Mansoura Engineering Journal (MEJ), Vol. 20, No. 1, March. 1995. M. 23.

Effect of Heat Treatment on the Corrosion Behaviour of Rapidly Solidified Al-8Ni-2Co Alloy in NaCl Solution

تأثير المعالجة الحرارية على سلوك التآكل فى محلول ٣,٥٪ كلوريد صوديوم لسبيكة Al-8Ni-2Co المبردة تبريدا سريعا من الحالة السائلة

*F.N. El-Sabbahy, *M.A. Kussem, **R.M. Ramadan

* Lecturer **Associate Prof.

Dept. of Metallurgy, Faculty of Pet. & Min. Eng.,
Suez Canal Univ., Suez, Egypt.

خلاصة عربى :

- تمت دراسة سلوك التآكل الكهروكيميائى لسبيكة الألمنيوم - ٨٪ نيكل - ٢٪ كوبلت المنتجة باستخدام تكنولوجيا التبريد الفائق السرعة وكذلك بعد معالجتها حراريا. وقد تم كذلك تتبع سلوك تحلل السبيكة المبردة سريعا من الحالة السائلة باستخدام كل من حيود أشعة إكس و الكالوميتر الحرارى المساح واختبار الصلادة الدقيقة والفحص الميكروسكوبى.
- هذا وقد أظهرت النتائج أن الأوجه المستقرة والتى تتكون عند معدلات التبريد التقليدية لا تتكون فى العينات المبردة باستخدام التبريد فائق السرعة وبدلا منها يتكون محلول صلب فوق مشبع للألمنيوم بالإضافة إلى مكورات دقيقة من المركب المعدنى $Al_9(Co\text{-}Ni)_2$.
- وقد أظهرت نتائج اختبار التآكل فى محلول مائى يحتوى على ٣,٥٪ كلوريد صوديوم أن السبيكة المبردة تبريدا سريعا لها أقل معدل تآكل ويزداد معدل التآكل بزيادة درجة المعالجة الحرارية لها نتيجة تكوين الوجه المستقر Al_3Ni وزيادة حجمه.

Abstract :

The corrosion behaviour of as-rapidly solidified and heat treated Al-8Ni-2Co alloy ribbons produced using melt spinning technique was investigated. The decomposition behaviour of the rapidly solidified ribbons was followed up using x-ray diffraction, differentialscanningcalometry, microhardness, and metallography. The stable phases which are generally formed in conventional solidified alloy in the as cast condition, were not detected in the as-rapidly solidified specimens. Instead, super-saturated solid solution α-Al was present in addition to fine dispersoids of $Al_9(CoNi)_2$. The corrosion behaviour was investigated through potentiostatic technique in 3.5% NaCl aqueous solution. The corrosion rate was the lowest in the as-rapidly solidified condition and increased with increasing the annealing temperature as a result of the formation and coarsening of the intermetallic Al_3Ni.

Introduction :

Although it is generally agreed that aluminium alloys acquire good corrosion resistance to marine environments, many are susceptible to localized corrosion [1-3]. Micro-constituents are usually the source of most problems with electrochemical corrosion as they lead to localized attack resulting from the potential difference between the micro-constituents and the aluminium matrix. Therefore a solid solution is the most corrosion resistance form in which an alloy may exist. Rapid solidification extends the solid solubility with a consequent homogeneous distribution of dispersoids in addition to the formation of microcrystalline alloys. Thereto, the corrosion behaviour of rapidly solidified aluminium alloys is of interest in connection with the formation of alloys in which the solid solubility is extended. Through the use of controlled rapidly solidified particulate [4] or flakes [5] and fabrication techniques, it is possible to obtain products with high volume fractions of finely-dispersed intermetallic phases. On one hand, these particles impart strength through dispersion strengthening and thermal stable structure through utilizing alloying additions with high liquid solubility, low solid solubility and low diffusion coefficients in the aluminium matrix [6-8]. On the other hand, the corrosion behaviour of these wrought P/M alloy products may be imparied or improved depending on the potential difference between the evolved dispersoids and the aluminium matrix.

Among rapidly solidified aluminium alloys, Al-Ni-Co alloys have been reported to be potential candidates for high temperature applications. In such alloys the main dispersoids evolved during aging or fabrications are Al_3Ni and $Al_9(Co, Ni)_2$ [6-8].

The purpose of the present work is to tharacterize the combined effect of rapid solidification and the aging temperature on the decomposition and corrosion characteristics of the Al-8Ni-2Co alloy.

Experimental :

Al-8Ni-2Co alloys was prepared by arc melting of pure elements on a water cooled copper hearth with a tungesten electrode in a partial pressure of titanium gettered argon. Rapid quenching from melt was performed by induction melting the alloy in a quartz tube placed in a helium atmosphere. The melt was then ejected by helium pressure onto a single copper roller with 145 mm diameter, and rotating at 2200 rpm.

Rapidely quenched ribbons of 5-8 mm width and 20-80 μm thick were produced.

Thermal stability of the rapidly solidified ribbons was investigated using several techniques : differential scanning calorimetry (DSC), microhardness measurements and X-ray diffraction (XRD) which was carried out on the wheel side ribbon's surface. The DSC was done by operating the calorimeter at constant heating rate of 10°C/min over the temperature range (25-700°C). The XRD using Cu-Kα, radiation was performed on Rigaku D-Max diffractometer at a scan speed of 2°/min and step angle of 0.1°. Vicker's microhardness measurements were made using Schimadzu microhardness testing machine at a load of 25 gm. Microhardness value was taken as an average of ten readings for each sample.

Polarization curves were constructed by a potentiostatic method, using a Wenking Potentioscan (POS 73). The corrosive environment used was an aerated solution of 3.5% NaCl prepared using analar grade chemicals and distilled water. A platinium electrode was used as a counter electrode and all the potentials were measured against saturated calomel electrode (SCE). The working electrode was coated by alcomit lacquer and free surface of 1 x 1 cm^2 of the wheel side surface was exposed. The experiments were performed in a 250 ml corning glass cell containing 200 ml of the test solution at room temperature. The specimen was held in the solution, at open circuit potential for 1 hr. for steady state corrosion potential (E_{corr}) and then cathodic and anodic polarization current were measured potentiostatically. Potential steps of 20 mV for the anodic polarization and 10 mV for the cathodic polarization were applied manually, specimen stabilize for about 5 min., and then current measurements were done. Corrosion rate, in mpy, was computed by extrapolation of the cathodic tafel line to corrosion potential.

Results and Discussion :

Thermal decomposition of the rapidly solidified materials :

In order to understand the corrosion behaviour of the rapidly solidified material as well as the annealed one, the decomposition behaviour of as rapidly solidified material was investigated. The DSC thermogram of as-melt quenched specimen at a heating rate of 10°C/min up to 700°C is shown in Fi.g 1a. There are two exothermic peaks spaning the temperature range of 305-490 and 510-590 with peaks maximum at 380 and 554°C respectively. The DSC results well agree with the microhardness measurements illustrated in Fig. 1b. The as rapidly solidified structure is observed to thermally decompose just above 300°C and stabilize over 500°C, .

There are two types of precipitations occure as can be deduced from the DSC results, Fig. 1a. The x-ray that diffraction results display the constituents of the as-rapidly solidified materials at each stage of annealing. The main micro-constituents of the as-rapidly solidified specimen are mainly the super saturated aluminium solid solution and a minor dispersoids of the monoclinic Al_9Co_2 [8,9]. The intermetallic Al_9Co_2 appears to result from direct nucleation from the melt as reported previously [9] and followed by subsequent growth. That can be infered from the increasing of Al_9Co_2 peaks and intensity with the annealing temperature, Fig. 2. Because the solubility of nickel in intermetallic Al_9Co_2 is extensive, more than two-third of cobalt atoms can be replaced by nickel [10], theseto, the primary intermetallic is $Al_9(Co, Ni)_2$. The X-ray results, Fig. 3. of annealed materials at 300 and 400°C for one hour show that the precipitation of metastable Al_3Ni (orthorombic . a = 6.4 , b = 7.56, and c = 9.56 A°) [11]. A few weak peaks of the hexagonal Al_5Co_2 [12] are detected too. Therefore, the first wide exthothermic peak, Fig. 1, can be assigned to the precipitation of metastable Al_3Ni and Al_5Co_2 and growing of $Al_9(Co, Ni)_2$. Annealed sample at 500°C shows the transformation of metastable AL_3Ni to the stable Al_3Ni (orthohombic : a = 6.598, b = 7.352, c = 4.802 A°) [13], Fig. 3. The present phases at each condition are summerized in Table 1, which are very important to explain the corrosion behaviour of each material.

Electrochemical behaviour :

The anodic polarization behaviour of the as-melt quenched and that annealed at 300, 400, and 500°C for one hour was investigated. Fig. 3. shows the anodic polarization curves for the investigated materials. The characteristics parameters of the anodic behaviour such as the free corrosion potential (E_{corr}), the critical current (i_{crit}) and passivity current (i_p), break down potential ($E_{b.d}$) and passivation range are listed in Table 2. It is observed that with increasing annealing temperature, the corrosion potential, breakdown potential and passivation range decrease, while passivation current, critical current and corrosion rate increase. The anodic current density in the region between the open circuit potential and the pitting potential is the lowest for the as-rapidly solidified sample and it increases with increasing the annealing temperature. Such behaviour is strongly related to the decomposition process that takes place during annealing of the as-rapidly solidified materials. The important trend in the electrochemical data, table. 2, indicate that the microconstituents, affect the corrosion characteristics of the investigated material. In particular, decomposition of the as-melt quenched microstructure which promote the formation of stable Al_3Ni dispersoid. The presence of this phase increase the susceptibility of the Al-8Ni-2Co alloy to attack in 3.5% NaCl solution. An understanding of the formation and growth of the intermetallics is central to the understanding of the corrosion behaviour. In order to make this connection as clear as possible a plot of free corrosion potential versus annealing temperature which results in a sigmodial curve, Fig.1c,compared with the decomposition curve deduced by microhardness, Fig. 1b. It indicates that a significant change in corrosion behaviour occurs when the annealing temperature exceeds 300°C. This coincides with the commence of the decomposition of the as-melt quenched solid solution. The detected phases at each stage of annealing are listed in Table 1. The electrode potential with respect to SCE of the aluminium matrix is -0.85 as compared with -0.52 for stable Al_3Ni [14]. The dispersoid Al_3Ni is cathodic with respect to aluminium. Therefore, it provides point at which the surface oxide film is weak, thereby promoting electrochemical attack, pitting corrosion [1,2,14]. The effect of precipitation is in turn reflected in the decrease of the pitting potential with the increase of annealing temperature. The rate of general corrosion (mpy) of as-melt quenched material is much less than that of annealed ones, table. 2, which is attributed to the increasing of the number of small size cathodic Al_3Ni through the structure.

Conclusions :

1- Rapid solidification of Al-9Ni-2Co alloy supresses the formation of the Al_3Ni phase. Thus only fine Al_9 (Co, Ni)$_2$ and unstable α-Al solid solution are present in the as-rapidly solidified alloy
2- The corrosion results show that rapid solidification is an effective method ennobling the corrosion parameters of the investigated alloy.

3- The increasing of the overall corrosion rate with increasing the annealing temperature is found to coincide with the decomposition of the super saturated solid solution (α'-Al) and the formation and coarsening of the cathodic-phase Al_3Ni make the passivation process less effective.

REFERENCES :

1- S.M. Skolianos, T.Z. Kattamis and O.F. Devereux, Metall. Trans., 20A (1989) 2499-2515.

2- H.Youshioka et al, Corrosion Sci., 26 (1986) 795-812.

3- E.Lunarska, E.Trela, and Z. Szklarska-Smialowska, Corrosion, 43 (1987) 219.

4- N.J.Grant, S.Kang and W.Wang, In. Proc. of 1st Int. Al-Li Conf., Eds., T.H. Sanders, Jr. and E.A. Starke, Jr., AIME, 1981, 171-188.

5- K.K. Sankaran, S.M.L. Sastry, and J.E. O'Neal, Ibid, 189-227.

6- Hamish, L.Fraser et al., In "Rapidly Solidified Powder Al-alloys" ASTM STP 890-, Eds., M.E. Fine and E.A. Starke, Jr, ASTM, Philadelphia, 1986., 186-210.

7- M.W. Griffith, R.E. Sanders, Jr, and G.J. Hildeman, in "High Strength Powder Metallurgy Al-alloys", Eds. M.J. Kazak and G.J. Hildeman. AIME, 1982, 209-224.

8- B.K. Garrett, Jr.and T.H. Sanders, Jr., Mater. Sci. & Eng., 60 (1983) 269-274.

9- G.Van Tendeloo, J.Menon, and C. Suryanarayana, J.Mater. Res., 2 (1987) 547-556.

10- L.F. Mondolfo, "Aluminium : Structure and properties", Butterworth London, 1976, P. 478.

11- T.R.Anartharaman et al, In "Proc. of 2nd Int. Conf. RQM, Eds. J.N. Grant and B.C. Giessen, 17-19 Nov., 1975 Massachusetts, 157-161.

12- JCPDS card file No. 3-1080.

13- JCPDS card file No. 2-416.

14- I.J. Polmear, "Light Alloys", Edward Arnold, London, 1981, 30.

Table 1. The detected phases in the investigated materials.

Condition	Detected phases
as-melt quenched	super saturated solid solution (α'-Al) + Al_9 $(Co,Ni)_2$
annealed at 300°C/1hr	α-Al + Al_9 (Co, Ni)2
annealed at 400°C/1hr	α-Al + Al_9 $(Co, Ni)_2$ + metastable Al_3Ni + Al_5Co_2
annealed at 500°C/1hr	α-Al + Al_9 $(Co, Ni)_2$ + Stable Al_3Ni + Al_5Co_2

Table. 2. Polarization test results for Al-8Ni-2Co in 3.5% NaCl solution at room temperature

Heat treatments conditions	E_{corr} mV/SCE	$E_{b.d}$ mV/SCE	Passivation range (mV)	Δ Ep ($E_{b.d}$-E_{corr})	Passivation current dens Ip μA/Cm^2	$I_{critical}$ μA/Cm^2	Corrosion rate mpy
as-rapidly solidified	- 717	+ 100	560	817	12	14	8.5
300°C	- 720	+ 50	450	770	23	25	17
400°C	- 735	+ 20	480	755	27	32	19
500°C	- 755	- 20	380	735	70	85	23

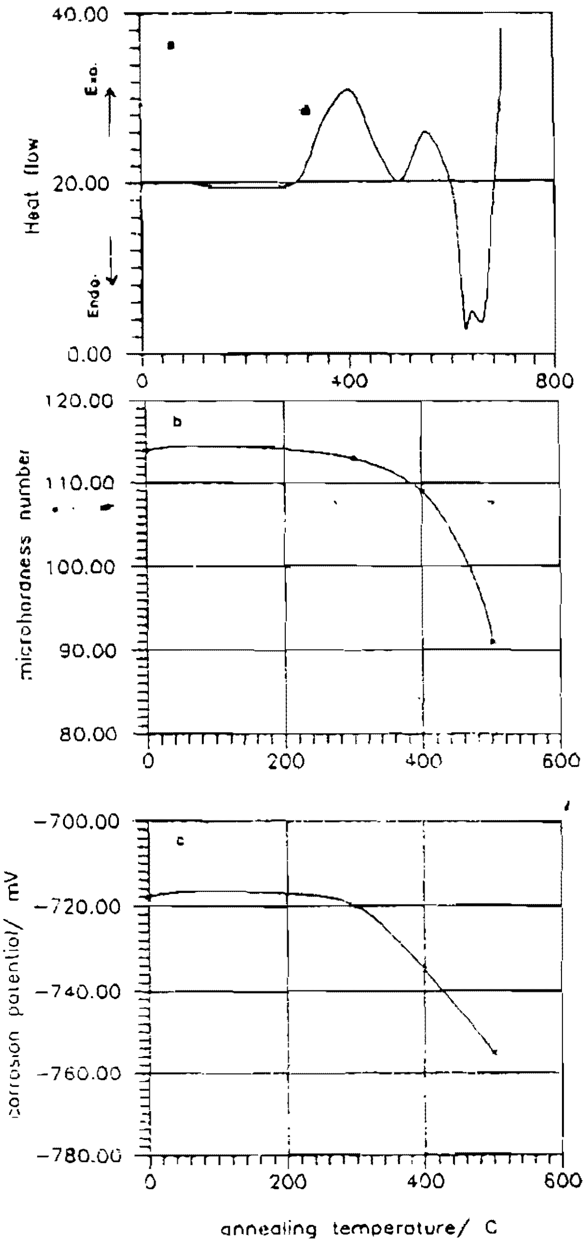

Fig 1 Thermal decomposition response of the as-melt quenched materials annealing at temperatures of 300, 400 and 500 C for on hour. a) DSC thermogram, (b) microhardness, and c) free corrosion potential response.

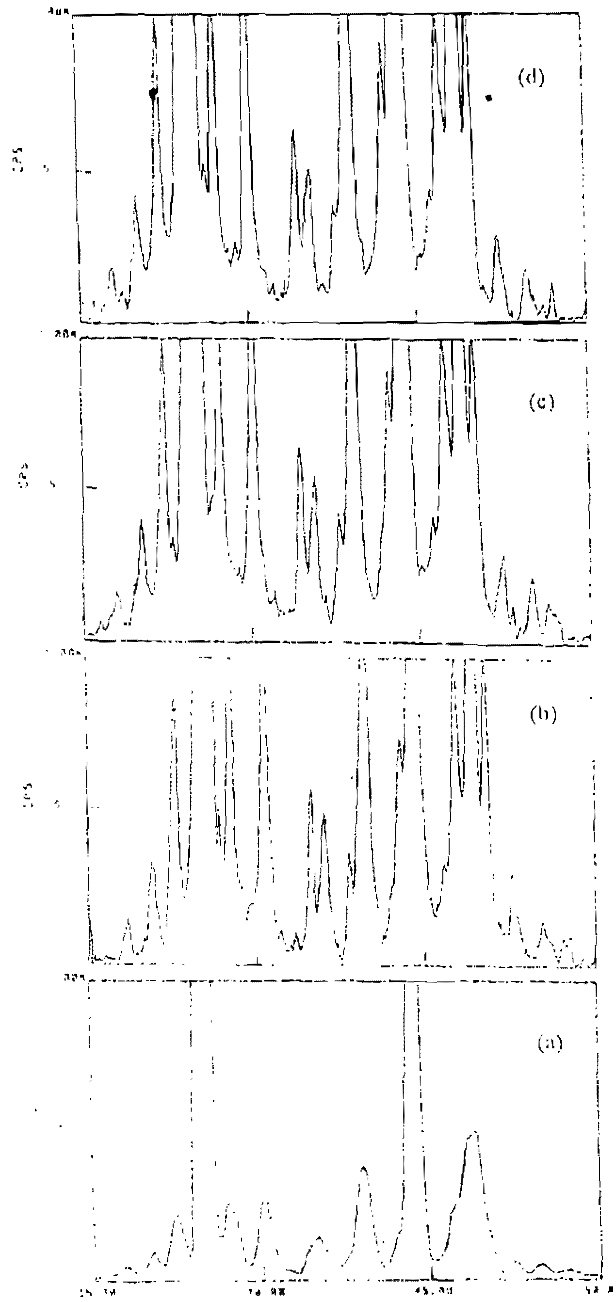

Fig. 2 X-ray diffraction of the investigated alloy (a) as-melt quenched (b, c and d) annealing at 300, 400 and 500°C respectively for one hour.

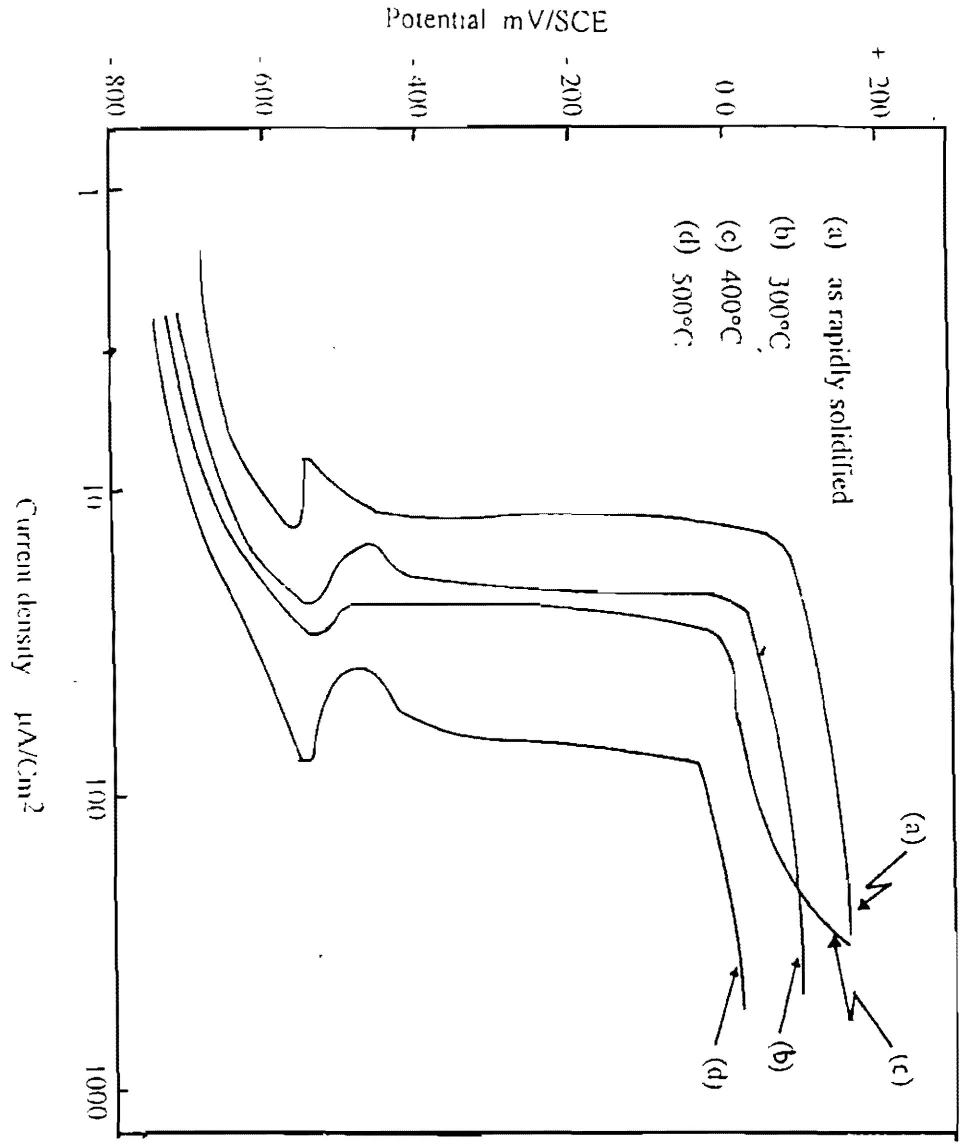

Fig. 3 : Anodic polarization behaviour of alloy Al-8Ni-2Co in several conditions