Application of Hydrogen for the Reduction of Bauxite Mineral

B. R. Parhi¹, S. K. Sahoo¹, B. Bhoi², B. K. Satapathy³ and R. K. Paramguru⁴

¹Department of Metallurgical & Materials Engg, NIT Roukela, Odisha, India, 769008
²Institute of Minerals & Materials Technology (IMMT), Bhubaneswar, Odisha, India, 751013
³R & D Centre, National Aluminium Company Ltd (NALCO), Bhubaneswar, Odisha, India, 751013
⁴Department of Mechanical Engineering, Kalinga Institute of Industrial Technology (KIIT), Bhubaneswar, Odisha, India, 751024

*E-mail:brporg@gmail.com

Abstract. Reduction of oxides present in bauxite through hydrogen was investigated in the present study. The bauxite samples were subjected to reduction through molecular hydrogen and hydrogen plasma at 650°C and 800°C with different flow rates of hydrogen for different time periods respectively. The samples, after the reduction processes, were characterized by X-ray diffraction technique and chemical analysis. It was observed that the oxides of iron present in bauxite were only undergone through reduction while other oxides remain unreduced. An attempt was then made to separate pure Al₂O₃ present in bauxite samples through acid leaching process.

Keywords: Bauxite, Reduction, Hydrogen, Plasma Processing, Leaching.

1. Introduction

Extraction of metals from their ores (mainly oxide ores) is primarily made through the process of carbothermic reduction [1, 2]. Such reduction process produces a great lot of CO₂ (carbon dioxide) which is responsible for greenhouse effect. Also carbon used in the reduction process has a limitation of future supply. Now-a-days research and development programs are dedicated to find out innovative solutions to minimize the emissions of CO₂ from different industries. It has been reported that hydrogen in place of carbon for the reduction process has several advantages [3,4]: (a) hydrogen is readily available, being the most abundant element in the universe; (b) the reaction of metal oxides with hydrogen is far more environmentally friendly, as the by-product being water rather than carbon dioxide (CO₂) or carbon monoxide (CO); (c) Theoretically very less amount of hydrogen compared to carbon is required for the reduction of metal oxides – only 6 tons of hydrogen in place of 18-36 tons of carbon is required for 112 tons of iron production; (d) Hydrogen in the form of plasma (consisting of H and H⁺) is a very powerful reductant that can reduce most metal oxides at temperatures below the melting point of metals; (e) A substantial decrease in the reduction temperature can be expected by using atomic/ionic hydrogen for extraction of metals; this can especially be significant for reduction of stable oxides, such as Al₂O₃, MgO, SiO₂ etc. Some studies have been reported for the reduction of metal oxides using hydrogen and hydrogen plasma respectively in the literature [4-10].

Extraction of aluminium from bauxite is initially purified by Bayer’s process which is then processed by Hall-Heroult electrolytic process [1,2]. Use of carbon during extraction of aluminium from bauxite is not an exception. In general, significant amount of energy is consumed in Hall-Heroult process by using carbon [11]. High quality carbon anodes are used in Hall-Heroult process and these are consumed during reduction of Al₂O₃ in the process. This consumption of carbon anodes need frequent replacement which makes the process expensive. Also smooth escape of carbon monoxide and carbon dioxide requires sufficient distance between the anode and cathode in the electrolytic cell which involves large energy consumption. The collection and the processing of effluent gases for minimizing environmental pollution are difficult and expensive. Keeping the above in mind, an attempt was made to investigate the reduction of bauxite using both hydrogen and hydrogen plasma in the present study. The reduced bauxite was then characterized by X-ray
diffraction (XRD) technique and chemical analysis. The present study summarizes the possible scopes for the reduction of bauxite mineral through hydrogen.

2. Materials and Methods

2.1 Materials and Sample Preparation

Bauxite samples of chemical composition (in wt. %) shown in Table 1 were obtained from National Aluminium Company Ltd., India. The bauxite samples were subjected to ball milling in a planetary ball mill for 1 hour. Pellets of 20 mm diameter and 4 mm thick were prepared from the bauxite powders by uniaxial cold compaction machine for hydrogen plasma processing. The powdered samples and the pellet samples were then calcined at 700°C for 4 hours to remove the moisture and volatile matters present in the samples. It may be noted that a series of calcination experiments were performed at different temperatures and time periods to remove entire moisture and volatile matters present in the samples. It was observed that the samples calcined at 700°C for 4 hours was sufficient to remove almost entire moisture and volatile matters present in the samples.

Table 1. Chemical composition (in wt. %) of bauxite used in the present study

|   | Al₂O₃ | Fe₂O₃ | TiO₂ | SiO₂ | LOI  |
|---|-------|-------|------|------|------|
|   | 43.0  | 23.0  | 3.0  | 4.0  | 22.5 |

2.2. Reduction by Hydrogen

The calcined samples were subjected to reduction through molecular hydrogen and hydrogen plasma at SLM Metal (P) Ltd, Rourkela and IMMT, Bhubaneswar respectively. Hydrogen gas was propelled at 650°C in a furnace (Fig. 1 (a)) with a flow rate of 1.5 m³/hr for 1hr 15min and 2 m³/hr for 1hr 30min respectively.

Hydrogen plasma processing was carried out in a microwave assisted hydrogen plasma reactor (Fig. 1 (b)). The bauxite pellets were treated with hydrogen plasma at a temperature of 800°C and pressure of 100 torr with hydrogen flow rates of 400sccm, 450sccm and 500sccm for 1hr 30min, 1hr 45min and 2hrs respectively.

Fig.1 (a) Muffle furnace for molecular hydrogen processing of bauxite samples and (b) Microwave hydrogen plasma reactor

2.3. X-Ray Diffraction (XRD)

A Panalytical PW 3040X’pert MPD system was used for XRD analysis. Bauxite samples before and after reduction processes were characterized by the XRD.
3. Result and Discussion

Fig. 2 shows the XRD plots of calcined bauxite powders before and after reduction processing by molecular hydrogen. It can be seen that, the samples after reduction processing had dominant iron (Fe) and Al$_2$O$_3$ peaks (Fig. 2(b) and (c)). However, the percentage reduction was higher in samples subjected to reduction processing of higher hydrogen flow rate as evident from the peak intensities of Fe. Although TiO$_2$ and SiO$_2$ were not observed in XRD plots of the bauxite samples, presence of TiO$_2$ and SiO$_2$ were observed in bauxite samples before and after reduction processing through chemical analysis.

XRD plots of reduced bauxite pellets through hydrogen plasma processing are shown in Fig. 3. The figures also showed non-reduction of Al$_2$O$_3$ present in the bauxite samples. Both Fe and Al$_2$O$_3$ peaks were observed in the samples. It may also be observed that the reduction percentage was different for different flow rates of hydrogen. However, increasing flow rates of hydrogen and time of reduction processing didn’t always increase the reduction percentages (Fig. 3). The chemical analysis of reduced bauxite samples processed by hydrogen plasma had also shown the presence of TiO$_2$ and SiO$_2$ in the samples.

From Ellingham diagram it can be found that the standard free energy change of formation ($\Delta G^o$) of Fe$_2$O$_3$ is -95 Kcal/mol which is very less as compared to that of other oxides like to Al$_2$O$_3$, SiO$_2$ and TiO$_2$ present in bauxite ($\Delta G^o$ for SiO$_2$, TiO$_2$ and Al$_2$O$_3$ are -203 Kcal/mol, -205 Kcal/mol and -252 Kcal/mol respectively) [1,2]. Hence, the reducibility of Fe$_2$O$_3$ through hydrogen is higher compared to that of SiO$_2$, TiO$_2$ and Al$_2$O$_3$. It was also observed that flow rate of hydrogen in plasma processing didn’t affect reducibility (Fig. 3). It was, therefore, attempted to separate Al$_2$O$_3$ from reduced bauxite samples rather than increasing the process parameters like hydrogen flow rate, temperature and time. Further, reduction of Al$_2$O$_3$ after separation through hydrogen plasma is in progress by the authors of the present study.

![XRD plots of calcined bauxite powders](image-url)
Fig. 2 XRD plots of calcined bauxite before and after reduction processing by molecular hydrogen; (a) Before reduction processing, (b) After reduction processing at 650°C with hydrogen flow rate of 1.5 m³/hr for 1hr 15min and (c) After reduction processing at 650°C with hydrogen flow rate of 2 m³/hr for 1hr 30 min.
Fig. 3 XRD plots of calcined bauxite after reduction processing by hydrogen plasma at 800°C and 100 torr; (a) Hydrogen flow rate of 400sccm for 1 hr 30 min, (b) Hydrogen flow rate of 450sccm for 1 hr 45 min and (c) Hydrogen flow rate of 500sccm for 2hrs.

Separation of Al₂O₃ from reduced bauxite was made through acid leaching by using concentrated hydrochloric acid. Acid leaching of reduced bauxite produced a filtrate containing chlorides of iron and a residue containing Al₂O₃ along with other minor oxides. The filtrate was subsequently treated with sodium hydroxide for the precipitation of iron hydroxide (Fe(OH)₃) which was converted to Fe₂O₃ on further heating. The residue after acid leaching was analysed by XRD and the analysis is shown in Fig.4. A dominant Al₂O₃ peak can be observed from the figure. The chemical analysis of the separated Al₂O₃ after leaching is shown in Table 2. A significant amount of Al₂O₃ was recovered by the process of leaching. Further reduction of Al₂O₃ obtained after acid leaching is an on-going research of the present authors.

Fig.4 XRD plot of the residue after filtration of the reduced bauxite leaching.
Table 2. Chemical composition (in wt. %) of the residue after filtration of the reduced bauxite leaching.

|        | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | SiO$_2$ | LOI  |
|--------|-------------|-------------|---------|---------|------|
| wt. %  | 89.10       | 2.10        | 2.95    | 3.59    | 2.26 |

4. Summary

Reduction of bauxite through hydrogen was investigated in the present study. The bauxite samples were subjected to reduction through molecular hydrogen at 650°C at hydrogen flow rate of 1.5 m$^3$/hr for 1 hr 15 min and 2 m$^3$/hr for 1 hr 30 min respectively. The samples were also reduced by hydrogen plasma (consisting of atomic and ionic forms of hydrogen) at temperature of 800°C and pressure of 100 torr with hydrogen flow rates of 400 sccm, 450 sccm and 500 sccm for 1 hr 30 min, 1 hr 45 min and 2 hrs respectively. In both the reduction processes, it was found that only iron oxide present in bauxite was reduced to iron while other oxides remain unreduced. It was also observed that the flow rate of hydrogen had significant effect on the reduction percentages. Acid leaching could separate Al$_2$O$_3$ from reduced bauxite in the present study.

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