Corrosion studies of high pressure die-cast Al-Si-Ni and Al-Si-Ni-Cu alloys

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ABSTRACT

Corrosion behavior of high pressure die-cast Al-Si-Ni alloys (Al-3Si-1Ni (SN31) and Al-3Si-3Ni (SN33)) with and without copper (Cu) addition has been investigated. Corrosion behavior was assessed in 3.5 wt% NaCl by electrochemical and immersion corrosion techniques. The presence of single phase pure Si and binary Al_3Ni phases were confirmed from the X-ray diffraction (XRD) and microstructural studies for SN31 and SN33 alloys. Interestingly, Cu addition (1 at.%) resulted in formation of Al_3Ni_2 phase along with a marginal decrease in Al_3Ni fraction and did not produce any Cu containing phases. Potentiodynamic polarization studies revealed an increase in corrosion current density (i_{corr}) value as the Ni content was increased. However, the addition of Cu to SN31 and SN33 alloys increased their corrosion resistance. Electrochemical impedance spectroscopy studies confirmed the higher charge transfer resistance (R_{ct}) values for the Cu added alloys. Immersion corrosion test results revealed that, the corrosion rate of Cu added alloys were three times lower than SN31 and SN33 alloys. In the SN alloys, increase in corrosion rate is attributed to the increase of Al_3Ni phase as the Ni content was increased. The added Cu dissolves in the Al alloys and also reduce the Al_3Ni fraction thereby improved their corrosion resistance.

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1. Introduction

Aluminum-silicon (Al-Si) based alloys are widely used in the automotive and aerospace industries owing to their high strength/weight ratio, exceptional castability, corrosion resistance, good wear resistance, thermal conductivity and recycling potential [1—7]. Silicon is used as one of the important alloying elements in Al alloys. Most foundry alloys for casting have 5—17 wt% of Si due to its high fluidity, low shrinkage and low density (2.34 g/cm³), which would also be helpful to reduce the total weight of the components [8,9]. Increasing the Si content reduces the thermal expansion coefficient of Al-Si based alloys and causes poor machinability [10]. Al-Si alloy system is mainly divided into three categories depending upon the Si content viz., hypoeutectic (<12 wt% Si), eutectic (12—13 wt%Si) and hypereutectic (14—25 wt%) [2].

Several alloying elements including, Ti, Mg, Cu, Fe, Ni, Sr, Sn, Ca, etc. are commonly added to Al-Si alloys to alter their mechanical and chemical properties. Transition elements can form intermetallics which will contribute to the improvement of high temperature properties [9,11—14]. Depending upon their concentration, solubility limits and intermetallic phases, each element has its own characteristics. On the other hand, achieving both mechanical and chemical stability by adding these elements is still a challenging task. Cu and Mg are generally used alloying elements in Al-Si alloys since they increase the strength at room temperature as well as at elevated temperatures by solid solution strengthening and dispersion strengthening mechanisms [15—17]. Nickel is used as a minor alloying element in Al-Si alloys and the formation of thermally resistant Ni-rich compounds such as Al_3Ni, Al_3Ni_2, Al_9FeNi, Al_3CuNi, etc. improve the strength and hardness at elevated temperatures [18—20].

In spite of the addition of these transition elements improved the machinability and mechanical properties, it significantly affects the corrosion behavior [21—25]. Though the addition of Ni improved the mechanical properties of Al based alloys, it severely affects the corrosion behavior [26,27]. The binary AlNi phase acts as cathode to Al matrix, thus accelerate the corrosion rate [28,29]. Recently we have studied the influence of Ca addition on the corrosion behavior of Al-Ni alloy and found that, Ca addition improved the corrosion resistance through grain refinement mechanism [30]. Addition of Ni and Cu found to improve the mechanical properties and thermal conductivity of the Al-Si alloy,

however the corrosion resistance need to be investigated. Research on these directions are scanty. Therefore, the present study investigates the influence of Ni and Cu addition on the corrosion behavior of Al-Si alloys. Electrochemical studies were mainly carried out to assess the corrosion resistance and immersion corrosion tests were also performed to substantiate the electrochemical corrosion results. Corrosion results were analyzed by observing the corrosion morphologies after immersion tests and compared with microstructures.

2. Experimental procedure

2.1. Alloy development and microstructural characterization

All the alloys used in the present investigation were prepared by procedure reported in our previous work [30]. A 125-ton die-casting machine BD-125V5EX, TOYO Co. Ltd. was used to produce specimens for all the alloys. The proposed chemical composition of all the alloys are listed in Table 1 and die-cast alloys were used for further studies. The produced alloys were named as SN31 (Al-3Si-1Ni), SN33 (Al-3Si-3Ni), SNC311 (Al-3Si-1Ni-1Cu) and SNC331 (Al-3Si-3Ni-1Cu). X-ray diffraction (XRD) studies were performed using a Bruker D8 Advance instrument with Cu Kα radiation in the 2θ range of 20−80 at a scan rate of 2°/min. In order to observe the microstructures, the samples were successively abraded and fine polished with 0.05 μm alumina (Al_2O_3), ultra-sonicated in ethanol and air-dried. Microstructures were observed using a ZEISS Merlin Compact field emission-scanning electron microscope (FE-SEM) attached with an energy dispersive X-ray analyzer (EDAX) at an accelerating voltage of 15 kV. EDAX chemical composition of matrix and the secondary phases were quantified by spot analysis and Al, Si, Ni and Cu EDAX elemental mappings were also performed to identify their distribution as well as the secondary phases.

2.2. Corrosion studies

Electrochemical and immersion corrosion tests were performed using the procedure mentioned in our earlier paper [30]. Samples were ground using silicon carbide (SiC) emery papers up to 2000 #, ultrasonicated in acetone for 10 min, air dried and used for further tests. Electrochemical tests were carried out using a Princeton Applied Research VersaStat 3 Potentiostat/Galvanostat with three-electrode flat cell comprising of Al alloy (1 cm^2) as working electrode, Ag/AgCl as reference electrode and Pt sheet as counter electrode. Electrochemical tests were performed after 1800 s of exposure to 3.5 wt% NaCl solution. Electrochemical impedance spectroscopy (EIS) studies were performed at an open circuit potential (OCP) in the frequency range of 100 kHz to 0.05 Hz with an amplitude of 10 mV. Equivalent circuit curve fitting analysis of EIS results was also performed using ZSimpWin software. Followed by EIS measurement, potentiodynamic polarization tests were carried out by polarizing the electrode ±250 mV from its OCP at a scan rate of 1 mV/s. Die-cast specimens with the dimension of

15 × 10 × 3 mm were used for immersion corrosion tests and corrosion rates were measured after 72 h of immersion. Corrosion rates were calculated based upon the following equations [30],

Weight loss corrosion rate = (K x W) / (A x T x D) mm/y

Where, $K = 8.76 \times 10^4$, W = Mass loss (mg), A - Area (cm^2), T - Time (h) and D - Density (2.7 g/cm^3).

Hydrogen volume corrosion rate $= (K \times 0.805\ V_H)/(A \times T \times D)$ mm/y
V_H - Volume of Hydrogen evolved (ml/cm^2/d)

Surface morphologies and elemental distribution after 72 h of immersion were also observed using FE-SEM and EDAX to explain the corrosion behavior of the alloys.

3. Results and discussion

3.1. Microstructural studies of SN31, SN33, SNC311 and SNC331 alloys

In order to find out the phase structures of the produced alloys, XRD studies were performed and XRD patterns of the SN31, SN33, SNC311 and SNC331 alloys are given in Fig. 1. The high intensity peaks appeared at 38.60°, 44.83°, 65.18° and 78.30° are attributed to primary α-Al (ICDD-00-001-1180). The presence of several peaks with relatively high peak intensities at 22.09°, 22.88°, 24.19°, 25.93°, 29.65°, 41.26°, 41.84°, 43.64° and 45.31° are attributed to Al_3Ni phase (ICDD-04-007-0402). The Al_3Ni peak intensities were higher as the Ni content was increased (SN33) confirming the presence of higher fraction of Al_3Ni phase and ternary Al-Si-Ni phase diagram also substantiated these results [31]. Peaks appeared at 25.28°, 31.21° and 45.06° are attributed to Al_3Ni_2 phase (ICDD-00-014-0648) and these peaks appeared only for the SNC311 and SCN331 alloys. Furthermore, the Cu addition decreased the Al_3Ni fraction and persuaded the formation of Al_3Ni_2 phase. These results are in accordance with the thermodynamic calculations. It is identified from the phase diagram that, the stable phases in the ternary phase diagram of Al-Ni-Cu are α-Al + Al_3Ni + Al_3Cu_2 at 500−700 °C [32]. Furthermore, it is also confirmed from the phase diagram that, Al_3Ni_2 phase can only be formed by the addition of Cu

Table 1
Proposed chemical compositions of high pressure die-cast SN31, SN33, SNC311, SNC331 alloys.

Alloy	Composition [at.%(wt.%)]			
	Si	Ni	Cu	Al
SN31	3.00 (3.08)	1.00 (2.15)	−	96.00 (94.77)
SNC311	3.00 (3.04)	1.00 (2.12)	1.00 (2.29)	95.00 (92.54)
SN33	3.00 (2.98)	3.00 (6.24)	−	94.00 (90.78)
SNC331	3.00 (2.97)	3.00 (6.22)	1.00 (2.24)	93.00 (88.57)
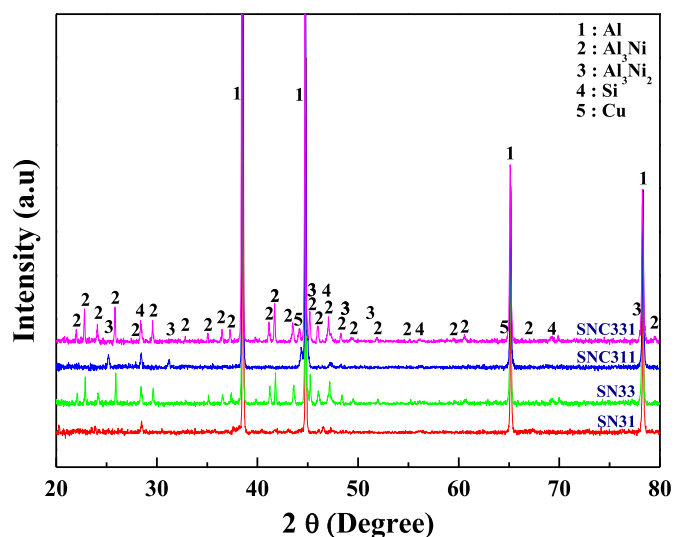
Fig. 1. XRD patterns of SN31, SNC311, SN33 and SNC331 alloys.