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Preparation of SiAlON and mullite-zirconia ceramics from aluminum dross

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ABSTRACT

Samples of Al dross collected from three different aluminum foundries were processed and characterized. A mixture of the three processed dross contains mainly Al_2O_3, Al, SiO_2, $MgAl_2O_4$ and AlN. This dross mixture was used as raw material to obtain high-grade ceramics composites such as SiAlON and mullite-zirconia. X-ray diffraction and electron microscopy analysis of the products obtained showed that SiAlON and mullite-zirconia composites were formed.

KEYWORDS

Aluminum dross;
Mullite;
Zirconia;
SiAlON.

INTRODUCTION

Aluminum dross is generated during recycling of aluminum scrap. Al dross contains mainly Al_2O_3, AlN, SiO_2, MgO and significant amounts of Al, Si, Fe, KCl, NaCl and $CaCO_3$[1-3]. Based on the chemical composition of dross, two types are recognized; white dross that contains mainly from 15 to 30 wt. % metallic aluminum and from 30 to 80 wt. % of alumina The black dross is produced mainly in reverberatory furnaces; its black appearance is acquired due to alkaline salts addition. Black dross may contain from 7 to 35 wt. % metallic aluminum, and from 30 to 50 wt. % alumina[4].

Dross processing procedures recover metallic aluminum that is trapped during the skimming process. Dross treatment is important for reduction of landfills; it avoids negative impacts to environment. For aluminum recovering, several processes have been developed such as the Salt-Cake, Press Ecocent, Altek, Alcan, Ltee/ Hydro, Alurec and Drostite processes[1,5]. Also, aluminum dross has been used for the elaboration high grade ceramics such as spinel-rich ($MgAl_2O_4$) refractories[6] and SiAlON ceramics[7]. In these papers, dross was obtained from one source only, and no detailed explication about of the dross treatment was given[6,7]. Moreover, a general method for the treatment of a variety of drosses has not been commercially available because dross composition changes for each foundry. In this work, a simple treatment process of aluminum dross was used in order to separate NaCl, KCl, $CaCO_3$ and Fe impurities. Subsequently, it was showed that purified Al dross can be an adequate precursor for the synthesis of high-grade ceramic materials.

EXPERIMENTAL PROCEDURE

Dross processing and characterization

Dross samples from three different foundries were collected, following the standard ASTM D346-90 procedure. The selected foundries are located in Saltillo, Coahuila, Mexico; where the secondary aluminum foundry is a common practice. The samples of dross were identified with the prefixes A, B and C.

The dross samples were processed as follows: Each sample was triturated in a jaw crusher to obtain aluminum particles of ~3.81 cm. After this, iron was removed by magnetic separation. Then, the samples were subjected to dry ball milling for 40 min. Materials with particle size higher than 1 cm (+12 mesh ASTM) was separated by sieving. Subsequently, the samples were treated separately as follow: 1kg of dross was milled for 180 min in a bar mill. Again, iron particles were removed by magnetic separation. The samples obtained after completing the milling time were sieved using a -150 mesh ASTM and analyzed by X-ray diffraction (XRD). Samples of material +150 and -150 mesh were mounted in resin, polished, and cleaned ultrasonically. Samples were gold coated and characterized by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis. Additionally, the dross chemical composition was determined by atomic adsorption spectrometry (AAS) using acids to dissolve the dross.

Samples of dross (-150 mesh ASTM) were washed in distilled water at 100 °C for 2 h in order to remove NaCl and KCl salts. Due to the presence of calcite ($CaCO_3$), dross samples were washed for 30 min in a 1:1 solution of acetic acid in distilled water at 80 °C. After washing, the samples were dried at 100 ºC for 12 h and characterized by XRD and AAS. After all the sample processing and characterization, samples A, B and C were mixed in a 1:1:1 ratio and homogenized for 12 h with acetone at room temperature; this blend is identified as dross mixture (DM).

Preparation of ceramics

The ceramic materials synthesized were SiAlON and mullite-zirconia composite. During the characterization, it was found that the dross samples contain Al, AlN and Al_2O_3; however, it is difficult to establish the amount of available alumina to produce SiAlON and mullite-zirconia composites. To known precisely the alumina content in dross is very important because it is a key precursor for preparation of SiAlON and mullite. For a more precise determination of alumina, the following process was realized. A sample of each dross was uniaxially pressed at 200 MPa and sintered at 1450 °C for 4h. The amount of phases was calculated by quantitative XRD analysis using the Rietveld method. This analysis was used to estimate the amount of available alumina. The final composition of DM was obtained by adding the individual composition of the three dross samples.

For the preparation of SiAlON, a mixture DM, silica and graphite was prepared according to the following reaction, which $\Delta G^o_{1450\,^\circ C}$ = -112.53 kJ.

$$3SiO_{2(s)} + 1.5Al_2O_{3(s)} + 7.5C_{(s)} + 2.5N_{2(s)} = Si_3Al_3O_3N_{5(s)} + 7.5CO_{(g)} \quad (1)$$

Where the Al_2O_3 source was DM. In order to adjust the stoichiometry of the reaction, extra silica was obtained from a geothermal waste. The reaction was carried out under the following conditions: the precursors were homogenized in plastic jars with acetone and dried at 80 °C for 12 h. After that, the mixture was compacted under uniaxial pressing at 20 MPa and synthesized in a tight closed tubular furnace at 1450°C, during the reaction a continuous flow of 1 L/min of N_2 was maintained for 5 h. The synthesized samples were characterized by XRD and SEM.

For the synthesis of mullite-zirconia composites, a mixture of DM and $ZrSiO_4$ were prepared according to the following stoichiometric reaction, which $\Delta G^o_{1500\,^\circ C}$ =:-43.88 kJ.

$$3Al_2O_3 + 2ZrSiO_4 = Al_6Si_2O_{13} + 2ZrO_2 \quad (2)$$

Where the Al_2O_3 source was DM and $ZrSiO_4$ was reactive grade. The mixture was homogenized in plastic jars with acetone and then dried at 80 °C for 12 h. Subsequently, the dryed powder was compacted under uniaxial pressing at 100 MPa and sintered at 1500 ºC for 6 h. The synthesized ceramics were characterized by XRD, SEM and EDX.

RESULTS AND DISCUSSION

Dross characterization

Figure 1 shows dross after different processing steps. Figure 1a shows the drosses as received with particles size greater than 6 cm. Using a jar crusher, the dross particle size was reduced ~3 cm. Figure 1b shows the dross after ball milling, where particles larger than

~1 cm were retaining in the ball mill (Figure 1c). Figure 1d shows sieved drosses (-12 mesh). The size reduction procedure facilitates the washing processes and iron separation. By AAS, it was found that the first products separated from dross were particles of an aluminum-rich phase. The AAS analyses are summarized in TABLE 1. The metallic material recovered from the different samples contain between 15.90 and 61.51 wt. % of total aluminum. It is important to note that this aluminum content is suitable for smelting[8].

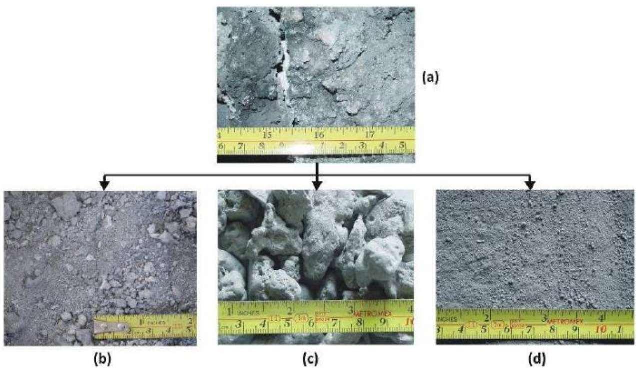

Figure 1 : Sequence of dross sample treatment: a) As-received, b) Milled c) Collected aluminum in ball milling, and d) Dross sieved to -12 mesh.

TABLE 1 : Metallic aluminum recovered from the aluminum dross samples after grinding and sieving.

Dross sample	Al* (%)	+12 mesh**$_{(Al)}$ (%)	Total aluminum recovered (%)
A	56.87	4.64	61.51
B	14.77	1.13	15.90
C	34.59	2.23	36.82

***Aluminum recovered within the ball mill; **Aluminum retained in 12 mesh of ASTM.**

The Figure 2 shows a SEM image of dross A before and after washing process. The part (a) of the figure shows two kinds of particles, ones very small of ~1 µm, and round shaped particles greater than ~10 µm. By EDX, it was found that the smaller particles correspond to salts such as NaCl, KCl and $CaCO_3$; on other hand, greater particles are Al rich materials. After washing process, SEM and EDX analysis reveled that Al-Si particles are imbedded in greater Al_2O_3 particles, see Figure 2b. The round-shaped Al-Si particles present a low Si content (~4 wt. %). Similar results were found in samples B and C.

Figure 3 shows X-ray diffraction patterns of dross A before and after washing process. The XRD also reveals that washing process is an effective method for the dissolution of KCl, NaCl, and $CaCO_3$. For samples B and C, the washing process was also effective. TABLE 2 shows the results of a quantitative XRD analysis for the three samples, before and after the washing process. It shows that NaCl, KCl and $CaCO_3$ were removed, it allows the fabrication of ceramic products. Additionally, TABLE 2 shows that after washing, part of AlN transforms to bayerite and gibbsite through a series of chemical reactions that generated ammonia. The reaction (3) is a representation of the washing process of AlN, which $\Delta G^o_{80\,°C}$ = -171.73 kJ:

$$AlN_{(s)} + 3H_2O_{(l)} = Al(OH)_{3(s)} + NH_{3(l)} \quad (3)$$

The negative ΔG indicates that the reaction is feasible. Reaction (3) is consistent with previous studies[10], where it was showed that the surface of AlN is hydrolyzed with water. Hydrolyzed products (bayerite and gibbsite) will be transformed into alumina during the sintering process[11].

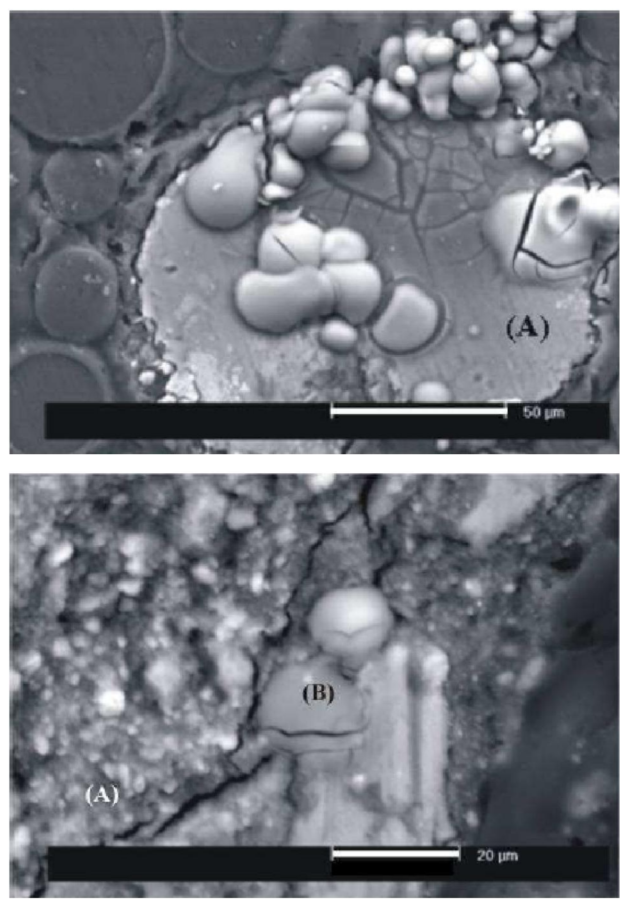

Figure 2 : SEM micrographs of dross samples a) before and b) after washing procedure.

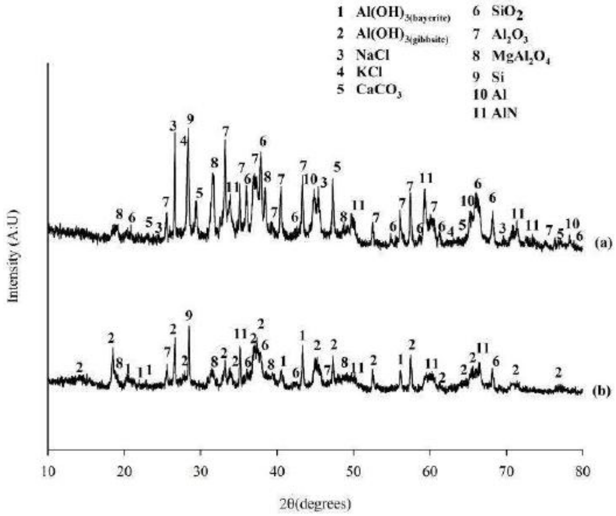

Figure 3 : X-ray diffraction pattern of a dross sample: a) as received, b) after washing process.

TABLE 2 : Phase composition of dross samples before and after washing.

Element or Compound (wt.%)	Source of dross					
	As received			After washing in a H_2O+$CH_3COOH_{(solution)}$		
	A	B	C	A	B	C
Al_2O_3	23	19	14	40	22	18
AlN (hexagonal)	23	14	30	-	-	16
AlN (cubic)	-	-	-	12	13	–
Al	5	11	8	-	12	9
Si	7	6	2	8	7	2
$MgAl_2O_4$ (spinel)	12	9	10	11	16	17
SiO_2 (quartz)	14	22	33	11	24	38
$CaCO_3$ (calcite)	6	10	3	-	-	-
NaCl (halite)	4	3	-	-	-	-
MgO (periclase)	-	2	-	-	-	-
KCl (silvite)	6	4	-	-	-	-
$Al(OH)_3$ (bayerite)	-	-	-	8	-	-
$Al(OH)_3$ (gibbsite)	-	-	-	9	6	-

TABLE 3 shows the phases present after sintering the dross samples. The following phases were identified by XRD: Al_2O_3, $MgAl_2O_4$ and $3Al_2O_3.SiO_2$. The concentration of each phase was quantified by the Rietveld method. According to TABLE 3, the content of total alumina from mullite + alumina and total silica from mullite were the following, respectively: A (74.72 wt.% and 10.11wt.%), B (76.46wt.% and 9.80wt.%) and C (72.63wt.% and 10.11wt.%). The content of alumina and silica were used to prepare in the mass balance to prepare SiAlON and mullite-zirconia ceramics. It is important to mention that the aluminum content found in the spinel ($MgAl_2O_4$) was no taken in to account in the mass balance.

TABLE 3 : Quantified phases calculated by Rietveld method from sintered drosses.

Compound (wt.%)	A	B	C
$Al_2O_{3(corundum)}$	48.96	61.90	46.87
$MgAl_2O_{4(spinel)}$	15.16	17.81	15.16
$3Al_2O_3.2SiO_{2(mullite)}$	35.88	20.29	35.88
$TiO_{2(rutile)}$	-	-	2.09

Preparation of ceramics

Figures 4 shows the XRD patterns of the powders obtained following the reactions (1) and (2). The XRD pattern shown in figure 4a reveals that the products of reaction (1) were two kinds of SiAlON, spinel and alumina. The presence of alumina after the reaction may be to its partial reaction. The obtaining of two different SiAlON products can be due to that the reactions conditions were not suitable for the synthesis of a single phase SiAlON. Otherwise, Figure 4b shows the XRD pattern where only mullite and zirconia are present; it is evident that reaction (2) predicts accurately the formation of this composite ceramic using as starting material Al dross.

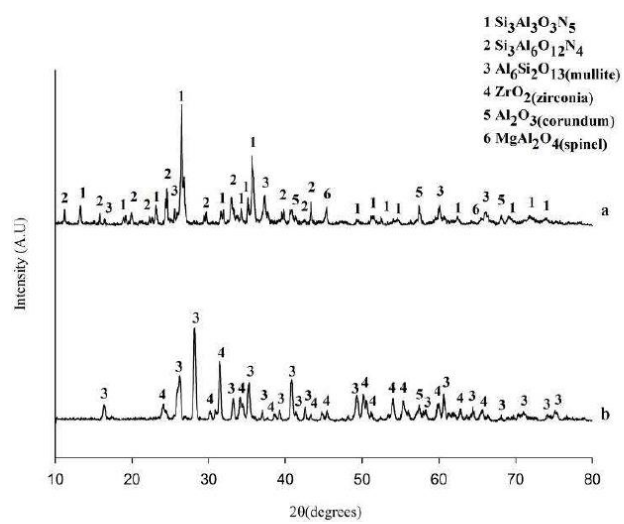

Figure 4 : XRD patterns of the synthesized ceramics: a) SiAlON composite and b) mullite-zirconia composite.

Figure 5 shows SEM images of the obtained ceramic composites. Figure 5a shows the typical belt-like morphology of SiAlON composites[12]. EDX analysis indicates the following composition (in wt. %): Si-26.6, Al-28.6, O-16.9, N-24.9, and Mg-2.8. This elemental composition is near to that of SiAlON phases. The presence of small amounts of Mg is due to the decomposition of $MgAl_2O_4$. Its presence is not considered as a detrimental of mechanical properties of SiAlON, because Mg promotes the stabilization of α-SiAlON[12]. Figure 5b shows the SEM image of the ceramic prepared from aluminum dross and zircon after heat treatment. It can be observed a continuous matrix of mullite (black background) and homogeneously distributed ZrO_2 particles (white particles). EDX microanalysis displayed an elemental composition (in wt. %) of Al-32.9, Si-13.7, O-52.1 and Mg-1.3 in the background (zone C); otherwise, the composition of white particles (zone B) was Zr-85.1 and O-14.9 wt. %.

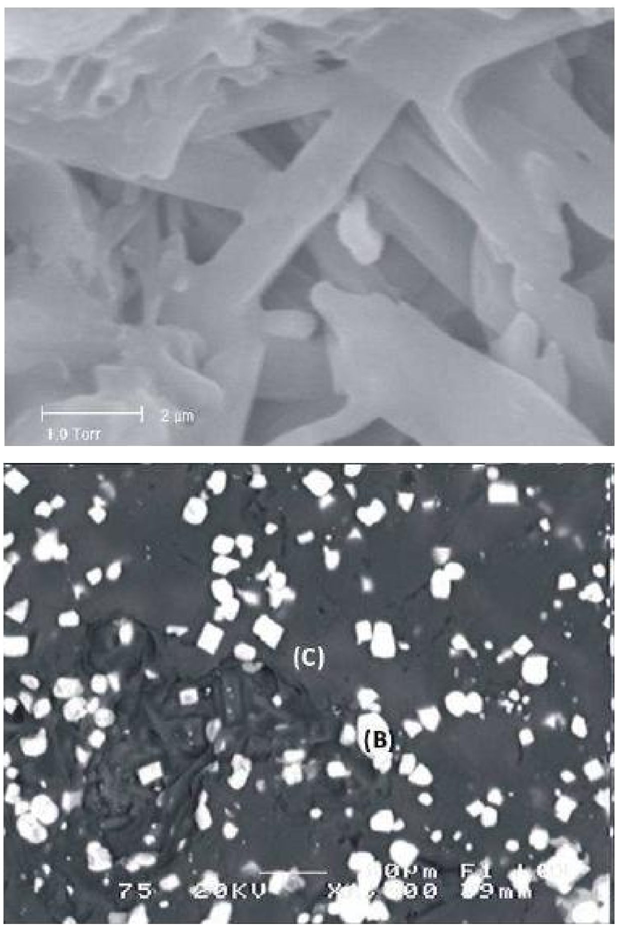

Figure 5 : SEM images of the synthesized ceramics: a) SiAlON composite and b) mullite-zirconia composite.

CONCLUSIONS

It was demonstrated that after an adequate purification process of Al dross, high grade ceramics such as mullite-zirconia or β-SiAlON can be prepared. The preparation of the ceramics was proposed following stoichiometric reactions were thermodynamic predictions were used.

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