EXPERIMENTAL MICROSTRUCTURE EVALUATION AND CORROSION BEHAVIOUR OF FLY-ASH REINFORCED ALUMINIUM COMPOSITE

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Abstract

The micro structural characteristics of aluminum matrix AK12 composites containing of fly ash particles (precipitator), obtained by gravity and squeeze costing techniques, pitting corrosion behavior and corrosion kinetics are presented and discussed. The present work concentrates on utilization of fly ash in useful manner by mixing it with Al6061 alloy with different weight fractions and particle size. Initially two sets of specimen are prepared using stir casting route technique. First set contains fly ash particle size below 50µm and second set consists fly ash particle size between 53-100µm. Mainly two sets of composite samples with the reinforcement weight percentages of 4, 8, 12 and 16% were used. One of the important thermal properties of the material, specific heat carrying capacity has been determined. It was found that(1) in comparison with gravity casting, squeeze casting technology is advantageous for obtaining higher structural homogeneity with minimum possible porosity levels, good interfacial bonding and quite a uniform distribution of reinforcement, (2) fly ash particles lead to an enhanced pitting corrosion of the AK12/9.0% fly ash (75-100 m fraction) composite in comparison with unreinforced matrix (AK12 alloy), and (3) the presence of nobler second phase of fly ash particles, cast defects like pores, and higher silicon content formed as a result of reaction between aluminum and silica in AK12 alloy and aluminum fly ash composite determine the pitting corrosion behaviour and the properties of oxide film forming on the corroding surface.

Key words: Aluminum, fly ash, Corrosion kinetics, Metal-Matrix Composites, Microstructure, Pitting corrosion.

1. Introduction

Aluminium-fly ash (ALFA) composites have been developed in recent years. Fly ash is a particulate waste material formed as a result of coal combustion in power plants. The use of fly ash as a filler or reinforcement for aluminum alloys, called Metal Matrix Composites (MMC's), is, therefore, very desirable from an environmental standpoint. Fly ash forms at temperatures in the range of 920-1200 ºC and is collected as precipitator ash (solid particles) and cenospheres (hollow microspheres) that float on collection ponds [1,2]. Cenosphere has a low density of about 0.6 g cm^{-3}, and can be used for the synthesis of ultra-light composites materials, whereas precipitator fly ash has a density in the range of 2.0-2.5 g cm^{-3}. It can improve various properties of selected matrix materials, including stiffness, strength, and wear resistance [3-5].

The published literature on advanced materials, such as Aluminium Fly Ash (ALFA) composites, is rather limited and is primarily concerned with applications of fly ash particles for synthesis of these materials. There is also a lack of information on the influence of fly ash particles on the susceptibility of ALFA composites to corrosion. Therefore, it was thought worthwhile to study:

(1) The microstructural characteristics of aluminium composites reinforced with fly ash particles, and

(2) The relationships between the composite microstructure and corrosion behaviour in a typical corrosive environment. The present work is dedicated to such an investigation.

The Metal matrix composites are dominantly in leading phase in the midst of different classes of composites. In last two to three decades this metal matrix composites (MMCs) has converted into a scientific topic. Also it gives intellectual awareness about material of extensive technological and commercial significance. MMCs deal with distinctive balance of mechanical and physical properties. Aluminium based MMCs have found increasing attention in last few decades as engineering material. From the literature review, it is concluded that in order to study and analyse the influence of the particle size of fly ash as reinforcement on the aluminium alloy (Al6061) composite is taken. To study its effect on thermal properties different sizes of fly ash have also been taken in this study. Some of the earlier investigations showed that the mechanical properties are enhanced with increase in fly ash percentage. It is true that with mechanical property thermal properties are also varying. Hence some consideration is given to study this thermal properties are given. It is known that the influence of these parameters on the various properties is maximum because due to the mixing of reinforcement its micro structural state changes which leads to increase in properties. In order to explore an interesting and useful engineering material this study is carried out.

2. EXPERIMENTAL SETUP

Setup used for the measurement of specific heat capacity is shown in below figure. It consists of voltmeter (0-200v), ammeter (0-2A), dimmer stat (4A load),thermocouples (0-250°C), temperature indicator (up to 1200°C), heater, insulated container etc. Electric flow diagram is also shown below. Before starting the experiment all the connections are properly checked. After this 200ml of water is filled in the insulated container and its temperature is noted down, with this the specimen weight is also noted down (6). Now specimen whose specific heat is to be measured is heated with the help of mica heater by supplying heat with dimmer stat, up to a temperature of 100°C. The dimmer stat is a device which is used to control temperature by supplying constant heat. The heat transfer will

takes place from metal piece to surrounding water. After some time interval both metal temperature and water temperature becomes equal. That temperature is used as the final temperature of water as well as metal. Now by usual proceeding i.e. by using the formula (Q= m Cp Δt) (By balancing the this equation) specific heat capacity of metal piece is calculated (7).

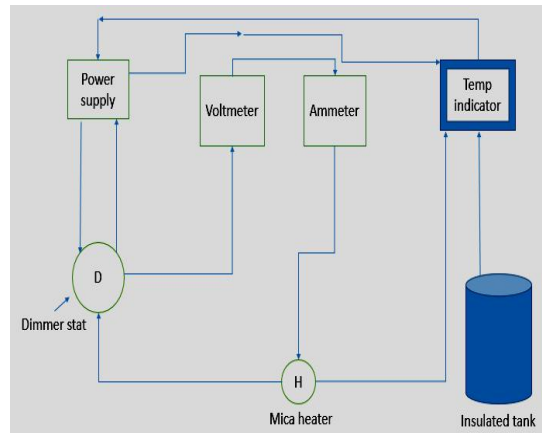**Figure –1:** Electrical Flow diagram of the experimental setup**.**

Figure -2: Experimental setup were used for the measurement of specific heat.

The corrosion behaviour of the materials was studied further by immersion tests. Samples in the shape of half-disc specimens of 18 mm radius and 3 mm thickness were cut from the composites and matrix alloy. They were ground to 800 grit and then cleaned with acetone, dried, weighed and immersed in an unstirred solution of 3.5 wt.% NaCl (pH 7.0) in distilled water exposed to atmospheric air. The test were performed at room temperature (22 ˚C). The solution-to-specimen area ratio was about 1 ml mm^{-2}. To avoid crevice corrosion, the

specimens were suspended in the solution with a plastic string passing through a 2 mm diameter hole through them. Every 5 days the specimen were first mechanically cleaned with a brush made of plastic strings, and then chemically cleaned in a solution of 2.0 wt.% chromic acid and 3.5 wt.% phosphoric acid at 98 ˚C for 10 s, dried and weighed. The accuracy in the determination of weight was ± 0.05 mg. The microstructure was studied using an optical microscope (ZEISS model) and a scanning electron microscope (Hitachi S-3500N).

2.1 Measurement of Specific Heat Capacity of composite solid (Cp):

Specimen no. 1: Pure Al6061 without fly ash

Mass of water = 200ml

Mass of specimen = 14.1g

Initial temperature of water = ?

Cp of water = ?

We know that,

$$Q = mCp\Delta t$$

TABLE1:

Voltage (V)	Current (A)	T1 Initial water temp. (˚C)	T2 Final water temp. (°C)	T3 Initial specimen temp(°C)	T1 Final specimen temp. (°C)
205	0.35	31	32	100	32

(mCpΔt) water = (mCpΔt) Specimen

$200 \times 4.187 \times (32-31) = 14.1 \times Cp \times (100-32)$

$837.4 = 958.8$ Cp specimen

Cp of Specimen= **0.8733** J/g°C

From literature survey the specific heat carrying capacity of Al 6061 is 0.896 J/g-°C. In this experimental work specific heat capacity is found as 0.8733 J/g-°C. The difference is very small and it is mainly due to some tiny experimental errors. Even though the result obtained from the experimental work is accepted. From the above table it can be observed that specific heat carrying capacity of composite is gradually increasing with increase in fly ash percentage. It is mainly due to the fact that fly ash particle exhibit higher specific heat capacity. As a result of this specific heat capacity of composite also increased. Enhanced specific heat capacity is most widely accepted in automobile and aerospace industries (7). Now if we see the variation of specific heat with respect to fly ash particle size then it is higher for small sized particles.

3. Metal matrix microstructure

Good retention of fly ash particles was clearly seen in the microstructures of AK12/fly ash composites. This feature is shown in Fig. 3. Coagulation of some fly ash particles and development of some primary silicon single crystals in the vicinity of fly ash colonies are also seen in this figure.
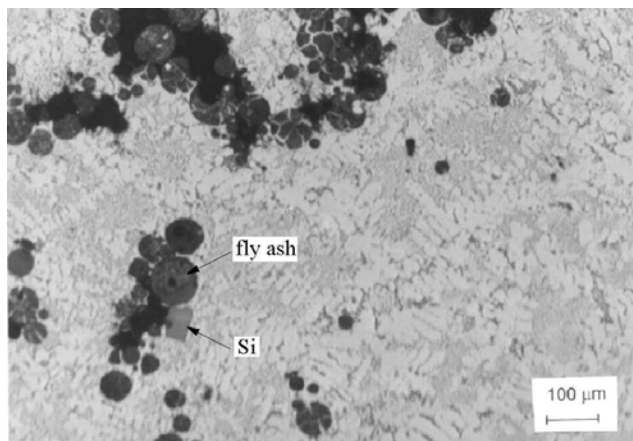

Fig. 3. Microstructure of ALFA AK12/9.0% fly ash (53-75m fraction) composite after gravity casting (as cast). Primary Si single crystals are also seen.

An important feature of the aluminium alloy composite containing fly ash particles is their distribution and interface between reinforcement and matrix [5]. In the case of composites after gravity casting, occurrence of agglomerations can be caused by a characteristic limitation of the stirring technique. Porosity located in the neighbourhood of interface is an effect of premature particle-matrix decohesion during crystallization. According to Rohatgi [5] the distribution of the fly ah particles is influenced

by the tendency of particles to float due to density differences and interactions with the solidifying metal. He also pointed out that fly particles are present in the interdendritic regions between -Al dendrites due to lack of nucleation of -Al on fly ash particles ad due to pushing on fly ash particles by growing -Al dendrites during solidification. Typical for all analysed composite structures is the presence of crushed fly ash precipitator particles, probably due to their high temperature treatment before incorporation into the melt and then vigorous mechanical stirring. The diversified chemical composition of fly ash particles and its high reactivity can form compounds by chemical reactions between fly ash particles and liquid aluminium during the synthesis of the composites [8]. The reaction between fly ash-reinforcement containing silica and liquid aluminium can lead to the formation of alumina and silicon[8].

$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si.$$
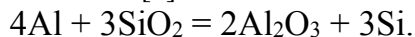
In the ALFA composites after squeeze casting the influence of pressure on microstructure of materials may be noticed [3,9]. During crystallization pressure reduces the energy of the phase interaction at the liquid metal-solid particle boundary. Additionally, there is a high probability of occurrence of wettability (inherently related with the surface tension) of fly ash particles by molten alloy when external pressure is applied, whereas it does not occur in traditional gravity casting. These factors affect the good bond of fly ash particles with aluminium matrix (Fig. 3). Squeeze casting technique is favourable for obtaining a uniform distribution of reinforcement phase in the metal matrix [3,8]. External pressure applied on the melt during crystallization increases the cooling rate, the number of crystallization centres, solidification temperature ranges, and the rate of undercooling. It also decreases dendrite arm spacing, solidification time, critical radius of nuclei, changes in surface tension, specific volume, diffusivity and other parameters of crystallization [9]. These processes lead to a refining of structural components (particularly -Al+Si eutectic), the changes of distribution and character of the phases, different structural and chemical homogeneity and elimination of any kind of structural discontinuities.

4. Corrosion behaviour

Corrosion characteristics represented by corrosion, pitting and repassivation potentials (denoted by E_{corr}, E_{pit} and E_{rp}, respectively) were determined from the electrochemical studies and analysis of anodic polarisation curves. The additional electrochemical parameters, given in the table, are: $E_{pit} = E_{pit} - E_{corr}$, and $E_{rp} = E_{pit} - E_{rp}$. The parameter E_{pit} is a measure of the width of the passive region on the polarization curve and provides an indication of the susceptibility to pitting. The parameter E_{rp} is used to assess the repassivation behaviour of propagating pits and hence, the ease with which locally active sites can be eliminated.

Pitting corrosion appears mainly on metals and alloys in the passive state as a result of disarrangement of passive layer by aggressive environment elements (frequently Cl^- ions) on the heterogeneities of metals. In the case of composites introduction of considerable amounts of alloy additions and reinforcing materials to the aluminium matrix releases intermetallic phases in the structure, which lead to the formation of galvanic couples favourable to corrosion. Moreover, factors influencing corrosion of the composites include porosity, segregation of alloying elements to the reinforcement/matrix interface, presence of an interfacial reaction product, high dislocation density around the reinforcement phase, voids at the reinforcement/matrix interface and electrical conductivity of the reinforcements [10,11]. Due to the increase in the concentration of Cl^- and H^+ ions passivation becomes difficult. Therefore, dissolution of metal in the pits is stimulated [12]. It is well known [12] that corrosion of metals involves the formation of a surface film of an oxide phase separating the metal from the corroding reactant. Growth of the surface film takes place as a result of migration of the reactant through the surface film. If the oxide film formed on the surface is porous, corrosion continues until the whole of the metal is oxidized. However, if the oxide film is compact, adherent and pore-free, then it prevents the metal surface from subsequent oxidation. Compact, pore-free and adherent films formed on metals are usually thin while porous films are thick.

5. RESULTS AND DISCUSSION:

Heat carrying capacity is the measure of the ability of the material to absorb thermal energy. Specific heat carrying capacity is another important thermal property that needs to be considered for a newly defined material(9). This is because higher the specific heat, more heat it must absorb before it raising its temperature.
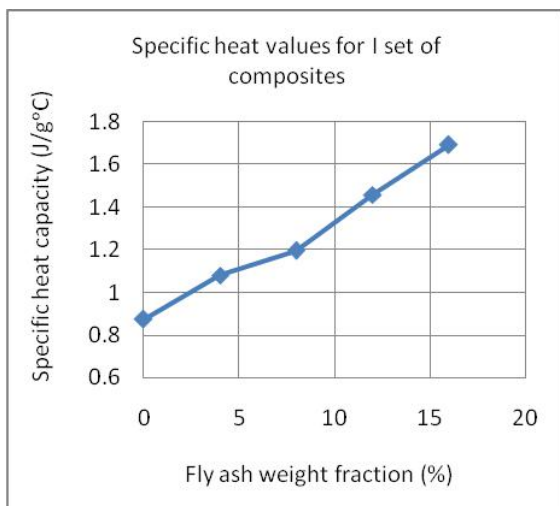
Figure 4 shows different values of Cp for different weight

fractions of fly ash particles sized below 50µm**.**

It is observed from the above table that specific heat carrying capacity is increased with addition of fly ash. It also observed that for first two compositions, percentage change in values of specific heat capacities are more for composite with fly ash particles sized below 50µm. For last two compositions, percentage change in values of specific heat capacities are more for composites with fly ash particles sized above 50µm(11). This may be due to higher thermal expansion of fly ash. This leads to decrease in values of thermal conductivity. Finally the result will be increase in values of specific heat capacity. It is known that specific heat capacity of Al6061 is 0.896 J/g-°C. In this experimental work it is observed that specific heat capacity of Al6061 is 0.8733 J/g-°C. From the above graph it is observed that specific heat carrying capacity of composite is gradually increasing with increase in fly ash percentage. It is mainly due to the fact that fly ash particle exhibit higher specific heat capacity(12). As a result of this specific heat capacity of composite also increases. This enhanced specific heat capacity is most widely accepted in automobile and aerospace industries. If we observe the variation of specific heat with respect to fly ash particle size, then it is higher for small sized particles. This is due to fact that fine powdered particles exhibit lower thermal expansion as a result of this specific heat carrying capacity increases. In this work up to 16% fly ash particles were added and results are obtained within acceptable range. From literature survey it is observed that only up to 20% weight fraction of fly ash particles can be successfully incorporated. Further increase in fly ash particles leads disadvantages rather than advantages.

6. CONCLUSION

Specific heat carrying capacity is one of the important thermal property that needs to be studied. This property is of prime concern because it gives ability of material to carry heat inside the material. This property is mainly related to inter atomic structure. In this work it is observed that composite with fly ash particles sized below 50µm exhibit higher specific heat carrying capacity than composite with fly ash particles sized above 50µm. This may be due to proper mixing of fly ash particles in composite and also due to fact that smaller fly ash particles exhibit higher specific heat carrying capacity. It is observed that for pure Al6061 specific heat carrying capacity is 0.8733 J/g° C. For Al6061+fly ash composite with 4% weight fraction specific heat carrying capacity is observed as 1.0811 J/g° C and 0.9835 J/g °C for fly ash sized below 50µm and above 50µm respectively. The percentage change occurred in specific heat of composite for case-I is 19.22%, for case II (Fly ash with particles sized above 50µm) is 11.20%. The difference is mainly due to size of fly ash particles. Higher the size of fly ash particle, lower will be the percentage change in specific heat capacity.

The following conclusions can be drawn from this study:

(1) Addition of fly ash particles as reinforcement in metal matrix composites and synthesis of ALFA composites by squeeze casting technology in comparison with gravity casting are advantageous for obtaining higher structural homogeneity with minimum possible porosity levels, good interfacial bonding and quite a uniform distribution of reinforcement.

(2) Fly ash particles lead to an enhanced pitting corrosion of the AK12/9.0% fly ash (75-100 m fraction) composite in comparison with unreinforced matrix (AK12 alloy). The enhanced pitting corrosion of ALFA composite is associated with the introduction of nobler second phase of fly ash particles, cast defects like pores, and higher silicon content formed as a result of reaction between aluminium and silica. The same factors (i.e. fly ash particles, cast defects and higher silicon content) also determine the properties of oxide film forming on the corroding surface.

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