Utilization of aluminum dross: Refractories from industrial waste

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Abstract. Aluminum oxide (Al₂O₃) and Magnesium-Aluminum oxides (MgAl₂O₄) are well known refractory materials used in engineering industries. They are built to withstand high temperatures and possess low thermal conductivities for greater energy efficiency. Dross, a product/byproduct of slag generated in aluminum metal production process is normally comprised of these two oxides in addition to aluminum nitride (AlN). Worldwide, thousands of tons of aluminum dross are generated as industrial wastes and are disposed of in landfills causing serious environmental hazard. This paper explores the potential to synergize the characteristics of the favourable contents of aluminum dross and its availability (in tons) via synthesis of refractories and thereby develop a value added product useful for the modern industries. In this work, Al-dross as-received from an aluminum industry which comprised of predominantly Al₂O₃, MgAl₂O₄ and AlN, was used to develop the refractories. AlN possesses high thermal conductivity values and therefore was leached out of the dross to protect the performance of the developed refractory. The washed dross was calcined at 700°C and 1000°C to facilitate gradual elimination of the undesired phases and finally sintered at 1500°C. The dross refractory pellets were subjected to thermo-physical and structural properties analysis: XRD (structural phase), SEM (Microstructure), EDS (chemical constituents) and thermal shock cycling test by dipping in molten aluminum and exposing to ambient (laboratory). The findings include the favourable prospects of using aluminum dross as refractories in metal casting industries.

Keywords: Aluminium dross, refractories, synthesis, AlN removal

1. Introduction

1.1 Dross: an industrial waste

Dross is the material that is found to be floating on top of molten metals during its refining operations and in general considered to have very limited commercial value and therefore presents a serious disposal problem. However, this may not be true about aluminum dross: provided efforts are made to understand its potential for utilization in an engineering industry. Aluminum dross (Al dross) is a by-product in the production of aluminum generated in electrolytic aluminum or cast aluminum

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production process. There are two types of dross. (1) The “white dross” which is obtained from primary melting operations and may be comprised of oxides of aluminum, magnesium and silicon etc. with about 15 – 70% recoverable metallic aluminum and (2) The “black dross” which is obtained from secondary smelting operations and typically comprised of a mixture of oxides of aluminum / alloys and slag, with smaller percentages (12 to 18%) of recoverable aluminum contents [1].

Although the technical and technological significance is very high and despite many recovery processes being practised throughout the world to reclaim aluminum metal from dross [2-5], the overall impact of dross utilization in metal recovery sector is limited, because environmental concerns are involved. Huge quantities (nearly five million tonnes/year) of aluminum dross are produced worldwide [6]. As in any industrial waste, the general composition or contents of the constituents may be variable. In addition to small quantity of metallic aluminum (Al), dross is generally comprised of oxides of aluminum (Al) and magnesium (Mg) i.e., MgO, Al2O3, MgAl2O4 and mostly nitrides of Al such as AlN as well [7, 8]. A typical quantification in the composition of dross is

(a) Aluminum: Al 2-15%,
(b) Corundum or Aluminum Oxide: α-Al2O3 7%
(c) Aluminum Nitride: AlN 15 - 28%
(d) Diaooyudaoite: NaAl11O17 6%
(e) Calcium fluoride: CaF2
(f) Silicon: Si (g) Defect Spinel: Mg$_{60.388}$Al$_{2.406}$O$_{3}$
(h) Spinel: MgAl2O4 and
(i) Quartz low: SiO$_2$

In today’s world most of the energy utilized or consumed in dross technology is to recuperate aluminum from the dross although the recovery process is highly energy intensive process. The ensuing salt cake is sent to landfills. Even though sealed, leaching of the constituents (fluorides and other salts) from the salt cakes into the environment cannot be ruled out. Any scope to utilize the Al dross, without diverting any fraction into landfills, would be a much more environmentally friendly alternative. Dross has deleterious effects on the environment either in a direct manner (for example, Pb even in very small amounts) or through subsequent changes which produce undesirable by products. Some examples are formation of Al$_2$C$_3$ and AlN, which react with water to produce methane and ammonia gases, respectively. Significant quantities of NH$_3$ (g) and CH$_4$ (g) are formed upon chemical interaction of dross with water and water vapour [9]. Many efforts are being directed worldwide to completely utilize Al dross as an engineering material without consuming much power and not land fill any fraction.

Some of the studies involved in engineering materials attempted to be produced from Al dross are (a) Synthesis of aluminum nitride from dross [9] (b) Synthesis of MgAl2O4 spinel from aluminum dross [10] (c) Production of high value η-Alumina[11] (d) Synthesis of aluminum oxides produced from aluminum dross recycling to be utilized together with other alternative materials to produce premixes for clinker production [12] (e) Usage of residues from aluminum dross recycling in cement – Smart-Waste [13] (f) Use as filler in concrete, cement and asphalt in order to improve properties like stiffness, abrasion resistance and control micro-cracking of construction products[14] (g) Synthesis of calcium aluminate cement mixes from aluminum sludge as a source of calcium oxide and Al$_2$O$_3$ and aluminum slag (dross) as a source of aluminum oxide, [15] (h) Study on dross utilization involving (i) refractory materials; (ii) aluminum composites; (iii) high temperature additive for de-sulphurizing steel. The use of dross waste to manufacture refractory material has been reported to have merit as well as the possibility for dross waste to be utilized as filler in concrete [16].

Alumina i.e. Al$_2$O$_3$ is an interesting ingredient in aluminum dross. Alumina has some significant properties like low thermal conductivity, resistance to many forms of chemical attacks, stability at high temperatures (~ 1500°C), resistance to corrosion and more. Alumina is also one of the prime ingredients in the production of any refractory product which is used in high temperature industrial
applications such as metallurgical, cement, ceramic, and glass and petro chemical manufacturing processes. The market potential for dross is present as an alternative for alumina source for refractory aggregate. This is because the world consumption of alumina is about 112 million tonnes per year [17].

1.2. Refractories in Industries
Resistant to thermal stress with capability to withstand any thermo-mechanical wear and being corrosion resistant to chemicals: refractories are usually synthesized from silica-alumina geo-materials. Mostly used in the lining of furnace walls, they are made of ceramic materials with an intention of withstanding high temperatures generally in the order of 500 to >1000°C, depending upon intended applications. Refractories find their usage in industries as they are more wear resistant compared to metals even at high temperatures. Refractories have several applications involving wide ranging engineering industries petrochemical, power generation plants, aero-space etc. They are used not only in brick kilns but also have their application as heat shields for re-entry in space shuttle. They are also used in places where processing machines or equipment’s are kept which require protection from heat or intense temperature. The properties that make a refractory more desirable than metals are [18]:

- High temperature stability
- Resistant to wear
- Corrosion resistance
- Refractories are found both as synthetic and natural materials. In general they are made up of non-metals. These days however refractories are being made with a combination of both minerals and compounds such as dolomite, magnesite, fireclay, zirconia and alumina. This work involves the development of refractories from Al dross.

1.3. Challenges in aluminum dross utilization.
Aluminum dross includes the presence of Aluminum nitride (AlN). A covalently-bonded ceramic, AlN does not occur naturally and is synthesized from the abundant elements aluminum and nitrogen. Stable in inert atmospheres at temperatures over 2000°C, AlN exhibits high thermal conductivity but is uniquely, a strong dielectric with high electrical resistivity. This unusual combination of properties makes AlN a critically advanced material for many future applications in optics, lighting, electronics and renewable energy. However, keeping in view the desired characteristics of a refractory material, it becomes necessary to remove the aluminum nitride from dross. Further AlN also gives health related issues to humans which includes irritation to the upper respiratory tract and should not be ignored [19].

Keeping all the above aspects of dross, its constituents, potential for industrial applications, some of their favourable and some non-favourable aspects etc. in view, this presentation explores the potential for utilizing the dross for refractory industry: the application being explored beginning with the most environmentally friendly metal in use today namely, aluminum.

2.0 Experimental Procedure

2.1. Processing of Refractories from Dross
The work carried out had a specific goal: to synthesise a value-added product from an industrial waste. Thus, it was important that the process should not comprise of many technically challenging steps. As received Aluminum dross powder (name of source industry withheld upon request) were sieved through ASTM 25 mesh sieves to remove the coarse particles. The sieved dross was used as the starting material for further processing which involved two methods. In one method (a) the sieved dross was used as it is for further processing, while in the second method (b) the sieved dross was cleaned/washed at 200°C, resulting in generation of pungent gases such as ammonia (NH₃) and processed further with a goal to remove the nitrides. Thereafter, the two parts were processed further, separately, which involved calcination, mixing with organic binder (PVA), compaction into pellets (15 mm diameter) and sintering followed finally by characterization. The flow chart of the material synthesis process and characterization involved is shown below.
As received aluminum dross powders (Al-dross): sieved
(Segregated into two parts)

Part 1: to be processed
further (continuation from above step)
Part 2: washed/cleaned and
processed further to remove nitrides

Part 1 and Part 2: processed further separately
calcination: 700°C and 1000°C

Structural phase analysis: XRD

Part 1 and Part 2: separately processed further.
Mixed with organic binders (PVA) and Oven Dried to remove moisture

Compaction into pellets (part 1 and Part 2 separately)

Sintering: 1000°C and 1500°C

Materials characterization: crystalline phase structure (XRD),
Microstructure (SEM-EDS), thermal shock test (molten aluminum)

Aluminum dross refractory synthesis and characterization (Flow chart)

Figure 1 shows a photograph of (a) the dross after removal of coarse particles via sieving (b) washing and (c) mixed with organic binder (PVA), green and sintered pellets.

Figure 1. Photos (a) raw dross (b) washing (c) L to R: powder, green & sintered pellets

2.2. Materials Characterization
The characterization at various stages of the development process involved (a) Study of structural phases via X-ray Diffraction (XRD), (b) micro-structural analysis employing Scanning Electron Microscope (SEM) (c) chemical composition analysis via Energy Dispersive X-ray spectroscopy (EDS) and (d) thermal shock testing. The sintered dross pellets were subjected to thermal shock testing by dipping the pellets into molten aluminum (@ 660°C). Figure 2 shows the photograph pertaining to thermal shock testing.

Figure 2. Sintered Dross pellet dip in molten aluminum (Thermal shock test)
The cycles involved dipping the pellets into molten aluminum, holding for 15 seconds and quenching in air for 15 seconds before re-dipping. This formed the experimental framework of one thermal shock cycle. The pellets were subjected to visual inspection at the end of each thermal shock cycle: this was done in order to detect if any cracks or defects had formed. The test was continued for a prefixed number of cycles or stopped upon the onset of defects or cracks.

3. Results and Discussion

3.1. Dross powder characteristics

3.1.1: Morphology and Chemical Composition (SEM and EDS)

The raw material powder morphology of the raw (as received) dross studied under the SEM is shown in Figure 3 (a and b).

Figure 3. SEM micrographs: Raw dross morphology (a: @ 500X and b@ 1,000X)

The SEM micrographs revealed the morphology of the dross powders which as expected, comprised of agglomerated particles of random shapes (round, oblong, individual and coalesced particles varying between few microns to few hundred microns). In order to remove the large particles, that would obstruct the sintering process, the as received dross powder was sieved through ASTM 25 mesh sieve. One fraction of the sieved dross powder was washed and dried. The SEM micrograph pertaining to the washed and dried dross is shown in Figure 4.

Figure 4. SEM micrographs: washed & dried dross morphology (a: @ 500X & b@ 1,000X)
Comparing the micrographs of the two dross powders from Figure 3 and 4, it is observed that although both the powder particles are agglomerates of several particles, the shape pertaining to washed samples is more uniform without the presence of very large particles. The EDS spectrum and composition pertaining to the raw and washed dross powders are shown in Figure 5 (a and b) respectively. Interestingly, a distinct N peak is evident in Figure 5a and is absent in Figure 5b.

![EDS spectrum and composition](image)

**Figure 5.** EDS spectrum and composition of (a) as received raw dross & (b) washed & dried dross

EDS has limitations in determining the percentages of elements with lower atomic numbers (Na, atomic number 11 and below) which means it cannot be used to make a quantitative analysis of elements such as Nitrogen (atomic number 7). However, a rough estimate was possible and the trend of lowered nitrogen content in washed and dried dross powder (N = 0.19 atomic% in washed dross: Figure 5a) when compared with N content = 3.63 atomic % (Figure 5b) was seen in the as received dross. This result indicated that Nitrogen content was reduced in dross after wash.

In contrast to EDS, XRD is a tool which can be used to confirm the presence (or absence) of a phase content fairly accurately, regardless of the elements involved. AlN content could be studied by analysing the intensity of AlN peaks in the XRD pattern, when compared with the peaks of the other phases present in it. The as-received and washed dross was subjected to XRD analysis.

### 3.1.2 XRD pattern Analysis

Figure 6 shows the XRD patterns of (a) as received dross and (b) washed and dried dross.
Detailed analysis of the XRD patterns shown in Figure 6 revealed the presence of three distinct phases in both the materials. They were Aluminum oxide (Corundum phase) Al$_2$O$_3$, (2) Magnesium aluminate (Spinel) MgAl$_2$O$_4$ and Aluminum Nitride AlN.

In the standard pattern of XRD for AlN, the 100% peak with h,k,l values (010) is observed at 2θ = 33.183° which has a d value of 2.69767Å (2.68 Å). This peak is highlighted with a blue arrow in Figure 6 (a & b). This was distinct and did not appear to be overlapping with any other major peaks i.e. corundum and spinel. From the appearance of the peak it could be confirmed that the percentage was not less that at least 10% (high approximation). Relatively, the 100% AlN peak of the washed and dried dross (Figure 6b) was reduced when compared with that shown in Figure 6(a). Furthermore, another distinct peak of 39.4% intensity and h,k,l values (112) found at 2θ = 71.337° with d value of 1.32105 (1.32 Å), was clearly visible (identified) in Figure 6a and was not seen in Figure 6b. This most likely is due to the reduction of the AlN phase due to the washing process. A detailed and complete quantitative analysis of any phase was beyond the scope of this investigation. Figure 7 shows the XRD pattern pertaining to the washed dross which was calcined at 800°C for 4 hrs. The
pattern did not reflect a highly crystalline nature; however the salient feature was intensities of peaks pertaining to AlN were negligible, indicating depleting AlN contents in the dross.

Figure 7: XRD patterns of washed and dried dross, calcined at 800°C for 4 hrs.

The disappearance of AlN was achieved by sintering the materials at 1500°C/4 hrs. This is reflected in the XRD patterns of sintered dross shown in Figure 8 (a) raw dross and (b) washed & dried dross.

Figure 8a: Raw dross
Sintered @1500°C

Figure 8b: washed dross
Sintered @1500°C

Figure 8. XRD patterns (a) raw dross and (b) washed and dried dross sintered @ 1500°C/4 hrs
While small peaks pertaining to AlN (100% peak of AlN at $2\theta = 33.183^\circ$ and $d= 2.69767 \ \AA$) is present in the XRD pattern shown in Figure 8a (raw dross sintered @ 1500$^\circ$C/4hrs), all peaks pertaining to AlN had completely disappeared confirming the presence of only Al$_2$O$_3$ and MgAlO$_4$ in washed dross sintered @ 1500$^\circ$C/4hrs. Such a material composition is expected to be highly suitable as a refractory.

3.1.3: Thermal Shock Test

The refractoriness of the developed product was verified by subjecting the sintered pellets to thermal shock cycling tests as described in previous section. Photograph of a typical specimen that has undergone 7 thermal shock cycles without failure in molten aluminum is shown in Figure 9. The pellets were intact without any deformation or cracks at the end of the shock cycle tests.

4. Concluding remarks

Aluminium dross, an industrial waste, comprised of Al$_2$O$_3$, MgAl$_2$O$_4$ and AlN phases was subjected to simple laboratory treatments to leach out the AlN with a goal to retain the oxides of Al and Mg (Al$_2$O$_3$, MgAl$_2$O$_4$) which are favored for use as refractories in many engineering industries. The undesirable phase (AlN) removal process involved washing (associated with evolution of pungent gases such as ammonia and perhaps chlorides) and high temperature calcination methods.

The Al dross pellets, calcined at 700$^\circ$ and 1000$^\circ$C to facilitate gradual elimination of the undesired phases and sintered at 1500$^\circ$C, were subjected to XRD, SEM, and EDS analysis which confirmed the complete removal of AlN from the dross and presence of desired phases most suitable for refractories for service in aluminum industries: i.e. Al$_2$O$_3$, MgAl$_2$O$_4$. The suitability of the developed product to suit a refractory application was confirmed by thermal shock cycling the sintered product in molten aluminum.

These findings strongly suggest the favourable prospects of using aluminum dross (after leaching out the undesirable phases) as refractories in metal casting industries. It is expected that they will withstand severe thermal shock cycling in molten steel as well. This is a subject of current research in this laboratory and publications later.

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