



SEPARATION AND RECOVERY OF ALUMINUM FROM ALUMINUM METAL MATRIX COMPOSITES BY SALT FLUX ADDITION

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ABSTRACT

Separation of matrix material and reinforcement has been attempted in pure Al – Graphite_p and pure Al – SiC_p composites. Complete separation of ceramic reinforcement particles and matrix alloy from composite has been achieved by salt flux addition and it is confirmed by the XRD analysis. This separation process also has been theoretically predicted using interface free energies, which is in good agreement with the experimental trend. The efficiency of separation has been improved by addition of small amount of NaF to equimolar mixture of NaCl – KCl salt flux.

Key words: Metal Matrix Composites, Salt flux, Separation, Aluminum, Recycling.

1. INTRODUCTION

The application of metal matrix composites (MMCs) in many engineering components has generally increased over the last few years, particularly in the automobile industry¹⁻⁴. It is mainly due to the ever increasing restrictions on the fuel consumption and pollutant emission which have forced the automotive manufacturers to look for new light weight materials for automobile components suitable for saving fuel. Among the various manufacturing processes available for MMCs production, liquid metallurgy technique is the most economical one and allows fabrication of very large sized components required for automobile parts. The amount of scraps (feed heads, runners and rejected components) generated during manufacturing MMC products by liquid state process will increase as the world consumption increases. According to Business Communications Company (BCC) market survey 1999, the world market for MMCs reached 2.5 million kg valued at \$102.7 million. BCC projects a rise of 4.9 million kg valued at \$173.3 million during the next five years corresponding to a 14.1% AAGR (average annual growth rate) from 1999 through 2004 (Table 1). Therefore, development of viable techniques for recycling of MMCs is critical to the commercialization of these advanced materials.

The problems associated with conventional recycling of MMCs by remelting are (i) amplified interfacial reaction between melt and reinforcement (mainly in low Si content wrought alloys) and (ii) tendency to the formation of large quantities of dross. An alternate approach is separate both matrix and reinforcement from the composites and reuse them effectively. The research on the recycling of aluminum alloys is becoming active to preserve the natural environment, save energy and conserve aluminum^{5,6}. The production energy of recycled aluminum alloy ingot is about 3 pct

of that of the new ingot⁵. This fact also strongly supports the necessity for the separation of aluminum from composites and its recycling.

Oxide films, insoluble metallic and non metallic inclusions are normally separated from the aluminum melt by salt flux addition. This technique can be used to separate the matrix material and reinforcement from composites. The most commonly used salt fluxes are mixtures of NaCl and KCl¹². Besides these chlorides, fluorides are also added to improve the fluxing efficiency. In the present study, the separation of matrix alloy and reinforcements from pure Al – Graphite_p and pure Al – SiC_p composites by using salt flux addition is theoretically predicted using interface free energies as well as experimentally verified.

2. THEORETICAL ASPECTS OF SEPARATION PROCESS

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

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

$$W = (\gamma_{rm} - \gamma_{ra}) dA \quad [1]$$

where γ_{rm} is the interface energy between reinforcement and matrix metal, γ_{ra} is the surface energy of the reinforcement surrounded by air before the fabrication of the composite, and dA is the total interface area between matrix metal and reinforcement in unit weight of the composite (Figure 1). When ceramic fibers 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° . Therefore, some work should be done to synthesis the composite. Supposing that γ_{rm} and γ_{ra} are independent of the location of the reinforcement surface, the surface free energy of the reinforcement before and after the fabrication of the composite is given by

$$\Delta G_2 = (\gamma_{ra} - \gamma_{rm}) dA \quad [2]$$

Generally, for metal – ceramic system, ΔG_2 in equation [2] is negative and total system will be in an unstable condition. 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 free energy of following reaction is negative.

$$dA \gamma_{rm} \rightarrow dA \gamma_{ra} + dA \gamma_{ma} \quad [3]$$

$$\Delta G_3 = (\gamma_{ra} + \gamma_{ma} - \gamma_{rm}) dA$$

where γ_{ma} is the surface energy of the matrix surrounded by air during fabrication of the composite. For metal – ceramic system, ΔG_3 is always positive, because the driving force available from ΔG_2 is compensated by the energy required to create two new surfaces (Figure 1). Hence, the separation of reinforcements from composite does not occur spontaneously.

In order to separate matrix alloy and reinforcement, salt fluxes are found to be candidate material. It makes an interface with reinforcements having smaller interface free energy than that of matrix metal. If the flux comes into contact with the interface between the reinforcement and matrix metal, the reinforcement can be absorbed at the flux/metal interface or directly into flux. Surface free energy of the salt flux before and after its addition in composite melt is given by

$$\Delta G_4 = \gamma_{rf} - \gamma_{fa} \quad [4]$$

where γ_{rf} is the interface energy between reinforcement and flux, γ_{fa} is the surface energy of the reinforcement surrounded by air before addition in the composite melt. ΔG_4 is always negative and total system will be in an unstable condition. The flux addition changes entire interface system as shown in Figure 2 and it can be written as

$$dA \gamma_{rm} \rightarrow dA \gamma_{mf} + dA \gamma_{rf} \quad [5]$$

$$\Delta G_5 = (\gamma_{rf} + \gamma_{mf} - \gamma_{rm}) dA$$

where γ_{mf} is the interface energy between metal and flux. When ΔG_5 is less than zero and the salt fluxes having little solubility in the matrix metal, separation of matrix metal and reinforcement from composite is spontaneous. It depends on the type of flux, reinforcement and matrix alloy.

On the other hand, when two different materials come into contact there seems to be no theoretical method to estimate the interface energy quantitatively. However, it is possible to consider that interface energy consist of two terms: the geometrical energy term (ΔH_g) and chemical energy term (ΔH_c)⁷. The interface energy between material A and material B, γ_{AB} is given by

$$\gamma_{AB} = \Delta H_g + \Delta H_c \quad [6]$$

The geometrical energy term ΔH_g , will be obtained approximately by summing the surface energies of both materials:

$$\Delta H_g = \gamma_A + \gamma_B \quad [7]$$

where γ_A is the surface energy of material A and γ_B is the surface energy of the material B. Since the value of ΔH_g , will be usually larger than the real interface energy (γ_{AB}). Then the chemical energy term ΔH_c should be negative, and the interface energy γ_{AB} is expressed by

$$\gamma_{AB} \leq \gamma_A + \gamma_B \quad [8]$$

If the contact angle between molten metal and ceramic reinforcement is about π rad, the interface energy formed by both materials will be close to the sum of surface energies of both materials given by Eq. [8]

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

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

$$\gamma_{rm} = \gamma_{ra} - \gamma_{ma} \cos\theta \quad [9]$$

data used are given in Appendix I.

2.2 Interfacial tension between ceramic reinforcement and molten salt flux (γ_{rf})

When the contact angle between two materials is rather low, it is possible to estimate the interface energy by Girifalco and Good's equation⁸

$$\gamma_{fr} = \gamma_r + \gamma_f - 2\phi (\gamma_r \gamma_f)^{1/2} \quad [10]$$

data used are given in Appendix I.

where γ_r is surface energy of reinforcement, γ_f surface tension of molten salt flux and ϕ is constant which is determined by the characteristics of the system. The real value of ϕ is about unity for the water/organic liquid system, about 0.7 for the mercury/non metallic liquid system⁸ and 0.41 for the molten salt flux/ceramic system^{9,10}.

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

When the interfacial tension changes due to adsorption of surface active elements, Girifalco and Good's equation⁸ in conjunction with expressions for the surface coverage of surface active species can be used to estimate the interfacial tension. Based on this approach, Raja R. Roy and Utigard¹¹ theoretically predicted interfacial tension between molten aluminum and various salt flux system (Figure 3), which is in good agreement with previous experimental results. In the present work, values of interfacial tension between molten aluminum and various salt flux system has been taken from Raja R. Roy and Utigard¹¹ theoretical prediction.

3. MATERIAL AND METHODS

Two different composites containing 10 vol. % of silicon carbide and graphite particles of size range 40 – 60 μm dispersed in electrical grade pure aluminum prepared by liquid metallurgy route have been chosen as the starting materials for the experiments. In order to change the interfacial energy between the ceramic reinforcement and matrix metal at molten state, equimolar mixture of NaCl – KCl salt flux with varying amounts of NaF has been used. The flux has been added to the remelted composite melt through mechanically stirred vortex at 720 °C. At a critical quantity of flux addition, separation of reinforcement particles starts leading to their floating on the melt surface, where they are skimmed off. Remaining metal in the crucible has been poured into a cast iron mold.

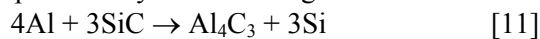
4. RESULTS AND DISCUSSION

The effect of equimolar mixture of NaCl – KCl salt flux addition to Al – 10 vol. % SiC_p and Al – 10 vol. % Gr_p composites on free energy for separation (ΔG_5) has been theoretically predicted (Figure 4(a)). Free energy for separation is slightly lower for Al – 10 vol. % Gr_p composite system, which means that separation of graphite particles from composite is easier than silicon carbide particles. The efficiency of separation in both systems has been quantified in terms of the quantity of salt flux required for separation as shown in Figure 4(b). It is clear that the quantity of salt flux required for separation is lesser in Al - 10 vol. % Gr_p system. The effect of NaF addition to equimolar mixture of NaCl – KCl salt flux on the optimum quantity of flux required for separation is shown in Figure 5. Addition of NaF brings down the optimum quantity of flux required for separation. This trend has been similar with the theoretically predicted free energy for separation. It has been observed that, the recovery of both metal and particle is more efficient with the increase of NaF addition (Figures 6 and 7).

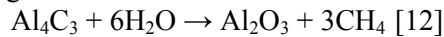
The increase in the separation efficiency promoted by the addition of NaF to the equimolar mixture of NaCl – KCl salt flux has been attributed to the simultaneous action of three factors (i) decrease in interfacial tension between molten salt and aluminum which favors the overall free energy for separation (ΔG_5) to become more negative (ii) decrease in flux viscosity that favors the aluminum coalescence and (iii) Alumina (Al₂O₃) film forming 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. Ye and shai¹³ observed that the fluorides of the molten salts attack the external oxide layer, allowing of chloride

ions to have access into the interface metal/oxide. The removal of the oxide layer is attributed to the formation of aluminum chloride, which is volatile at the temperature of recycling.

Figure 8 illustrate the XRD patterns of base and reclaimed aluminum (separation process by addition of equimolar NaCl – KCl + 5 wt % NaF). Complete separation of matrix metal and reinforcement from composites has been confirmed by the XRD pattern. It also reveals that the separation process by salt flux addition does not lead to any contamination of the reclaimed aluminum by Na, K or other products. It has been observed from Figure 9 that there is no appreciable contamination or degradation of reclaimed particle as well. The examination of the reclaimed SiC particles by SEM micrograph (Figure 10) did not show any particle breakage during fabrication and separation process due to the combined effect of heating and stirring. But sharp corners of the particles are rounded off. It may be due to the interfacial reaction occurred at the sharp corners of particles by the following reaction^{14, 15}.



The sharp corners are chemically more reactive because of their high surface energy. The detection of reaction products (Al_4C_3) in the particle surface is difficult, because the carbide formed in this reaction is hygroscopic in nature and reacts with moisture in the air or any other water source as per the following reaction



The occurrence of the reaction [11] can also be assessed by measuring the intensity of silicon XRD peaks. Because the reaction [11] is accompanied by the rejection of silicon in the melt. In the present investigation XRD pattern of reclaimed matrix material does not show any silicon peaks which indicates the amount of silicon released by the interfacial reaction is well below the detection limit of XRD analysis. Hence, there is no significant amount of reaction between the reinforcement and the matrix material during fabrication and separation process.

5. CONCLUSIONS

1. The separation and recovery of matrix alloy and reinforcements from pure Al – Graphite_p and pure Al – SiC_p composites by using salt flux addition has been theoretically predicted using interface free energies.
2. Complete separation of SiC and graphite particles and matrix material from the composite has been achieved.
3. The efficiency of separation process has been improved by the addition of small amount of NaF to equimolar mixture of NaCl – KCl salt flux.

Appendix I

Interface energies:

$$\gamma_{\text{ra}} \text{ for SiC} = 1844 \text{ mJ/m}^2 \text{ }^{16}$$

$$\gamma_{\text{ra}} \text{ for Graphite} = 1022 \text{ mJ/m}^2 \text{ }^{16}$$

$$\gamma_{\text{ma}} \text{ for Aluminum} = 840 \text{ mJ/m}^2 \text{ }^{17}$$

$$\text{Contact angle between Al and SiC} = 120 \text{ deg} \text{ }^{18}$$

$$\text{Contact angle between Al and Graphite} = 130 \text{ deg} \text{ }^{19}$$

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TABLES

Table 1. Worldwide Market for Metal Matrix Composites by End-Use Industry, 1999-2004 (Kg Thousands)

	1999	2004	AAGR % 1999-2004
Automobile	1,566	3,430	17.0
Thermal Management	668	1,067	9.8
Aerospace	137	161	3.3
Industrial	76	130	11.3
Recreational	72	90	4.6
Total	2,519	4,878	14.1

FIGURES

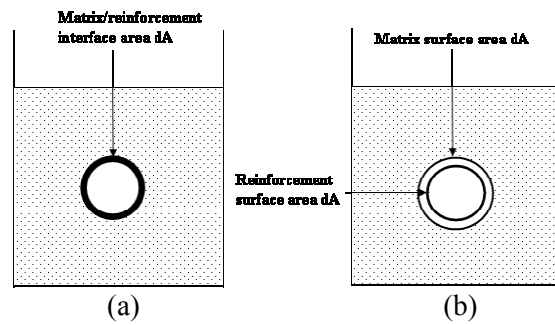


Figure 1. Surface area at the interface without flux addition (a) Before separation (b) After separation

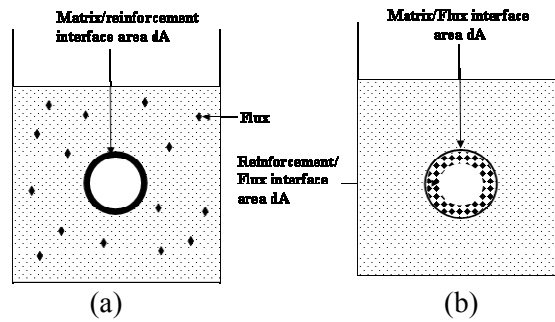


Figure 2. Surface area at the interface with flux addition (a) Before separation (b) After separation

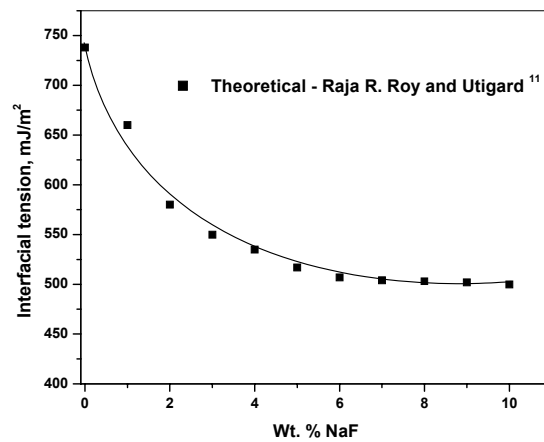


Figure 3. Variation of interfacial tension between aluminum and equimolar NaCl – KCl as a function of NaF addition

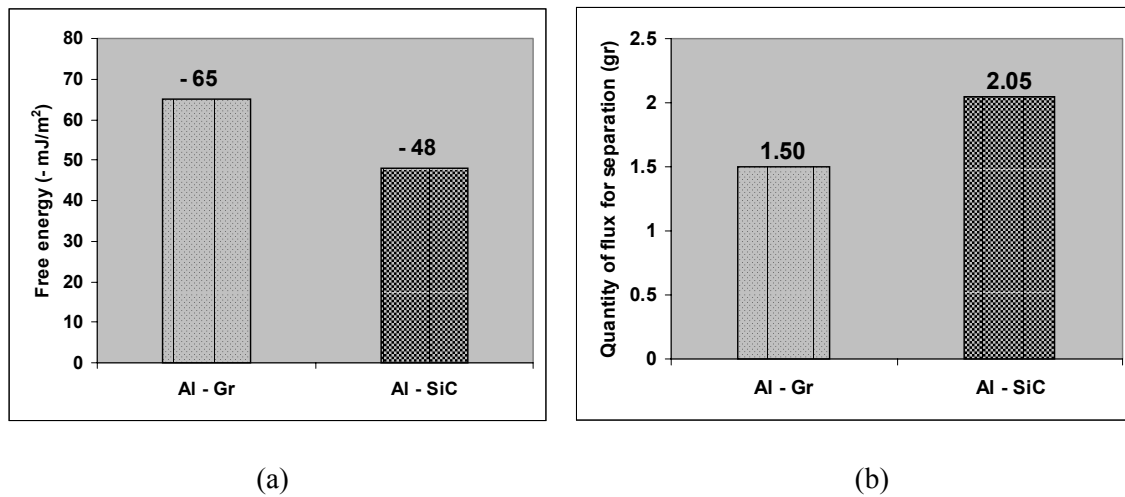


Figure 4. Comparison of Al – Gr_p and Al – SiC_p system (a) Free energy for separation (b) Quantity of flux required for separation

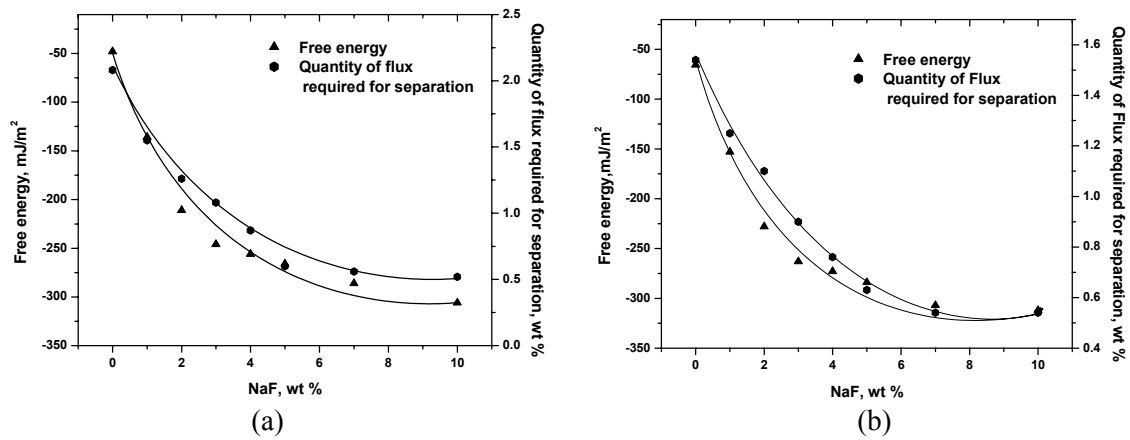


Figure 5. Variation of free energy and quantity of flux required for separation from composites as a function of NaF addition to equimolar NaCl – KCl salt flux (a) Al – SiC_p (b) Al – Gr_p

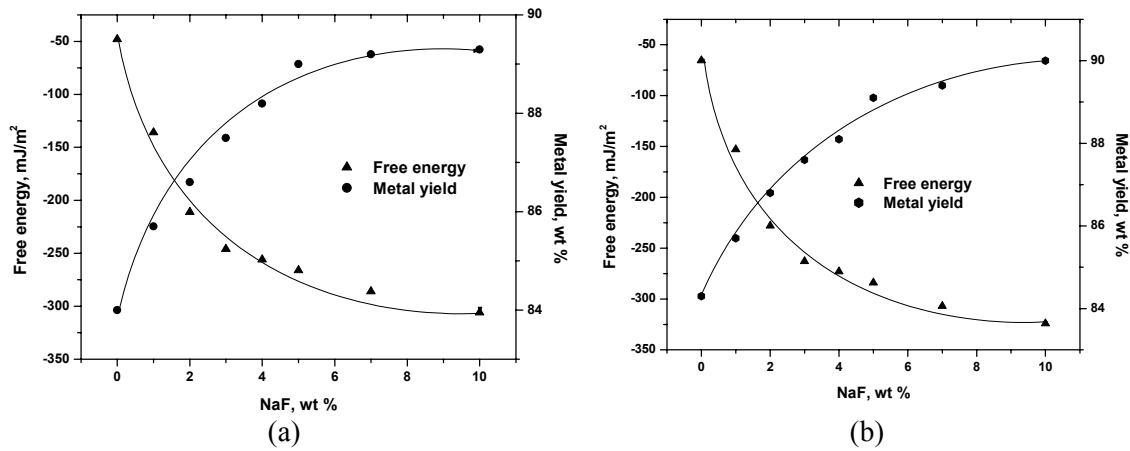


Figure 6. Variation of free energy for separation and metal yield in (a) Al – SiC_p (b) Al – Gr_p composites as a function of NaF addition to equimolar NaCl – KCl salt flux.

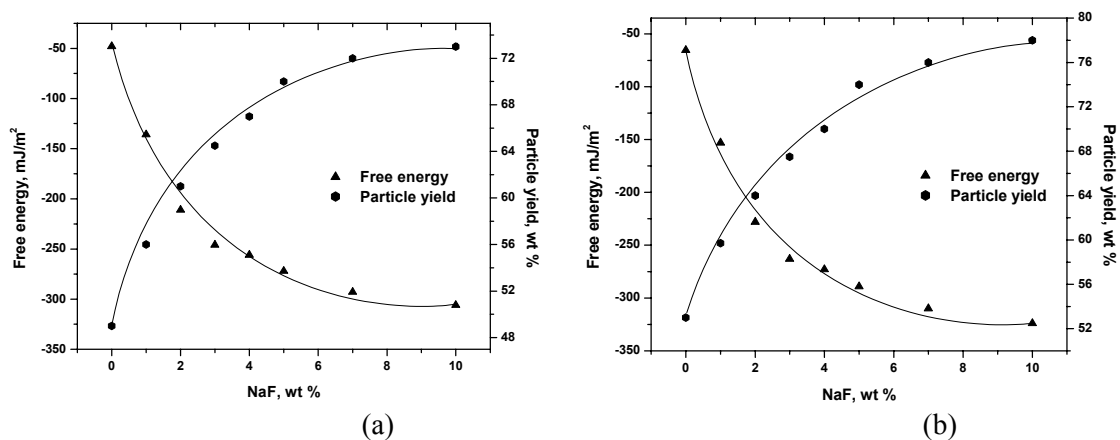


Figure 7. Variation of free energy for separation and particle yield in (a) Al – SiC_p (b) Al – Gr_p composites as a function of NaF addition to equimolar NaCl – KCl salt flux

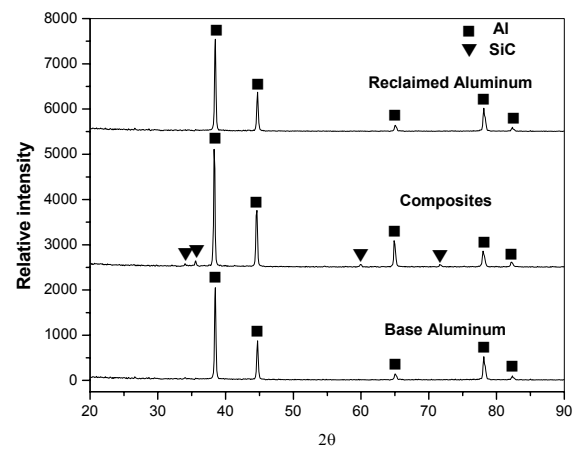


Figure 8. Comparison of XRD patterns of aluminum matrix metal separated by equimolar NaCl – KCl + 5 wt %NaF salt flux addition with those of base aluminum and composites.

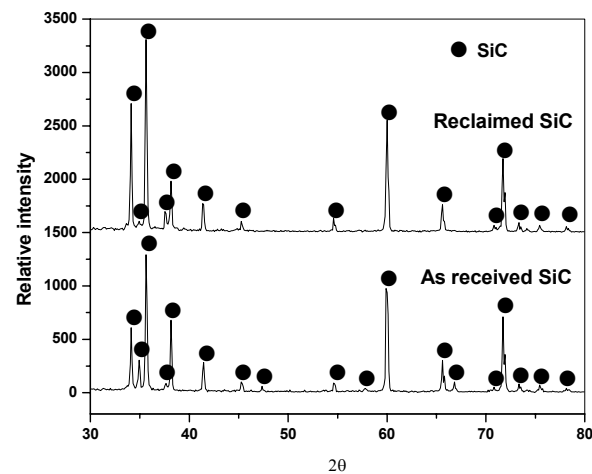


Figure 9. Comparison of XRD patterns of SiC particles separated by equimolar NaCl – KCl + 5 wt %NaF salt flux addition with that of as received SiC particles

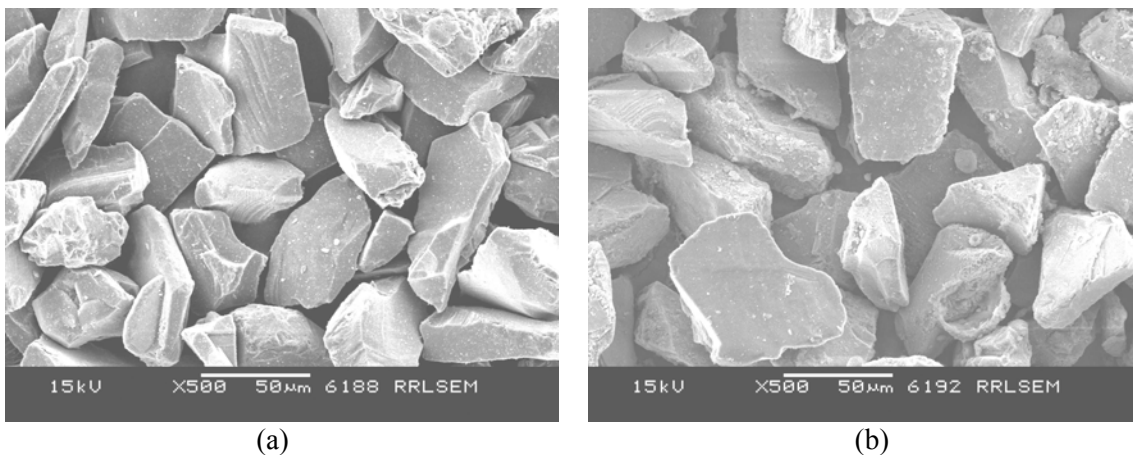


Figure 10. SEM micrograph of SiC particles (a) As received (b) Reclaimed from composites (separation by equimolar NaCl – KCl + 5 wt %NaF)