown in Fig.(1b,c,d) respectively. The outer layer consists of equi axed α -aluminum grains while the inner grains are more or less elongated.

X-ray results of as solidified Al7Mn2Ni alloy shown in Figure(2) reveals the formation of α -Al super saturated solid solution and G-phase .The alloy annealed at 500 °C shows an increase in a-aluminum lattice parameter of about 0.25% due to the rejection of the smaller Mn atoms. Also, Stable Al6Mn shows up.

Differential thermal analysis of as rapidly solidified Al7Mn2Ni alloy in the temperature range between room temperature and 600 °C results in a two exothermic peaks as shown in Fig.(3).the first peak at 499 °C represents the formation of the metastable phases of AlMnNi .The second exothermic peak is an indication of transformation of the transition phases to stable Al₆(MnNi).

Cyclic potentiodynamic polarization tests were performed in 0.1N NaCl on rapidly solidified Al-7%Mn , Al-7%Mn-2%Ti, Al-7%Mn-2%Ni and Al-7%Mn-2%Cr in as-received and annealed conditions . The results are given in Fig. 4(a) for as received Al-7%Mn and the annealed alloy at 300°C and 500°C for one hour. For the as-received and annealed alloys a negative loop is formed (i.e backward scan current density values are higher than the corresponding forward scan current density values at the same potential). The current density values were observed at potential +100 mv higher than the corrosion potential. From Fig.4(a), the current density values of forward scan for as-received, heat treated at 300°C/1h and heat treated at 500°C/1h are 8×10^{-3} , 1×10^{-4} and 3×10^{-7} A/cm² , respectively. The current density values for backward scan at the same potential are 2×10^{-4} , 2×10^{-4} and 1×10^{-4} A/cm² , respectively. As can be seen that the width of the cyclic loop for the three different conditions is different. The corrosion potentials of the tested alloy are -918, -805 and -1000mv for as-received, heat treated at 300°C/1hr and 500°C/1hr ,respectively. Similar cyclic potentiodynamic polarization runs (i.e same test solution and scan rate) were carried out on rapidly solidified Al-7%Mn alloy with addition of one more alloying element. The added alloying elements were 2%Ti ,2%Ni and 2%Cr. The results of the electrochemical runs

on the as-received and annealed Al-7%Mn-2%Ti alloy are presented in Fig. 1(b), it is observed that the alloy exhibited negative loop, the equipotential forward scan current density values are 2×10^{-4} , 2×10^{-7} and 2×10^{-4} A/cm² for as received, treated at 300°C and 500°C, respectively. The backward scan current density values at same potential are 4×10^{-4} , 1×10^{-4} and 5×10^{-4} A/cm², as can be seen for the three conditions, backward scan currents are greater than forward. The corrosion potentials for as received, treated at 300°C and 500°C are -736, -620 and -1040mv, respectively, the corrosion current densities are 1×10^{-6} , 8×10^{-8} and 5×10^{-6} A/cm² in the same sequence.

The electrochemical behavior of the as-received and annealed Al-7%Mn-2%Ni is given in Fig.4(c), it is obvious that the alloy exhibited a negative loop for all conditions. The forward scan current density values are 3×10^{-8} , 1×10^{-8} and 3×10^{-6} A/cm² for as-received, treated at 300°C and at 500°C, respectively and the back scan current density values are 1×10^{-3} , 7×10^{-4} and 6×10^{-4} A/cm², The corrosion potentials for the alloy were -637, -580 and -766mv, for as-received, treated at 300°C and at 500°C, respectively. The corrosion current density values were 1×10^{-7} , 2×10^{-9} and 8×10^{-7} A/cm². The electrochemical behavior of as-received and annealed Al-7%Mn-2%Cr is shown in Fig.4(d), the corrosion potentials were -600, -568 and -1060mv for as received, treated at 300°C and at 500°C, respectively. The corrosion current density values were 3×10^{-8} , 7×10^{-9} and 1×10^{-6} A/cm², respectively. It is observed from Fig.4(d) that the alloy annealed at 500°C have the smallest loop width. The forward scan current density values were 1×10^{-6} , 3×10^{-8} and 1×10^{-3} A/cm², for as received, treated at 300°C and at 500°C, respectively. The backward scan density values were 1×10^{-4} , 4×10^{-4} and 2×10^{-4} A/cm². The reason for the change in the corrosion resistance of the as received, annealed at 300°C and 500 °C was confirmed by the DSC results. As can be seen from Figure(3) annealing at 300C for one hour results in the relief of the stress created due to rapid quenching. However, annealing at 500 °C results in higher corrosion rates due to the formation of the metastable phases confirmed by DSC.

The surface of the tested samples reveals the nature of attack as shown in Fig.(4) for the as received Al7M alloy there is a discrete particles of corrosion product, however, in case of annealing at 500°C /1 hour the corrosion pits demarcates the grain boundaries due to the dissolution of the precipitates formed at the grain boundaries at this temperature. Corrosion in AlMnTi and AlMnCr is less than in AlMnNi due to the

dissolution of Al₃Ni precipitates which is more anodic than the aluminum matrix. The electron micrograph shown in Figure(7)c for AlMnNi annealed at 500°C/1 hour shows large pits due to the dissolution of Al₃Ni and small pits which define the grain boundaries due to dissolution of AlMn intermetallics. In case of AlMnCr the attack is more general than the other cases, however attack beneath the large precipitates is more clear.

SEM surface examinations after the cyclic potentiodynamic polarization runs are presented in Figs.(5-7), it can be observed that the corrosion attack increases with heat treatment temperature.

4. Discussion

Rapid solidification refers to cooling of melts at rates exceeding 10^4 - 10^6 K/s. Rapid solidification processing results in refinement of grain size, second phase particles or segregation patterns[9]. In rapid solidified aluminium alloys, a solid solubility limit is extended. Manganese has a relatively high solubility in aluminium and in case of avoiding the formation of competing phases, large extensions of the solubility limit would be expected even without any departure from equilibrium at the solid-liquid interface[10]. In Al-Mn alloys rapidly solidified a phase with composition Al₁₂Mn appears during annealing of these supersaturated solution and at temperatures below 500°C, this phase exists with the phase Al₆Mn[10]. During rapid solidification of alloys at composition greater than 5wt%Mn, a cellular or subgrain structure was present in the as-received ribbons. Very small (<10nm diameter) precipitates were present along the cell or subgrain boundaries, and the concentration of Mn in solid solution within the cells was slightly less than the nominal composition of the sample[10]. Annealing of these fine-grains, supersaturated solid solutions leads to higher volume fractions of precipitates[11,12]. Up on annealing at 300°C the precipitates do not grow and the stress are partially relieved, up on annealing at 450°C precipitates grow rapidly along the subgrain boundaries. when more than 4 wt% Mn is in solid solution, precipitates also form within the subgrains, but a denuded zone occurs adjacent to the grain boundary[10].

The surface examinations by SEM of the corroded surface of as received and annealed Al-7%Mn specimens at 300°C and 500°C are shown in Fig.5(a-c), it can be observed that there is a selective dissolution at grain boundaries and inside the grains in

the alloy annealed at 500°C, Fig.5(c). While in case of as received specimen, Fig.(5a), the corrosion attack was less and the dissolution was adjacent to precipitates. However, in case of annealing at 300°C some selective dissolution of precipitates can be observed but less than that in case of annealing at 500°C.

Normally the transient metals (Fe, Mn, Ti, Ni, V) have very low diffusivity in aluminium[8]. By rapid solidification processing, the solubility of these elements increases, and the rapid solidification of Al-base alloys with addition of small quantities of transient elements capable of precipitating in a form of a small dispersoids[13].

During solidification of the Al-base alloys, the aluminids particles do not grow and can not keep up the growth velocity of aluminium cells, so they are found as individual discrete particles[14]. The corrosion surface of as received and annealed Al-7%Mn-2%Ti alloy as examined by SEM are shown in Fig. 6(a-c). It is observed that the corrosion attack is concentrated in the adjacent areas of the precipitates in all cases, but it is more dense in case of alloy annealed at 300°C, these observations are supplemented by corrosion current density values at potential +100mv (SCE) higher than corrosion potential, Fig.4(b).

In a study of X-ray diffraction pattern of rapidly solidified $Al_{93}Mn_5Ce_1M_1$ ($M \approx$ Mn, Fe, Co, Ni) alloys, showed that half-width of peak increased in the order of $Ni \approx Co > Fe > Mn > Cr$ indicating that the particle size of the icosahedral phase is considerably smaller and amount of the phases defects is greater for the alloys containing Ni or Co as M element[15]. Addition of the transient element Ni to rapidly solidified Al-Mn alloys, will form an intermetallic and its distribution will be responsible for dispersion strengthening of the alloy[16]; and, the intermetallic phase dispersed in the matrix, was identified as Al_3Ni by X-ray diffraction[16]. The SEM examinations of as received and annealed specimens of alloy Al-7%Mn-2%Ni after corrosion, Fig.7(a-c) showed that the corrosion attack is severe in case of alloy annealed at 500°C, and there is a selective dissolution around the dispersoids and at grain boundaries, Fig.7(c), while the attack is less in case of alloy annealed at 300°C, and the dissolution is around the dispersoids only. These results are supported by corrosion current density values in Fig.4(c).

The rapidly solidified aluminium-chromium alloys containing up to 4wt% Cr, are characterized by a supersaturated solt-free structure, with distributed

dispersoids[17]. The corroded surface of as-received and annealed specimens of alloy Al-7%Mn-2%Cr, Fig.8(a-c), showed that the corrosion attack is mainly in the areas adjacent to the dispersoids in grains in case of as received and annealed at 300°C alloy. In case of the alloy annealed at 500°C the attack is in the areas adjacent to dispersoids in grains and at grain boundaries.

5. Conclusions

The DSC measurements show that Al7Mn2Ni is thermally stable up to 500C which was also confirmed by X-rays.

The results of the electrochemical tests applied in 0.1N NaCl at ambient temperature supplemented by microscopic surface examination showed that :

- The corrosion of the alloy Al-7%Mn is less than the alloys with additions,
- The degree of the severity of corrosion attack due to presence of additions is Ni > Ti > Cr.
- The annealing temperature at 500°C increases the severity of the corrosion attack while less attack is observed on annealing at temperature 300°C.

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Fig.(1) Optical Micrographs of as Rapidly Solidified Al₇Mn₂Ni.
a) Whole crosssection(x200)
b) Central Part of the Rippon(x800)
c) Air Side of the Rippon (x800)
d) Wheel Side of the Rippon(x800)

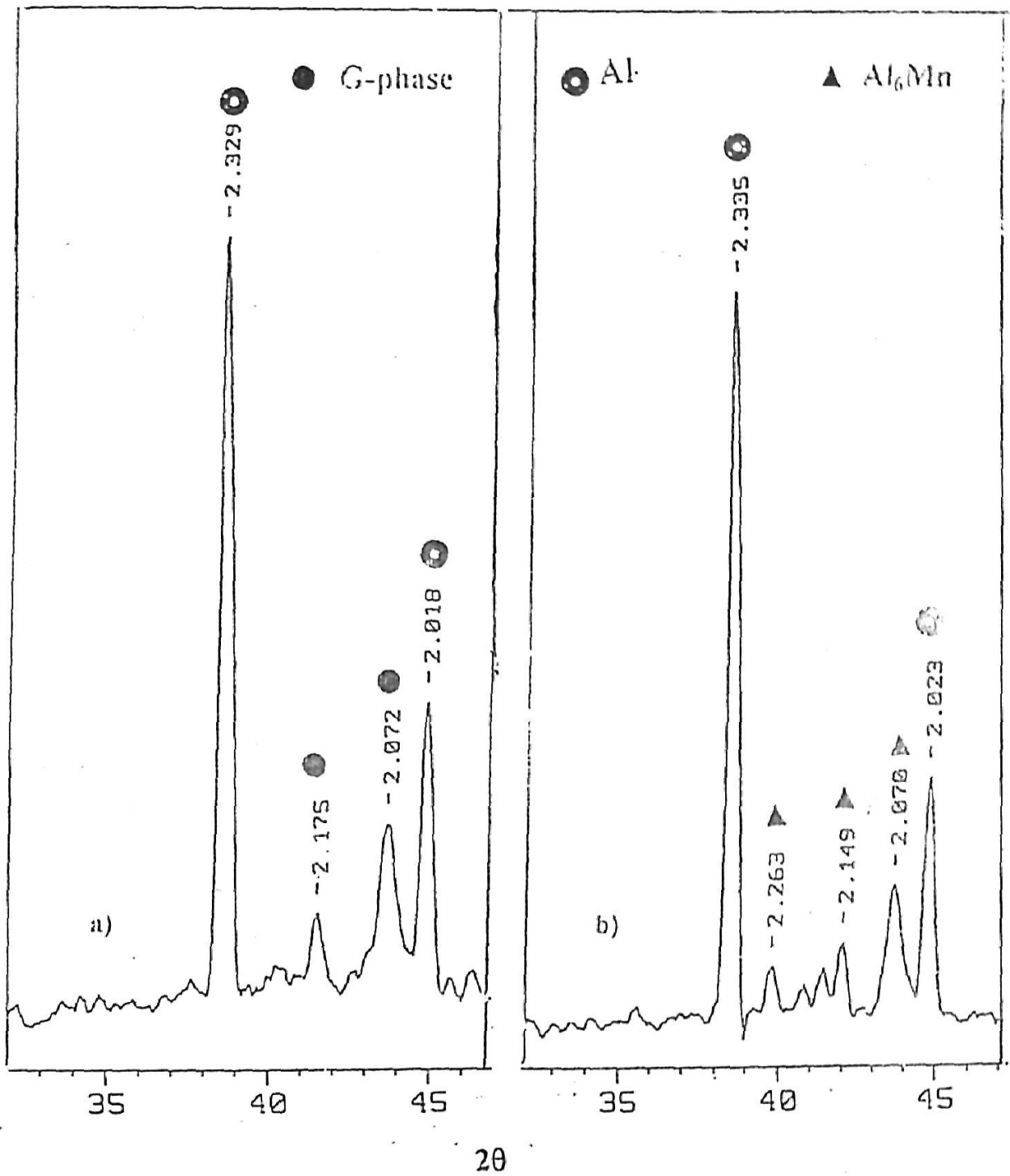


Fig.(2) a) X-ray diffraction of as rapidly solidified $\text{Al}_7\text{Mn}_2\text{Ni}$ alloy.
 b) X-ray diffraction of $\text{Al}_7\text{Mn}_2\text{Ni}$ alloy after annealing at 500°C for 1 hour.

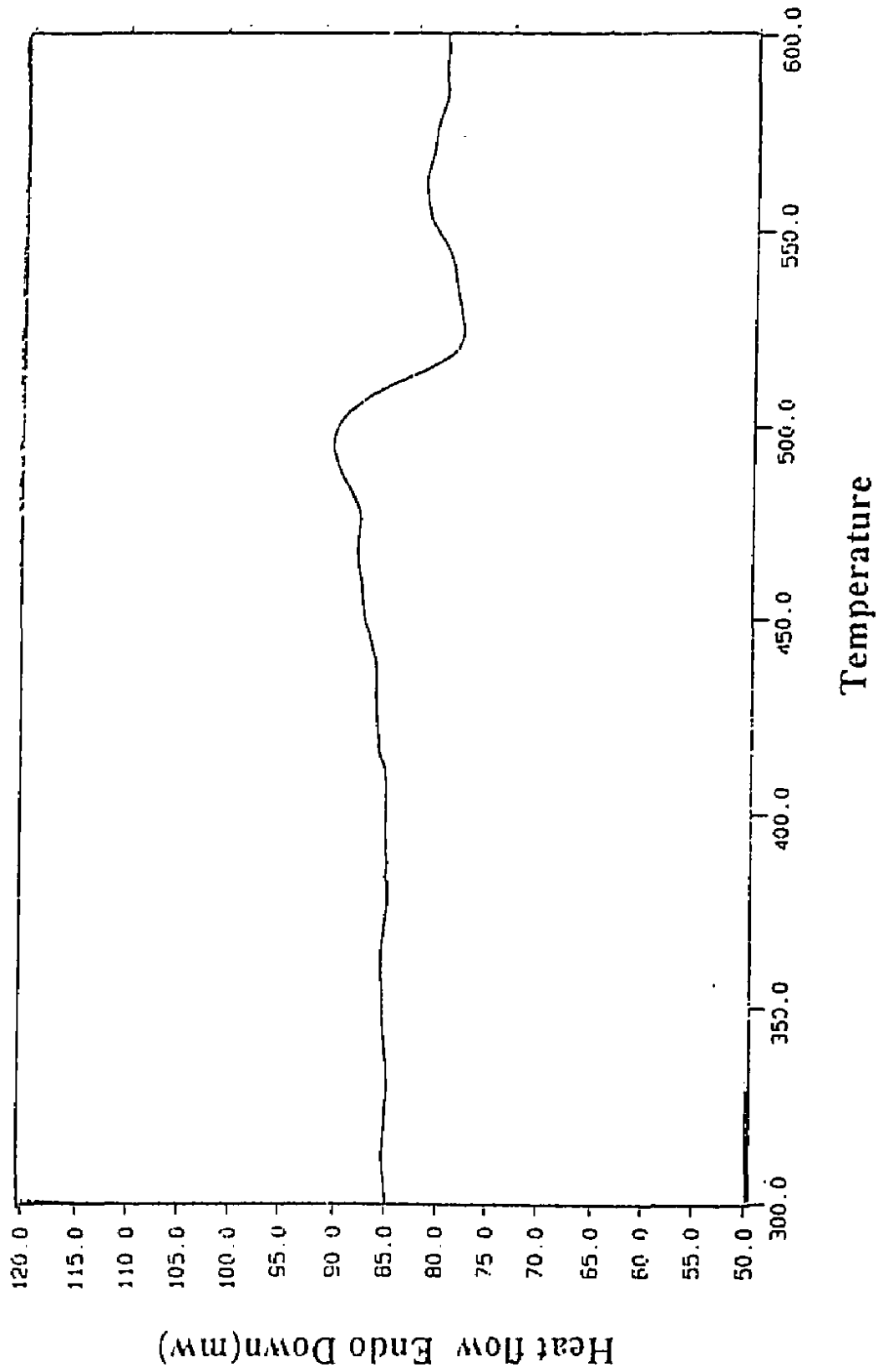
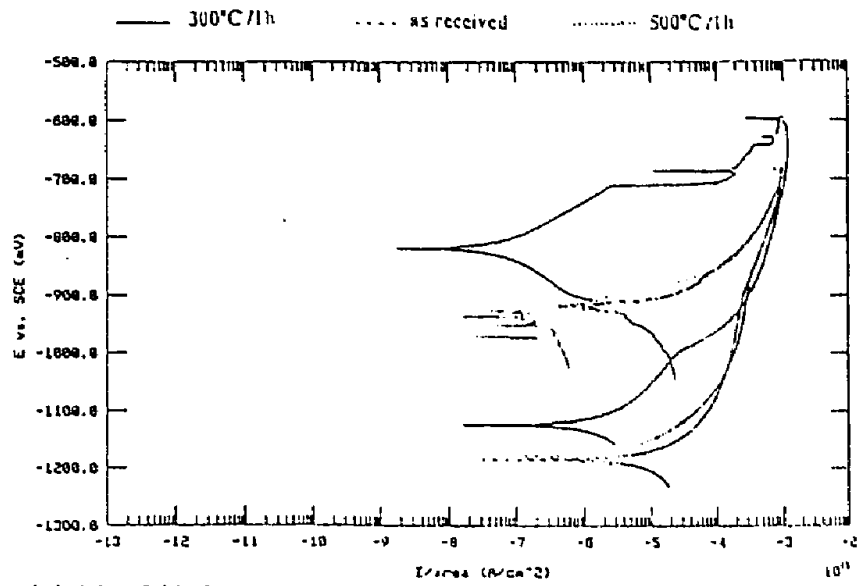
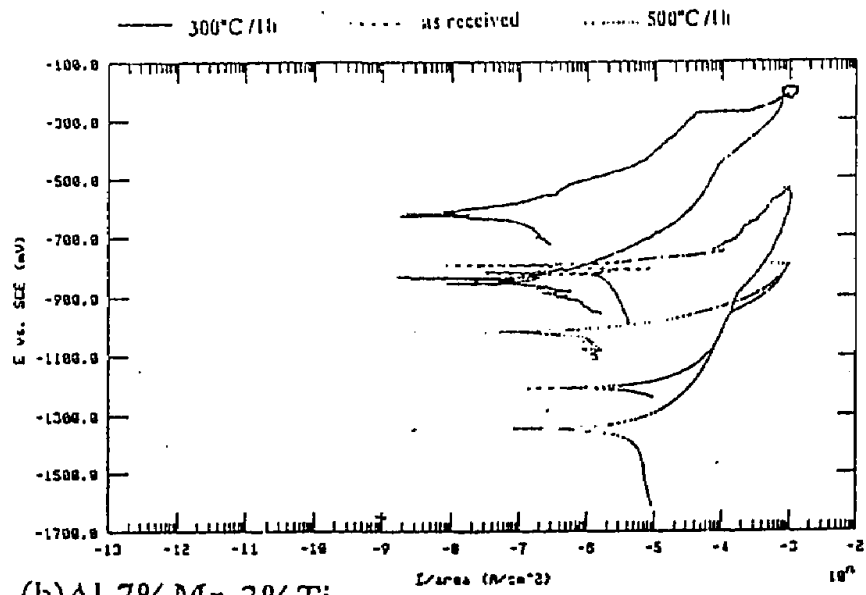


Fig.(3) DSC thermogram of as rapidly solidified Al₇Mn₂Ni alloy at 20deg/min.

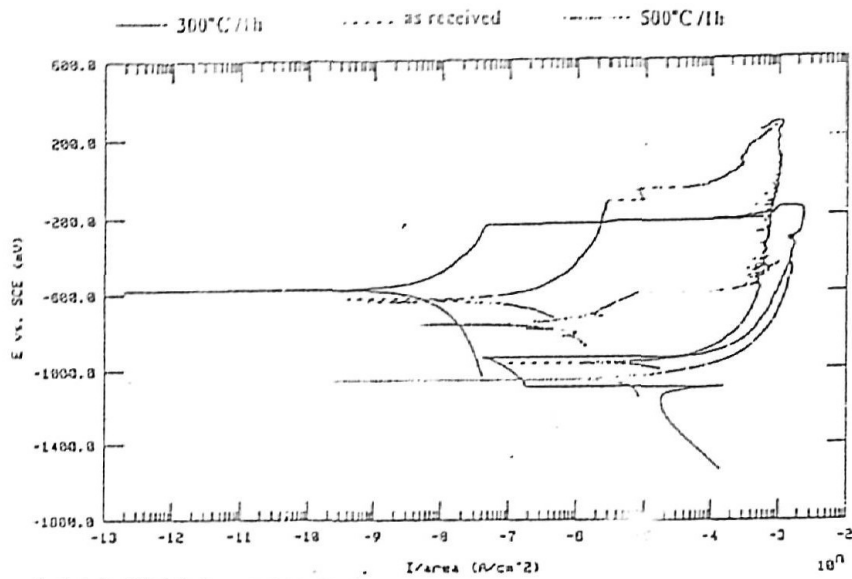


(a) Al-7%Mn

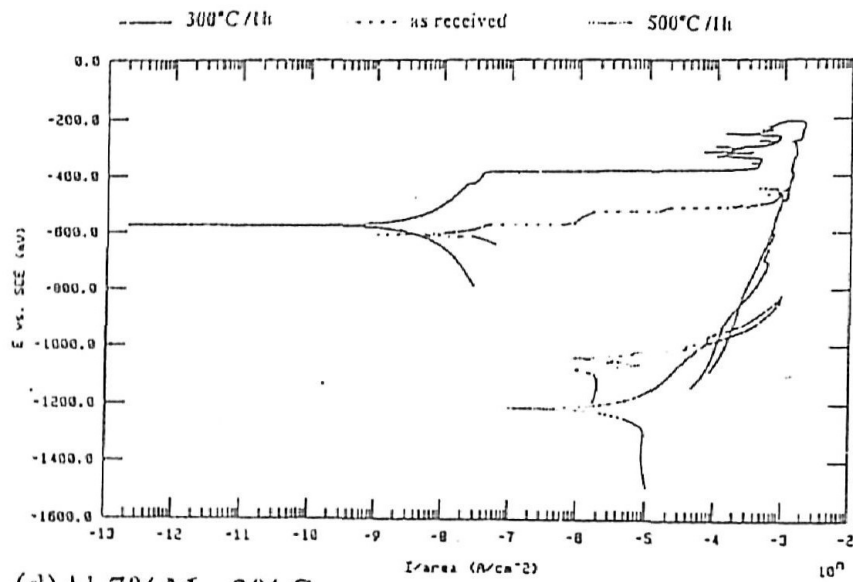


(b) Al-7%Mn-2%Ti

Fig.(4) Cyclic potentiodynamic polarization Of aluminium alloys tested in 0.1N NaCl solution at ambient temperature.



(c) Al-7%Mn-2%Ni



(d) Al-7%Mn-2%Cr

cont. Fig.(4) Cyclic potentiodynamic polarization Of aluminium alloys tested in 0.1N NaCl solution at ambient temperature.

(a) as received



(b) heat treated
at 300°C / 1h



(c) heat treated
at 500°C / 1h

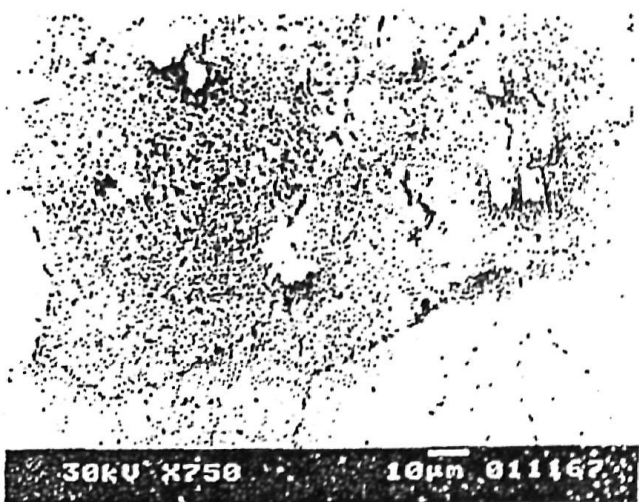


Fig.(5) SEM micrographs of Al7Mn after testing in 0.1N NaCl .

(a) as received



(b) heat treated
at 300°C / 1h



(c) heat treated
at 500°C / 1h



Fig.(6) SEM micrographs of Al₇Mn₂Ti after testing in 0.1N NaCl.

(a) as received



(b) heat treated
at 300°C /1h



(c) heat treated
at 500°C /1h

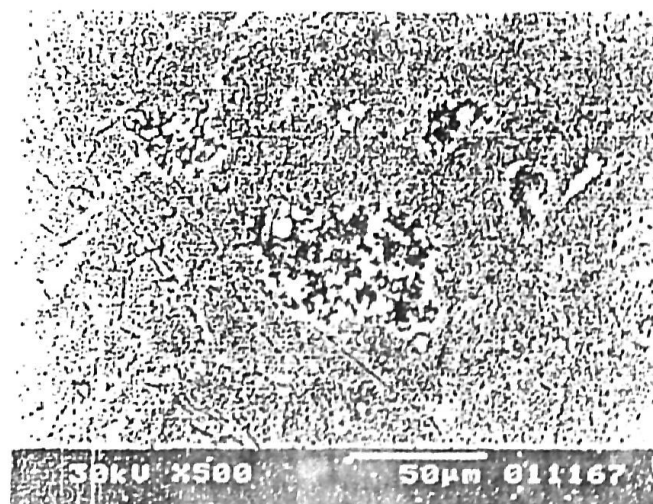
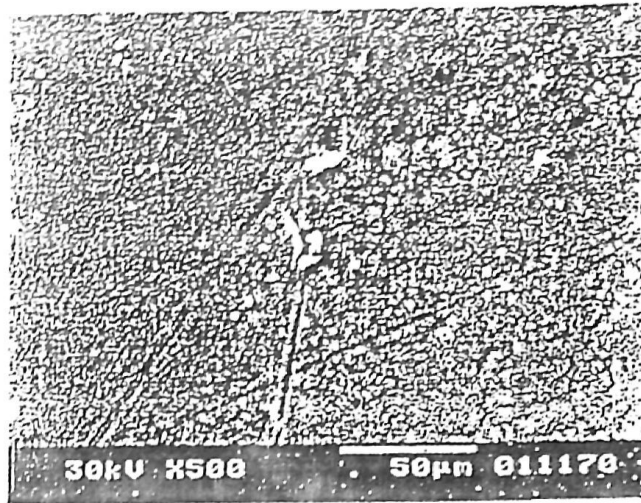
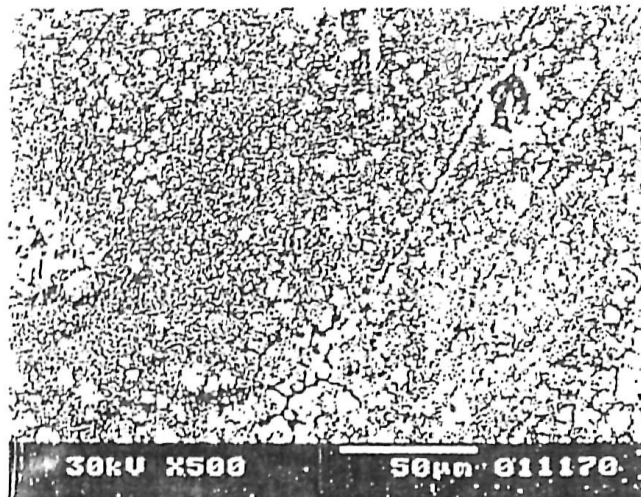


Fig.(7) SEM micrographs of Al₇Mn₂Ni after testing in 0.1N NaCl.

(a) as received



(b) heat treated
at 300°C /1h



(c) heat treated
at 500°C /1h

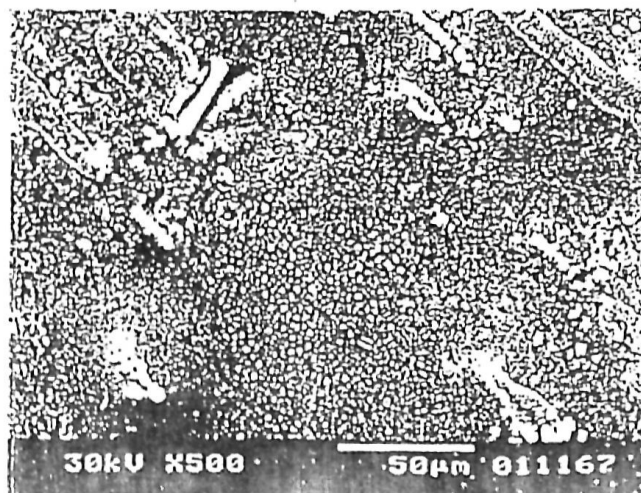


Fig.(8) SEM micrographs of Al₇Mn₂Cr after testing in 0.1N NaCl.