



Production of metals and oxygen from coal fly ash by aluminothermic and electrochemical reduction process



Aimin Liu ^a, Zhongning Shi ^{a,*}, Xianwei Hu ^a, Blanka Kubikova ^b, Miroslav Boca ^b, Bingliang Gao ^a, Zhaowen Wang ^a

^a School of Metallurgy, Northeastern University, Shenyang 110004, PR China

^b Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava 845 36, Slovakia

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ABSTRACT

In-situ utilization of lunar resources for the production of metals and oxygen is essential for lunar exploration. The main emphasis of this article is on a candidate approach that combined aluminothermic reduction and electrolysis process in cryolite molten salts to produce both Al-based alloy and oxygen from lunar soil simulants. The influences of reductant amount and reaction time on the aluminothermic reduction of coal fly ash in cryolite melts at 1233 K (960 °C) were studied. The results obtained by XRF, XRD, SEM and EDS analysis show that the products mainly contain Al, Si, Fe, and little Ti, while the main phases of the products are Al and Si. With the increase of reaction time, the content of Si in alloy products increases from 4.43 wt% to 7.47 wt%. In addition, the remaining alumina-rich cryolite melts was electrolyzed at 1233 K (960 °C) using 56 wt%Fe-44 wt%Ni alloy inert anode. The cathode product obtained by galvanostatic electrolysis for 4 h was characterized, and the results showed that the phase composition of the cathode product was pure Al, while the highest aluminum content in the cathode product is 99.431 wt%. Besides, the outlet gas at the anode during electrolysis is pure oxygen according to the analysis of gas chromatography.

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1. Introduction

When considering the establishment of a manned self-sufficient lunar base, both construction metals and oxygen are required. Transporting metals and oxygen from the surface of the Earth is rather costly (ca. $\$10^5 \text{ kg}^{-1}$) [1], and a large number of inventory are indispensable to be housed on the lunar surface just in case there is a suspend with the Earth supply. On the other hand, there is plenty of oxygen on the Moon (up to 40% by weight), although it is tightly bound to metallic elements in the form of stable compounds [2]. Therefore, in-situ resource utilization (ISRU) will be a key component of human lunar mission, and it is advantageous to develop a process that achieves the combined winning of oxygen and metal from solid lunar soil [3].

Lunar soils and rocks collected during Apollo program demonstrate the existence of pyroxene-type minerals ((Mg, Ca, Fe)- SiO_3), ilmenite (FeTiO_3), and silicates such as anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) [4].

Additionally, ilmenite and silicates are two excellent candidates for lunar oxygen production, and corresponding lunar soil simulants such as JSC-1 (Johnson Space Center 1) and MKS-1 (Japan, Shimzu Corporation) were prepared for ISRU studies [5,6]. As seen in Table 1 [5–13], both Apollo 14 lunar regolith and lunar soil simulants such as JSC-1, MKS-1, and CAS-1 (Chinese academy simulant 1) are mainly composed of SiO_2 , Al_2O_3 , FeO, MgO, and CaO. Besides, coal fly ash that comes from the coal-fired plant especially in Shanghai of China has properties essentially similar to Apollo lunar regolith.

At present, there are diversified candidates for the extraction of oxygen from lunar regolith, including chemical reduction (hydrogen, methane, carbon), vapor phase pyrolysis, sulphuric acid reduction, and molten oxide electrolysis [7–12]. By contrast, abundant solar and nuclear energy make electrolysis process attractive because it does not require a continues supply of terrestrial reagents such as hydrogen and carbon from the Earth. The concept of molten regolith electrolysis (also called magma electrolysis, molten oxide electrolysis) for extracting iron metal from molten silicate was first patented by Aiken in 1906 [14]. Since the Apollo landings, a significant number of laboratory studies have

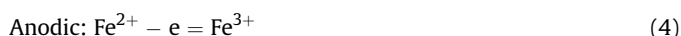
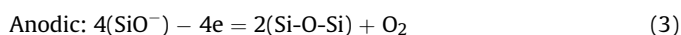
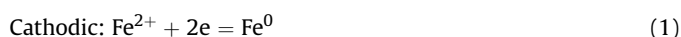
* Corresponding author.

E-mail address: znshi@mail.neu.edu.cn (Z. Shi).

Table 1
Element composition of JSC-1, MKS-1, CAS-1 lunar soil simulants, and Apollo 14 lunar regolith.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO/Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
Apollo 14	48.1	1.70	17.40	10.40	0.14	9.40	10.70	0.70	0.55	0.51	–	99.60
JSC-1	47.71	1.59	15.02	10.79	0.18	9.01	10.42	2.70	0.82	0.66	0.11	99.01
MKS-1	52.69	1.01	15.91	12.28	0.22	5.41	9.36	1.90	0.58	0.14	0.50	100
CAS-1	49.24	1.91	15.80	11.47	0.14	8.72	7.25	3.08	1.03	0.30	0.43	98.14
Coal fly ash	45.77	1.30	26.56	11.80	–	1.98	7.28	0.73	1.18	–	–	96.6

been concentrated on molten regolith electrolysis [11,12,15,16]. One of the recent was performed by Sirk et al. using iridium anode and molybdenum cathode for electro-winning of oxygen from JSC-1 at 1873 K (1600 °C) [11]. In addition, the major cathodic and anodic reactions were suggested as follows [11]:



As shown in reaction (4), oxidations of Fe²⁺ and formation of Fe³⁺, which would decrease current efficiency and increase electrical conductivity, can be expected when Fe²⁺ was present in the melt. Moreover, as molten oxide cells were operated at temperature above 1573 K (1300 °C), many inert anode materials such as iridium and 50:50 (wt%) iridium/tungsten alloys [11,15] were demonstrated, but they were not suitable for large-scale production due to their extraordinary high cost. On the other hand, the electro-deoxidation approach was developed that directly convert JSC-1 into oxygen and metallic by-product (Al, Si, Mg, Fe) in molten CaCl₂-CaO at temperature around 1173 K (900 °C) [12]. However, the disadvantages of the electro-deoxidation process are its low current efficiency and fresh salt supplement from Earth.

Another approach was suggested that aluminum-silicon alloy and oxygen could be obtained by electrochemical reduction of CAS-1 in cryolite melts [17]. Besides, it was reported that aluminum-silicon alloy was deposited at the cathode and CO₂ generated at the anode by electrolysis of coal fly ash in molten cryolite [18]. However, the highest reported current efficiency is relatively low (40.7%) for a potential industrial process [18]. In this study, an alternative approach for the production of alumina-silicon alloy and oxygen from lunar soil simulant is proposed. As shown in Fig. 1, alumina-rich cryolite and aluminium-base alloy could be obtained

via aluminothermic reduction of lunar regolith simulant in Hall–Héroult aluminum reduction cell. After aluminum-base alloy is removed from the bottom of the bath, oxygen and metal aluminum could be simultaneously produced by electrolysis using inert anode [19,20]. In this paper, coal fly ash was used as a lunar soil simulant to investigate the feasibility of extraction oxygen and metals by aluminothermic reduction combined with inert anode electrolysis, and influences of reaction time and aluminum dosage on product composition were investigated.

2. Experimental

Coal fly ash used in present study comes from the Datang International Recycling Resource Development Company Limited (Inner Mongolia, China). The components of the coal fly ash that analyzed by X-ray fluorescence (XRF; ZSX 100e; Rigaku Corporation, Tokyo, Japan) are Al₂O₃ (52.75 wt%), SiO₂ (38.05 wt%), CaO (3.88 wt%), TiO₂ (1.97 wt%), Fe₂O₃ (1.86 wt%), and K₂O (0.51 wt%). Besides, the main phases of the fly ash are mullite (Al₆Si₂O₁₃) and alumina via the X-ray diffraction (XRD, PW3040/60, Panalytical, Netherlands) analysis. Aluminium fluoride trihydrate (AlF₃·3H₂O, 99% pure) and sodium fluoride (NaF, 99% pure) were purchased from Sinopharm Chemical Reagent Company Limited (Shanghai, China). Anhydrous AlF₃ was prepared from AlF₃·3H₂O by vacuum sublimation process, and sodium fluoride was heated at 673 K (400 °C) for 24 h to drive off moisture and other volatile impurities. Aluminum block (99.9% pure) was obtained from the Fushun aluminum smelter of China.

The reactant mixture composed of coal fly ash with mass of 25 g and cryolite media were poured into a hermetically sealed high purity graphite crucible. The cryolite media was 52.7 wt%NaF-47.3 wt%AlF₃ with mass of 500 g. Then the graphite crucible was placed inside a stainless steel crucible with a continuous argon circulation during the experiment. Aluminium block was added in the melts after coal fly ash totally dissolved in the molten cryolite. The aluminothermic reduction process was carried out in a SiC resistance furnace at temperature of 1233 K (960 °C). After natural cooling, the alloy products were characterized by XRF, XRD, scanning electron microscopy (SEM; SSX-550; Shimadzu corp., Kyoto, Japan), and energy-dispersive spectrometer (EDS, Shimadzu corp.).

After aluminothermic reduction process, the alloy was removed from the bottom of the bath, and electrolysis experiments were performed using the separated cryolite melts at 1233 K (960 °C) with a two-electrode cell. As seen in Fig. 2, the anode was 56 wt% Fe-44 wt%Ni alloy with a gas-collecting hood, which was also made of 56 wt%Fe-44 wt%Ni alloy, in order to collect and analyze the gas products obtained by electrolysis, while a high pure graphite crucible was served as the cathode as well as the container for the electrolyte. The anode-cathode distance is 40 mm, while anode current density is 0.9 A/cm². The electrolysis products obtained at the cathode was analyzed by XRD, XRF, SEM, and EDS. In addition, the outlet gas collected at the anode during electrolysis experiment was monitored by a gas chromatography instrument (GC7890T, Shanghai Kechuang Chromato graph Instruments Co., Ltd., China).

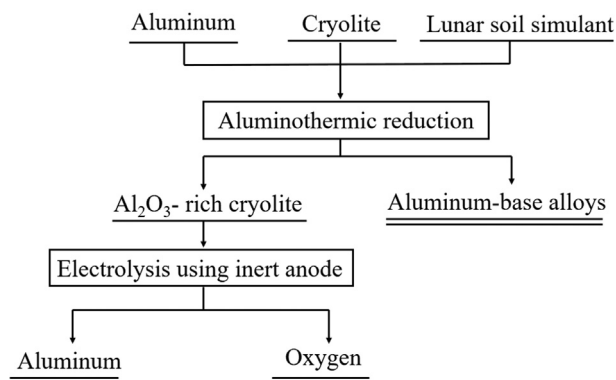


Fig. 1. Flow chart of metal and oxygen extraction from lunar soil simulant by aluminothermic reduction and molten salt electrolysis.

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