

Separation of matrix alloy and reinforcement from aluminum metal matrix composites scrap by salt flux addition

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Abstract. Separation of matrix alloy and reinforcements from pure Al–SiC_p composite scrap by salt flux addition has been theoretically predicted using interface free energies. Experiments performed confirm the theoretical prediction. Complete separation of matrix aluminum and reinforcement from metal matrix composites (MMCs) scrap has been achieved by addition of 2.05 wt% of equimolar mixture of NaCl–KCl salt flux with a metal and particle yield of 84 and 50%, respectively. By adding 5 wt% of NaF to equimolar mixture of NaCl–KCl, metal and particle yield improved to 91 and 73%, respectively. Reusability of both the matrix aluminum and the SiC separated from Al–SiC_p scraps has been analysed using XRD, SEM and DTA techniques. The matrix alloy separated from Al–SiC_p scraps can be used possibly as a low Si content Al–Si alloy. However, the interfacial reaction that occurred during the fabrication of the composites had degraded the SiC particles.

Keywords. Metal matrix composites; salt flux; separation; recycling.

1. Introduction

The application of metal matrix composites (MMCs) in many engineering components has increased over the last few years, particularly in the automobile industry as drive shafts, engine and brake components (Chawla and Chawla 2006). It is mainly due to the ever increasing restrictions on the fuel consumption and emission, which have forced the automotive manufacturers to look for newer light weight materials. Recent MMCs market survey released by the Business Communications Company (BCC) confirms that MMCs consumption in automotive sector increased from 1.57–2.03 million kg during the period 1999–2004 (Chawla and Chawla 2006). BCC projects a rise from its 2004 level of 2.03–2.9 million kg by 2010, which corresponds to an average annual growth rate of 6.2%. The amount of MMCs scraps (feeder heads, runners and rejected and worn out components) generated during manufacturing and service will increase as the world consumption increases. Therefore, development of viable techniques for recycling and reclamation of MMCs is essential and critical to the commercialization of these advanced materials.

The problems associated with conventional recycling of Al MMCs by remelting are (i) amplified interfacial reaction between the melt and the reinforcement (mainly in low Si content wrought alloys) and (ii) tendency to the formation of large quantities of dross. Separation of both the matrix aluminum and the reinforcement from Al MMCs

scrap and reuse them individually is an alternate approach. The energy requirement for recycled aluminum alloy ingot is only about 3% of that of primary ingot (Ohnishi 1996). This fact also strongly supports the separation process.

Generally, oxide films and insoluble metallic and non-metallic inclusions are separated from aluminum melt by salt flux addition (Roy and Sahai 1998). This technique can also be used to separate the aluminum alloy and reinforcement from Al MMCs scrap. The most commonly used salt fluxes are mixtures of NaCl and KCl (Schuster *et al* 1993). Besides these chlorides, fluorides are also added to improve the fluxing efficiency. In the present study, separation of the matrix alloy and the reinforcements from pure Al–SiC_p composites by salt flux addition has been theoretically predicted using interface free energies followed by experimental validation. Further, the reusability of both the matrix aluminum and SiC separated from pure Al–SiC_p composites scraps has been analysed using XRD, SEM and DTA techniques.

2. Theoretical aspects of separation

MMCs consist of a matrix metal and a reinforcement, which have their own crystal structure and interfaces between them. The entropy of mixing in the fabrication of MMCs does not change much because MMCs are not mixtures at atomic level. This indicates that there should be a way to separate reinforcements from the matrix.

During the fabrication of MMCs, the minimum work, W , required is given by

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$$W = (\gamma_{rm} - \gamma_{ra})dA, \tag{1}$$

where γ_{rm} is the interface energy between reinforcement and matrix metal, γ_{ra} the surface energy of the reinforcement surrounded by air before the fabrication of the MMCs, and dA the total interface area between matrix metal and reinforcement of an unit weight of MMCs (figure 1(a)). When ceramic fibres or particles are used as the reinforcement, γ_{rm} is much larger than γ_{ra} , because the contact angle between the molten matrix metal and the reinforcement is larger than 90° . Hence, when some stimulus is given to the interface, the separation of the reinforcement might occur because the interface has a driving force. However, the separation occurs spontaneously only when the interface free energy (ΔG_1) is negative.

$$\Delta G_1 = \gamma_{ra}dA_1 + \gamma_{ma}dA_2 - \gamma_{rm}dA, \tag{2}$$

where γ_{ma} is the surface energy of the matrix surrounded by air during fabrication of the composite and dA_1 and dA_2

are surface area of reinforcement and matrix metal at the interface, respectively after separation (figure 1(b)). For metal–ceramic system, ΔG_1 is always positive, because the driving force available according to (1) is compensated by the energy required to create two new surfaces. Hence, the separation of reinforcements from composite does not occur spontaneously.

In order to separate matrix alloy and reinforcement, it is important to find a material that makes an interface having smaller interface energy than the matrix metal, when the material contacts the reinforcement. The salt fluxes are found to be candidate material for separation process (Ohnishi 1996). When it comes into contact with the interface between reinforcement and matrix metal at the molten state (figure 2(a)), it infiltrates into the interface instead of the matrix metal as shown in figure 2(b). The interface free energy of this case is given by

$$\Delta G_2 = \gamma_{rf}dA_3 + \gamma_{mf}dA_4 - \gamma_{rm}dA, \tag{3}$$

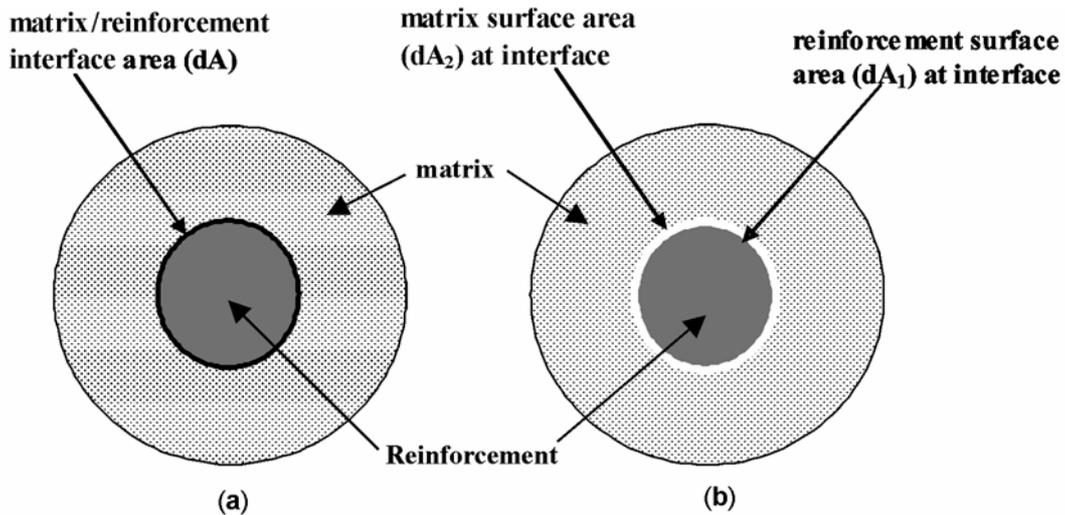


Figure 1. Surface area at the interface prior to flux addition: (a) before separation and (b) after separation.

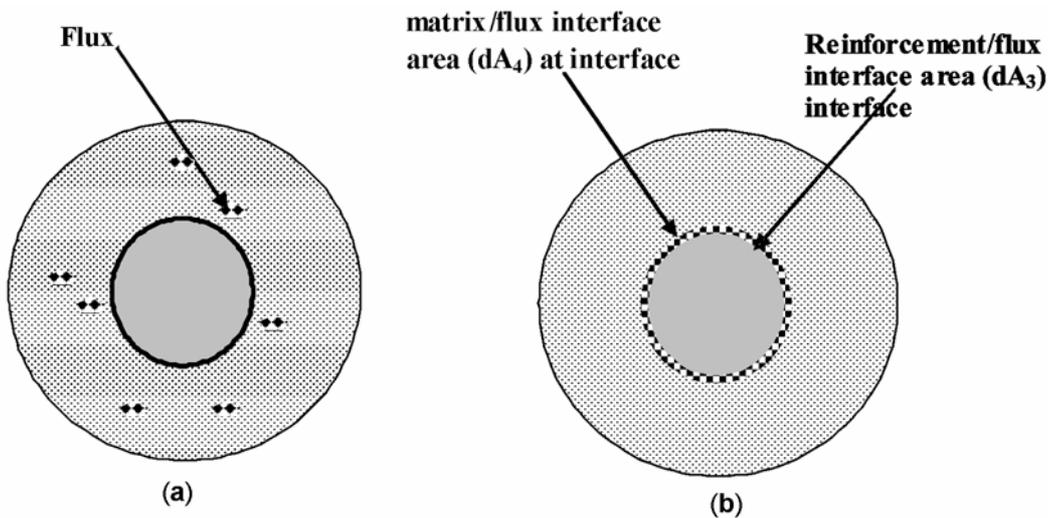


Figure 2. Surface area at the interface after flux addition: (a) before separation and (b) after separation.

where γ_{if} is the interface energy between the reinforcement and the flux, γ_{mf} the interface energy between the metal and the flux, dA_3 the total interface area between reinforcement and flux and dA_4 the total interface area between matrix and flux.

Assuming $dA = dA_3 = dA_4$, since the difference between these three interface areas is very small,

$$\Delta G_3 = (\gamma_{if} + \gamma_{mf} - \gamma_{m})dA. \quad (4)$$

When ΔG_3 is less than zero and the salt fluxes have only little solubility in the matrix metal, separation of the matrix metal and the reinforcement from composite is spontaneous.

2.1 Interfacial tension between ceramic reinforcement and molten salt flux (γ_{if})

When the contact angle between two materials is rather low, it is possible to estimate the interface energy by Girifalco and Good's (1957) equation

$$\gamma_{if} = \gamma_{ra} + \gamma_f - 2\phi(\gamma_{ra}\gamma_f)^{1/2}, \quad (5)$$

where γ_f is the surface tension of molten salt flux and ϕ a constant which is determined by the characteristics of the system.

2.2 Interfacial tension between molten aluminum and salt flux (γ_{mf})

When the interfacial tension changes due to the adsorption of surface active elements, Girifalco and Good's (1957) equation in conjunction with expressions for the surface coverage of surface active species can be used to estimate the interfacial tension. In the present work, interfacial tension between molten aluminum and various salt flux systems has been taken from the plot showing the variation of interfacial tension between aluminum and equimolar NaCl–KCl as a function of NaF addition (Roy and Utigard 1998).

2.3 Interfacial tension between ceramic reinforcement and molten aluminum (γ_{rm})

The interfacial tension between the ceramic particles and the liquid aluminum, γ_{rm} is calculated using Young's equation

$$\gamma_{rm} = \gamma_{ra} - \gamma_{ma}\cos\theta. \quad (6)$$

3. Materials and methods

Pure Al–SiC_p composites used in the present study have been fabricated by stir casting technique. Entire composite fabrication process (particle addition, stirring and pouring) has been carried out at 720°C. The time of contact of the

aluminum melt with SiC at this temperature did not exceed 30 min. In order to change the interfacial energy between the ceramic reinforcement and the matrix metal at molten state, equimolar mixture of NaCl–KCl salt flux with varying amounts of NaF (1, 2, 3, 4, 5, 7 and 10 wt%) has been added to the composite melt through vortex created by mechanical stirring at 700°C. At a certain quantity of flux addition, separation of reinforcement particles starts leading to their floating on the melt surface and skimming off. The left over matrix melt in the crucible has been poured into a cast iron mold.

4. Results and discussion

4.1 Comparison of theoretical model and experimental results

The effect of equimolar mixture of NaCl–KCl salt flux addition to pure Al–SiC composites on free energy for separation (ΔG_3) has been theoretically calculated using the values of various parameters given in appendix 1. According to the theoretical result, the free energy for the separation in Al–SiC composites is negative (-48 mJ/m^2) dA with equimolar mixture of NaCl–KCl salt flux addition. It indicates that separation of SiC particle from Al–SiC composites melt should occur with equimolar mixture of NaCl–KCl salt flux addition. Experiments performed confirm the theoretical results. Addition of 2.05 wt% equimolar mixture of NaCl–KCl salt flux results in complete separation of the matrix material and the reinforcement from MMCs scrap with metal and particle yield of 84 and 50%, respectively. The balance metal and particle form a part of the dross generated.

The effect of NaF addition to equimolar mixture of NaCl–KCl salt flux on the free energy and optimum quantity

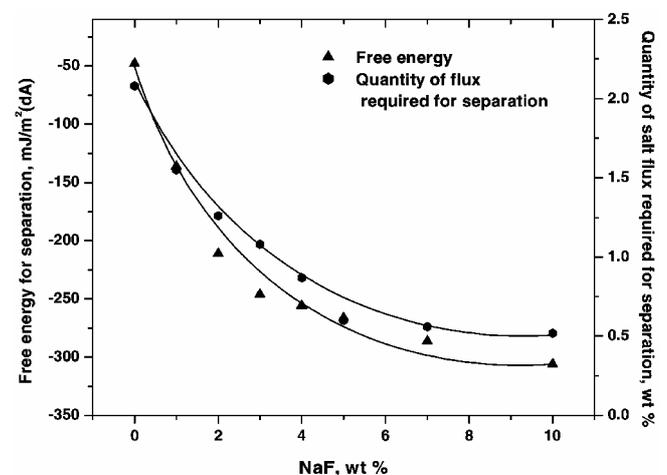


Figure 3. Influence of NaF addition to equimolar mixture of NaCl–KCl salt flux on the free energy and optimum quantity of flux required for separation in pure Al–SiC_p composites.

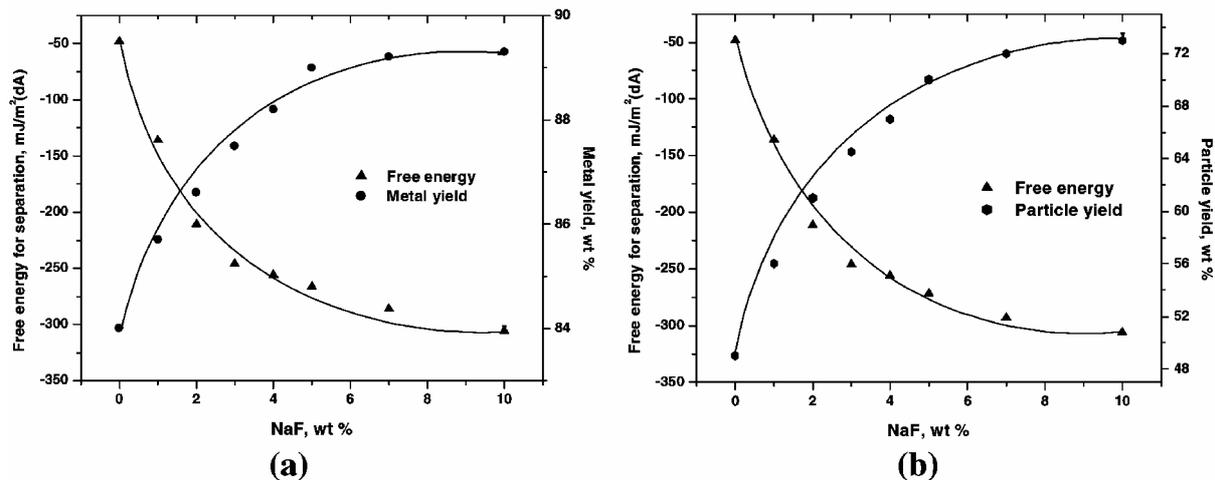


Figure 4. Influence of NaF addition to equimolar mixture of NaCl-KCl salt flux on (a) metal yield and (b) reinforcement yield in pure Al-SiC_p composites.

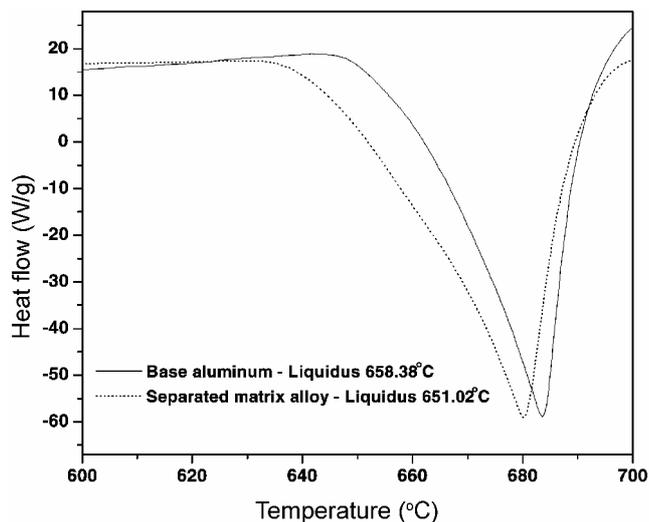


Figure 5. DTA heating curves of pure aluminum and matrix alloy separated from pure Al-SiC_p composites (as processed) by salt flux (equimolar NaCl-KCl + 5 wt% NaF) addition.

of flux required for separation in pure Al-SiC composites is shown in figure 3. The free energy for separation decreases rapidly from $(-48 \text{ mJ/m}^2)dA$ to $(-266 \text{ mJ/m}^2)dA$ up to 5 wt% of NaF addition to equimolar mixture of NaCl-KCl salt flux and thereafter, it decreases slowly from $(-266 \text{ mJ/m}^2)dA$ to $(-306 \text{ mJ/m}^2)dA$ with further 5 wt% of NaF addition. Similarly, optimum quantity of salt flux required for separation decreases from 2.05 wt% to 0.6 wt% with 5 wt% of NaF addition to equimolar mixture of NaCl-KCl salt flux and with further 5 wt% of NaF addition it decreased to 0.52 wt%. Further, metal and particle yield improved to 91 and 73%, respectively with 5 wt% of NaF addition to equimolar mixture of NaCl-KCl salt flux (figures 4(a) and (b)). These results indicate that the free energy for separation calculated based on the

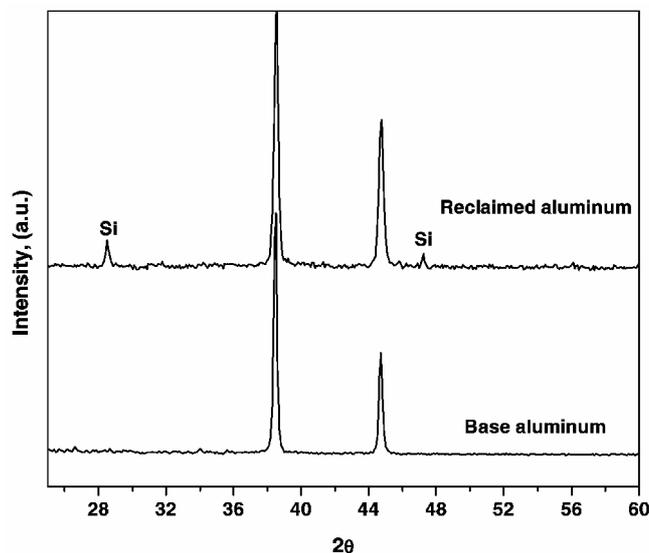


Figure 6. Comparison of XRD patterns of matrix alloy separated from pure Al-SiC_p composites (as processed) by salt flux (equimolar NaCl-KCl + 5 wt% NaF) addition with that of pure aluminum.

interface energy is in qualitative agreement with the efficiency of separation process. The increase in the separation efficiency promoted by NaF addition to the equimolar mixture of NaCl-KCl salt flux has been attributed to the simultaneous action of three factors: (i) the free energy for separation (ΔG_3) becoming more negative, (ii) decrease in flux viscosity favouring the coalescence of aluminum (Roy and Sahai 1997) and (iii) removal of alumina (Al_2O_3) film formed on the melt surface acting as a physical barrier to the transfer of separated particles to the melt surface. Hence, continuous stripping of oxide layer from the melt surface is necessary for effective separation of reinforcement. This observation is in agreement with that of

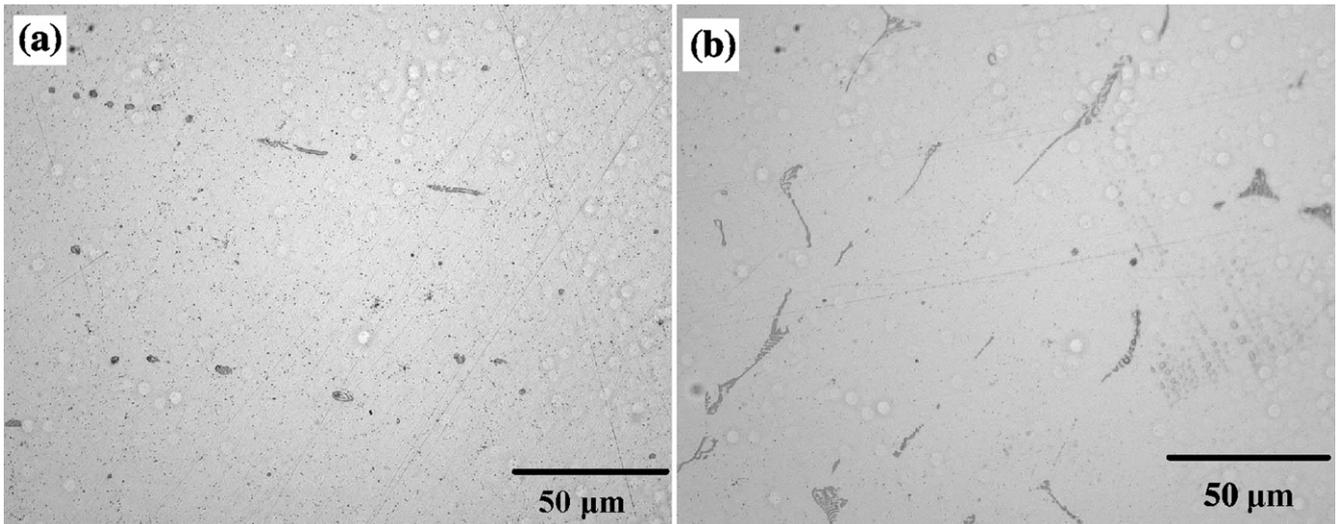


Figure 7. Optical microstructure of (a) pure aluminum and (b) matrix alloy separated from pure Al-SiC_p composites (as processed) by salt flux (equimolar NaCl-KCl + 5 wt% NaF) addition.

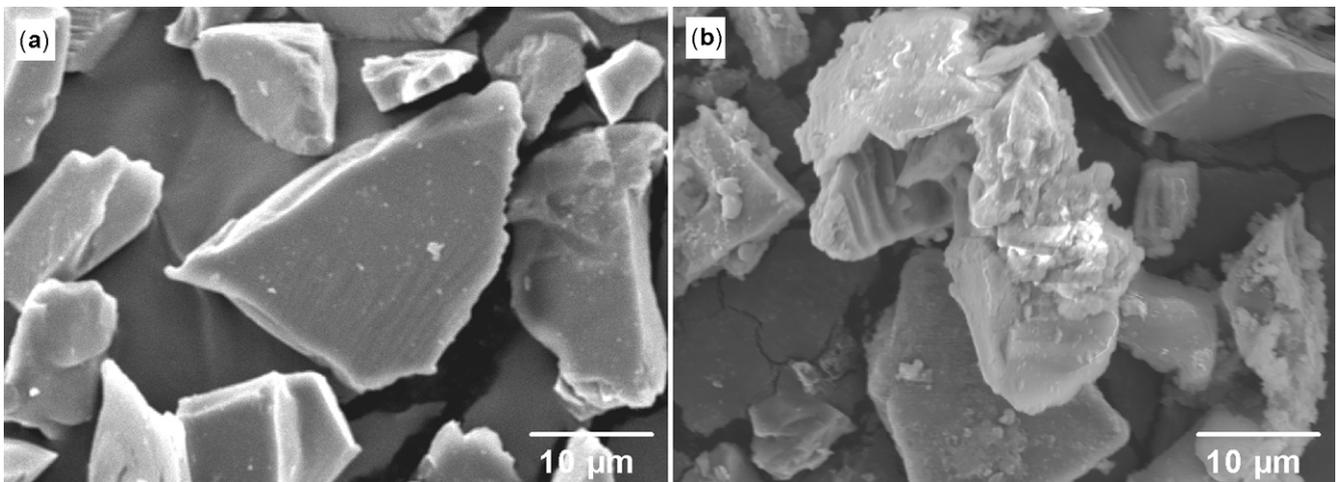
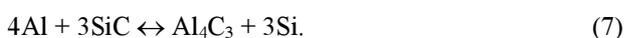


Figure 8. Scanning electron micrograph of (a) as received SiC particles and (b) SiC particles separated by equimolar NaCl-KCl + 5 wt% NaF salt flux addition.

Ye and Sahai (1996), who have also added NaF to equimolar mixture of NaCl-KCl salt flux to remove the external oxide layer of aluminum melt more efficiently.

4.2 Recycling of separated matrix alloy

During the fabrication of pure Al-SiC_p composites via stir casting process, it is impossible to avoid the interfacial reaction totally due to the low Si contents within the matrices (Lee *et al* 1999). Interfacial reaction between Al and SiC to form Al₄C₃ and Si takes place according to the reaction



Si released during this interfacial reaction changes the matrix alloy composition resulting in a decrease in liquidus temperature. This decrease in liquidus temperature

can be ascertained by differential thermal analysis (DTA). Figure 5 shows the DTA heating curves of pure aluminum and the matrix alloy separated from pure Al-SiC_p composites (as processed) by salt flux (equimolar NaCl-KCl + 5 wt% NaF) addition. In the case of pure aluminum, upon heating, a strong endothermic peak appears at around 658.38°C, corresponding to the melting of the matrix alloy. Considering that the melting of pure Al occurs at 660°C, the measured melting temperature of the Al/SiC_p composite in its as processed condition is slightly lower, which may be attributed to the presence of small amounts of impurities within the matrix. In the case of separated matrix alloy, the thermal response observed is similar to that for the pure aluminum except at a lower melting temperature of 651.02°C. XRD of separated matrix alloy shows diffraction peak of the released Si (figure 6), which is responsible for the decrease in liquidus tempera-

ture in DTA curve of separated matrix aluminum. It indicates that interfacial reaction has occurred during processing of composite at 720°C for 30 min.

Figure 7 shows the optical microstructure of pure aluminum and matrix alloy separated from pure Al–SiC_p composite, the latter showing the typical microstructure of low Si content hypoeutectic Al–Si alloy. In the separated matrix alloy, no reinforcement particle is observed. This shows that complete separation of matrix metal and reinforcement from Al–SiC_p composites scrap has been achieved by salt flux addition. Hence, the separated matrix aluminum can be reused possibly as a low Si content Al–Si alloy.

4.3 Recycling of separated SiC particles

Figure 8(a) shows the sharp edges and smooth surface morphologies of SiC_p in as-received condition, while figure 8(b) reveals the rounded edges and degraded surfaces of the SiC_p separated from pure Al–SiC_p composites (as processed) by salt flux (equimolar NaCl–KCl + 5 wt% NaF) addition indicating the occurrence of interfacial reaction during processing of the composites. The sharp corners are chemically more reactive due to their high surface energy. XRD results obtained from SiC_p separated from pure Al–SiC_p composites shows Al₄C₃ peak (figure 9), further confirming the interfacial reaction. Thus, the interfacial reaction taking place during the fabrication of the composite degrades the SiC particles limiting its recyclability.

5. Conclusions

(I) Theoretically predicted separation of matrix alloy and reinforcements from pure Al–SiC_p composite scrap by salt flux addition has been confirmed by experiments.

(II) Addition of equimolar mixture of NaCl–KCl salt flux results in complete separation of matrix material and reinforcement from MMCs scrap with metal and particle yield of 84% and 50%, respectively.

(III) Addition of 5wt% NaF to equimolar mixture of NaCl–KCl, metal and particle yield has been improved to 91 and 73%, respectively.

(IV) Separated matrix aluminum can be reused possibly as a low Si content Al–Si alloy.

(V) Interfacial reaction taking place during fabrication of the composites degrades the SiC particles limiting their recyclability.

Appendix I

Interface energies:

$$\gamma_{ra} = 1844 \text{ mJ/m}^2 \text{ (Barsoum and Ownby 1981);}$$

$$\phi = 0.41 \text{ (Silny and Utigard 1997; Ho and Sahai 1990);}$$

$$\gamma_f = 106 \text{ mJ/m}^2 \text{ (Silny and Utigard 1997; Ho and Sahai 1990);}$$

$$\gamma_{ma} = 1007 \text{ mJ/m}^2 \text{ (Anson et al 1999).}$$

Contact angle between Al and SiC = 120 deg (Laurent et al 1987).

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References

- Anson J P, Drew R A L and Gruzleski J E 1999 *Met. Mater. Trans.* **B30** 1027
- Barsoum M W and Ownby P D 1981 *Surfaces and interfaces in ceramic metals systems* (New York: Plenum Press) p. 463
- Chawla N and Chawla K K 2006 *JOM* **58** 67
- Girifalco L A and Good R J 1957 *J. Phys. Chem.* **61** 904
- Handbook of Chemistry and Physics 1981 CRC Press, 66th edn. p. F-20
- Ho F K and Sahai Y 1990 *Light Met.* 717
- Laurent V, Chattain D and Eustathopoulos N 1987 *J. Mater. Sci.* **22** 244
- Lee J C, Seok H K and Lee H I 1999 *Mater. Res. Bull.* **34** 35
- Ohnishi T 1996 *J. Jpn Inst. Light Met.* **46** 525
- Roy R R and Sahai Y 1997 *Mater. Trans. JIM* **38** 568
- Roy R R and Utigard T A 1998 *Met. Mater. Trans.* **B29** 821
- Roy R R and Sahai Y 1998 *Light metals* (Warrendale, Pennsylvania: TMS Annual Meeting) pp 1237–1243
- Schuster D M, Skibo M D, Bruski R S, Provencher R and Rivierin G 1993 *JOM* **46** 26
- Silny A and Utigard T A 1997 *Light Met.* 871
- Ye J and Sahai Y 1996 *Mater. Trans. JIM* **37** 175

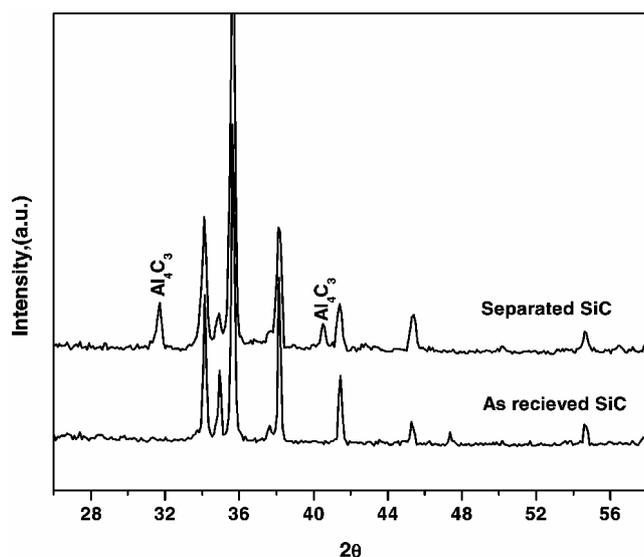


Figure 9. Comparison of XRD patterns of SiC particles separated by equimolar NaCl–KCl + 5 wt% NaF salt flux addition with that of as received SiC particles.