Nano Structured Red Mud – Synthesis and XRD Studies

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Abstract. The micro sized red mud particles have been modified to nano structured red mud particles using High Energy Ball Mill. Micro sized red mud obtained from the NALCO, Bhubaneswar was analyzed and milling was carried out for the total duration of 30 hours. The samples were taken out after every 5 hours of milling and characterized for the crystallite size and lattice strain by using X-Ray Diffractometer. It was found that for the 30 hrs, milling the crystallite size was reduced from 400nm to 42 nm. The fresh Red mud powder particles were mostly angular in shape. The shape of the 30h milled particles is irregular and the surface morphology is rough. The obtained nano structured red mud can be effectively used as reinforcement in MMCs to produce product with high wear resistance.

Keywords: Red mud, nano structured, ball milling, XRD

1. Introduction

Nanoscience and nanotechnology has become the buzz-word in recent years. It has appeal of miniaturization: also, it imparts enhanced electronic, magnetic, optical and chemical properties to a level that cannot be achieved by conventional materials[1,2]. A variety of ways have been reported to synthesize nano level materials such as plasma arcing, chemical vapor deposition, electro deposition, sol-gel synthesis, high intensity ball milling etc [3]. Among these methods, high-energy milling has advantages of being simple, relatively inexpensive to produce, applicable to any class of materials and can be easily scaled up to large quantities [4]. In this mechanical treatment, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the balls and the powder. This produces novel crystalline and amorphous materials with crystallite sizes at the nanometer scale [5]. Metal matrix composites are advanced materials resulting from a combination of two or more materials in which tailored properties are realized. However the ductility of the MMCs deteriorates with high ceramic particle concentration [6, 7]. It is of interest to use nano sized ceramic particles to strengthen the metal matrix, so called metal matrix nano composites (MMNC) while marinating good ductility [6, 8]. Currently, there are several fabrication methods of MMNCs, including mechanical alloying with high energy milling [9], ball milling [10], nano sintering [11], vortex method, spray deposition, electrical plating, sol - gel synthesis, laser deposition etc. Spark Plasma Sintering is the most advanced sintering technique used to produce products with complex shapes at low temperatures. Red mud is a residue or solid waste of bauxite processing for the production of alumina and it mainly consists of alumina, iron oxide, silica, calcium oxide, titania and trace components of gallium and scandium. Generally 1-1.5 tons of red mud is generated for every ton of alumina and due to its caustic nature, it poses a major environmental problem such as unsightly, undesirable and a non-productive use of land resources, as well as posing a non-going financial burden through their long-term maintenance. Therefore, utilization of red mud will produce significant benefits in terms of environmentally and economically by reducing landfill volume, contamination of soil and ground water, and release of land for alternative uses. In the present investigations, as received Red mud is reduced to nano structured level and characterized using X-Ray diffraction techniques.

2. Experimental Procedure

2.1. High energy ball milling

Red mud used in the present investigations is the waste obtained during the processing of Bauxite for the production of alumina at National Aluminum Company, Bhubaneswar. The as received Red mud is subjected for sieve analysis using mechanical sieve shaker and the particles of uniform size are collected. The reduction in particle size of Red mud from micron level to the nano level is carried out using a high-energy planetary ball mill (Model: Retsch, PM 100, Germany) in a stainless steel chamber using tungsten carbide and zirconia balls of 10 mm Φ and 3 mm Φ ball sizes respectively. The milling is carried for 30 hours by maintaining the rotation speed of the planet carrier at 200 rpm. The ball mill is loaded with ball to powder weight ratio (BPR) of 10:1. Toluene is used as the medium with an anionic surface active agent to avoid agglomeration. The milled sample powder is taken out at after 6hrs, 24 hours and 30 hours of milling and dried with mechanical drier.

2.2. X-Ray diffraction studies

The fresh as well as milled Red mud is characterized with an X-Ray Diffractometer (Model: 2036E201; Rigaku, Ultima IV, Japan). JADE software is used to investigate the structural changes and phase transformations of powders occur during mechanical milling. Sample preparation of XRD is done as per the standard practice. Sample packing is carried out by filling the Red mud on a glass slit of 12 X 12 X 2 mm size. Precautions are taken to have a tight powder packing on the glass slit and no manual contamination with the powder specimens. The X-ray diffraction measurements are carried out with the help of a Goniometer model 2036E201 using Cu Kα radiation (Kα= 1.54056 A0) at an accelerating voltage of 40 kV and a current of 20 mA. In this test the sample is kept in stationary condition, only the arms of the X- ray tube was rotating in the opposite direction up to 90^0 of 2θ during the test. The samples were scanned in the range from 30 to 90^0 of 2θ with a scan rate of 2^0 / min. The analysis is carried out to find out crystallite size, peak height, and amount of induced strains in the milled Red mud.

2.3. Results and Discussion

The average crystallite size is calculated from the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherer's equation (Cullity, 1978).

$$D = (k \lambda) / (B \cos\theta)$$

Where D is the particle diameter, λ is the X – Ray wavelength, B is the FWHM of the diffraction peak, θ is the diffraction angle and K is the Scherer's constant of the order of unity for usual crystals. The existence of stress in the materials results in lattice distortions of crystals; consequently, the diffraction peaks of the crystals are broadened. The relationship between the half width of the broadened diffraction peaks, Bd and the distortion of lattice, (Δd/d) was described by Yang et al. (2000). The lattice distortion (Δd/d) can be obtained from the following equation.

$$(\Delta d/d) = Bd / (4 \tan\theta)$$

Where Bd, is half width of the broadened diffraction peaks, θ is half of the diffraction angle. During ball milling the intense mechanical deformation experienced by the Red mud leads to generation of lattice strains, crystal defects. The balance between cold welding and fracturing operations among the powder particles is expected to affect the structural changes in the powder. The measurement of crystallite size and lattice strain in the mechanically milled powders is very important since the phase constitution and transformation characteristics appear to be critically depending on them [12]. A steady decrease in the crystallite size is observed and it is found that the crystallite size get reduced from 400 nm to 40 nm for 30h milling time. The relative lattice strain is increasing with increasing the duration of milling time. This lattice strain is increased from 0.12 to 0.28 for as received and 30 h milled Red mud respectively.

The X-Ray diffractograms obtained after 6, 24 and 30 hours of milling are shown in Figures 1-3 respectively. From this figure there is a confirmation of small tungsten carbide contamination in the milled Red mud sample. This entry might be from the tungsten carbide balls which were used as milling media during milling; also from the figure 3, it clearly observed that the intensity of the peaks in the XRD pattern

got reduced and the peak broadening increased as the duration of milling increases. Three major phases were identified for all the milling times; which are $MnSiO_2$, $MgAl_{.79}Fe_{1.21}O_4$ and $Al_2Mg\,O_4$.

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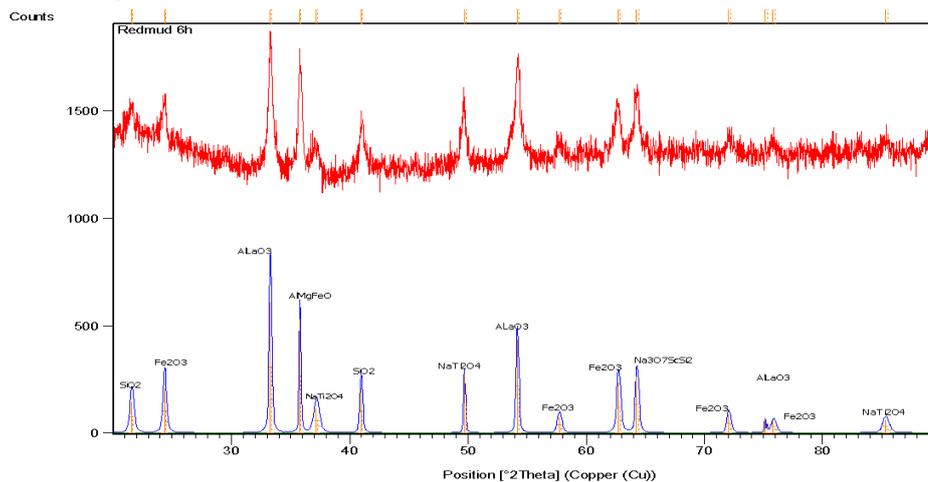

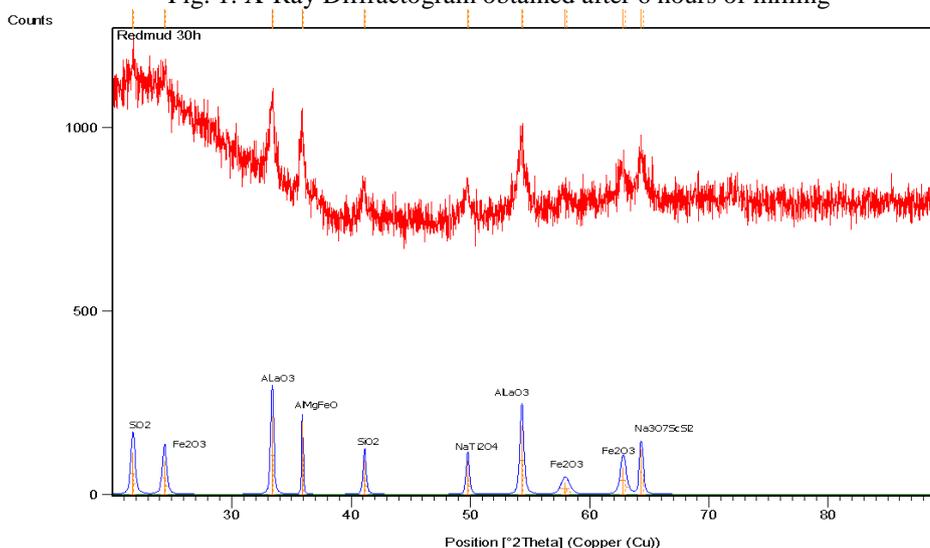Fig. 1: X-Ray Diffractogram obtained after 6 hours of milling

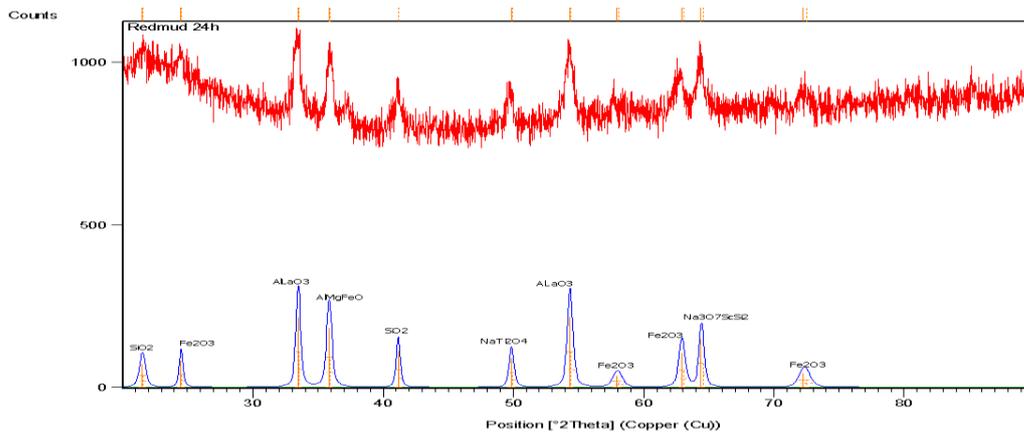Fig. 2: X-Ray Diffractogram obtained after 24 hours of milling

Fig. 3: X-Ray Diffractogram obtained after 30 hours of milling

Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peaks positions. From the shift in peak positions, one can calculate the change in d-spacing, which is the result of the change of lattice constants under a strain. Inhomogeneous strains vary from crystallite to crystallite or within a single crystallite and this cause a broadening of the diffraction peaks. The XRD graphs illustrate that with increasing milling time the peak height intensity shift slightly to the lower heights and increasing the peak broadening. This is the indication of high energy milling decreases the crystallinity of the Red mud, thus increasing the amorphous phase in it.

2.4. Conclusions

The following conclusions can be drawn from the investigations

1. It was found that for the 30 hrs milling, the crystallite size was reduced from 400nm to 42 nm.
2. The fresh Red mud powder particles were mostly angular in shape. The shape of the 30h milled particles is irregular and the surface morphology is rough.
3. A steady decrease in the crystallite size is observed and it is found that the crystallite size get reduced from 400 nm to 40 nm for 30h milling time. The relative lattice strain is increasing with increasing the duration of milling time. This lattice strain is increased from 0.12 to 0.28 for as received and 30 h milled Red mud respectively.
4. The intensity of the peaks in the XRD pattern got reduced and the peak broadening increased as the duration of milling increases. Three major phases were identified for all the milling times; which are $MnSiO_2$, $MgAl_{.79}Fe_{1.21}O_4$ and $Al_2Mg\,O_4$.

3. Acknowledgements

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