

Iron Deposition from Aluminosilicate Containing Trace Amount of Iron Oxide by Borate-Enhanced Hydrogen Reduction

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Aluminosilicate containing 0.50 wt% of iron oxide as impurity yields metallic iron deposit by heating with sodium borate ($3\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$) in H_2 at 950°C , while it remains unchanged by heating without the borate under the same condition. The SEM and EDX measurements indicate that the metallic iron deposit is formed on the sodium borate glass layer. We first find that the reduction in minor constituents in oxides is enhanced by the addition of borate as a flux.

I. Introduction

METAL deposition by reduction in metal oxides has been a fundamental and essential process in metallurgy from ancient times. Ore refining is generally performed above the fusion temperatures of the metal and gangue,¹ and thus it would be desirable for energy conservation to produce metals below their melting points. The reduction to metals thermodynamically occurs even below the melting points on the condition that the reactants and products satisfy $\Delta G < 0$ at the temperature, but kinetically the reaction rates in actual reactions are extremely small below the melting points except for the case with fine particles.² This is because the deposition occurs only locally in the vicinity of grain surfaces and remains without aggregation.³ Reduction kinetics of iron oxides by H_2 has been extensively studied for the energy conservation and CO_2 emission reduction.^{4–7} While many reports have appeared on the reduction in pure iron oxides such as hematite, magnetite,^{8–10} there have been no reports on the reduction in trace iron oxides in solid solutions. It is highly desirable to enhance the reduction kinetics of trace elements in solid solution matrix, and this will lead not only to the energy conservation in ore refining, but also to selective reduction in trace elements existing as a solid solution in metal complex oxides. This will be beneficial for separation and recovery of valuable metals from urban waste and for extreme purification to remove some trace metals.¹¹

In this study, we first found that the metallic iron was formed from 0.50 wt% of iron oxide existing as a solid solution in aluminosilicate (AS) by heating with sodium borate ($3\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$) in H_2 at 950°C . Heating AS without borate under the same condition brought about no change on the sample except for a slight color change, and thus the reduction from solid phases was enhanced by the addition of borate as a flux. We report here the reducing

conditions in details, and the analysis of the metallic iron deposit.

II. Experimental Section

(1) Preparation

Sodium borate at Na/B molar ratio of 3.0 was prepared by dissolving 11.0 g of NaOH and 5.7 g of H_3BO_3 into 1 L of water and drying it at 115°C in air for 24 h. The dried residue consisted of amorphous sodium borate, $\text{NaBO}_2\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$, and these act as a sodium borate flux above its melting point around 600°C – 700°C . The powder sample of AS was prepared by crushing and grinding a crucible boat (CB, Nikkato, Osaka, Japan) in a tungsten carbide mill. The composition from X-ray fluorescence (XRF) analysis is shown in Table I. The XRD pattern of AS indicates that it consists of mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, PDF-4 00-006-0259) and an amorphous phase. A slight amount of iron oxide at 0.50 wt% was considered to exist as a solid solution in AS. Ordinary portland cement (OPC; The Japan Cement Association, Tokyo, Japan) was also used for the sample containing a slight amount of iron oxide as a solid solution. The iron oxide at 2.00 wt% in OPC was contained in the cement mineral phase, C_4AF ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$), as a solid solution. The iron oxides in these samples are considered to be not intentionally added in production processes, but originally derived from their raw materials. The powder samples of sodium borate and AS were mixed at a weight ratio from 1:3 to 3:1 in agate and mortar, and heated at 950°C in 100% H_2 for 2 h. In the heating process, we used a crucible boat made of alumina (Al_2O_3) with high purity 99.7% (ACE-997; TGG, Tokyo, Japan) in order to avoid contamination.

(2) Characterization

The powder XRD patterns were measured with a diffractometer (XD-D1; Shimadzu, Kyoto, Japan) using graphite-monochromatized CuK_α radiation ($\lambda = 0.15406$ nm). The X-ray profiles were collected between 5° and 120° of 2θ angles with a step interval of 0.02° . The morphology and element distribution were observed by a scanning electron microscope (SEM) in back-scattered electron (BSE) mode equipped with an energy dispersive X-ray spectrometer (EDX; Swift ED3000, Hitachi, Tokyo, Japan) without carbon coating. The compositions were determined by a wave-dispersive XRF spectrometer (XRF-1700; Shimadzu). Resistance was measured coarsely at a distance of 2 mm by the DC two-probe measurement.

III. Results and Discussion

The powder mixtures of sodium borate and AS at a ratio from 1:3 to 3:1 turned black by heating at 950°C in 100%

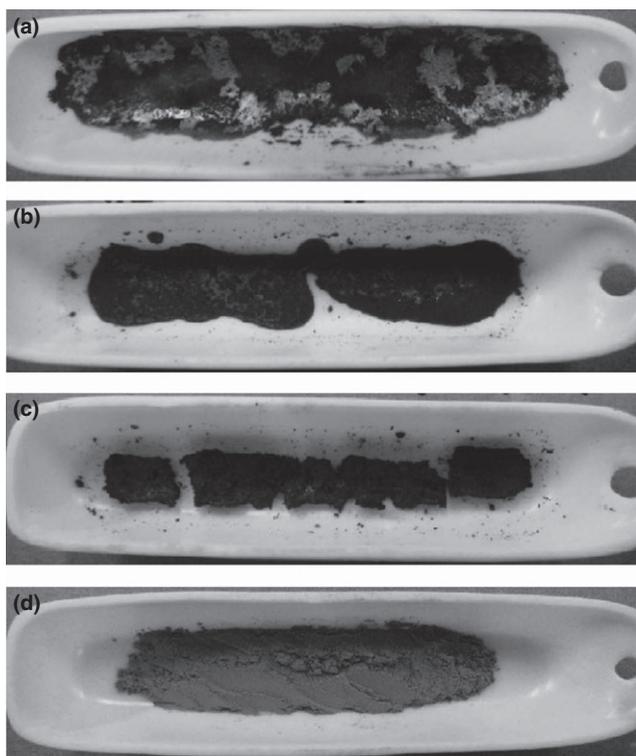
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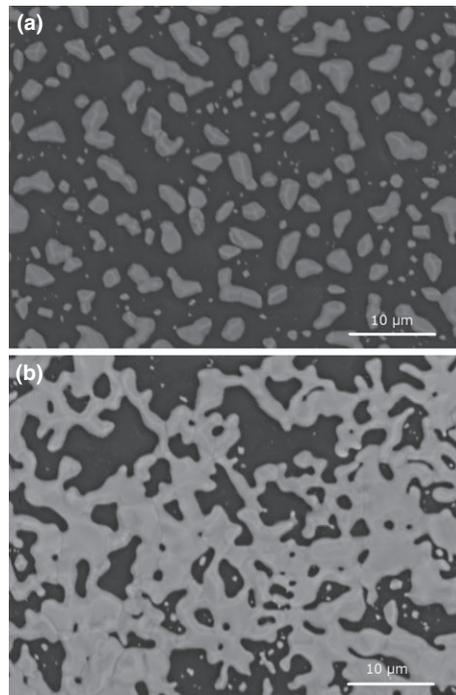
Table I. Compositions of the Aluminosilicate (AS) and the Ordinary Portland Cement (OPC) Determined by the XRF Analysis

Component	AS (wt%)	OPC (wt%)
SiO ₂	59.01	21.58
Al ₂ O ₃	37.35	6.74
K ₂ O	2.14	0.66
Fe ₂ O ₃	0.50	2.00
CaO	0.32	63.26
Na ₂ O	0.21	0.27
MgO	0.19	2.42
TiO ₂	0.19	0.24
CoO ₂	0.03	—
SO ₃	—	2.37
P ₂ O ₅	—	0.17
MnO	—	0.06
ZnO	—	0.05

**Fig. 1.** Appearances of the products obtained by heating the powder mixture of sodium borate and AS at a ratio of 1:1 (a), 1:2 (b) and 1:3 (c) at 950°C in 100% H₂ for 2 h, along with that by heating the AS alone (d) under the same condition.

H₂ for 2 h, and furthermore, the mixtures at a ratio from 1:1 to 3:1 yielded silver - colored deposit with metallic luster (Fig. 1). The silver - colored products were formed among black products on glass phase, which was newly generated on the boat. The AS powder without the addition of sodium borate showed only a slight color change from light gray to gray when heated at the same condition. The silver-colored deposit showed a small resistance approximately from 2 to 30 Ω, while the resistance of the black product varied widely, depending on the measurement point, from 30 Ω to over 20 MΩ. The gray product from AS alone showed a resistance over 20 MΩ. These results indicate that the formation of the conductive deposit from the raw materials is enhanced by the addition of sodium borate.

Figures 2(a) and (b) show the SEM - BSE images of the conductive deposits obtained by heating the mixture of

**Fig. 2.** SEM-BSE images of the deposits with black color (a) and metallic luster (b).

sodium borate and AS at a ratio of 1:1. Figure 2(a) is the black deposit with a resistance ranging widely from 1 k to 32 kΩ, and Fig. 2(b) is the deposit with metallic luster with a resistance approximately from 3 to 14 Ω. Figures 3(b)–(g) are the element distribution maps for O, Na, Al, Si, Fe, and Co, respectively, along with the BSE image of the same area in Fig. 3(a). Table II shows the EDX point analysis of the marked areas in Fig. 3(a). The conductive deposits with the metallic luster proved to be Fe and Co, and these metallic deposits were considered to be formed on oxide glass phase containing Al, Si, Na, and B. The resistance difference between the areas of Figs. 2(a) and (b) was due to the difference in the amount of the deposits, and the percolation of the deposits brought about by the low resistance. The tungsten and carbon detected in the metallic deposit in Table II were derived from the tungsten carbide used in the crushing and grinding process. Figure 4 shows the powder XRD pattern of the conductive deposit removed with the glass phase from the boat. A sharp peak due to 110 reflection of the metallic iron (Fe, PDF-4 04-003-3884) was observed with a broad peak from the glass phase, and this also confirms the formation of metallic iron. In short, a small amount of oxide impurities, 0.35% Fe and 0.02% Co, in AS was reduced and concentrated to a metallic deposit of 87.1% Fe and 0.4% Co by heating with sodium borate at 950°C in H₂. We first found that the sodium borate acts as a flux and enhances the reduction in metal oxide solid solutions to metals. Furthermore, the same phenomena were also observed for the OPC. The powder mixture of sodium borate and OPC at a ratio from 3:1 to 5:1 formed a mixture of black powder and small metallic grains by heating at 950°C in 100% H₂ for 2 h, and the products showed a low resistance in the range from 1.3 to 1700 Ω. The OPC without the addition of sodium borate showed only a slight color change and a resistance over 20 MΩ after heating at the same condition. Small amounts of iron oxide in a matrix of oxides, existing as a solid solution, were easily separated from the matrix by heating in H₂ with the sodium borate flux. This suggests that iron can be extracted from iron ores at 950°C much lower than the conventional refining processes and in gen-

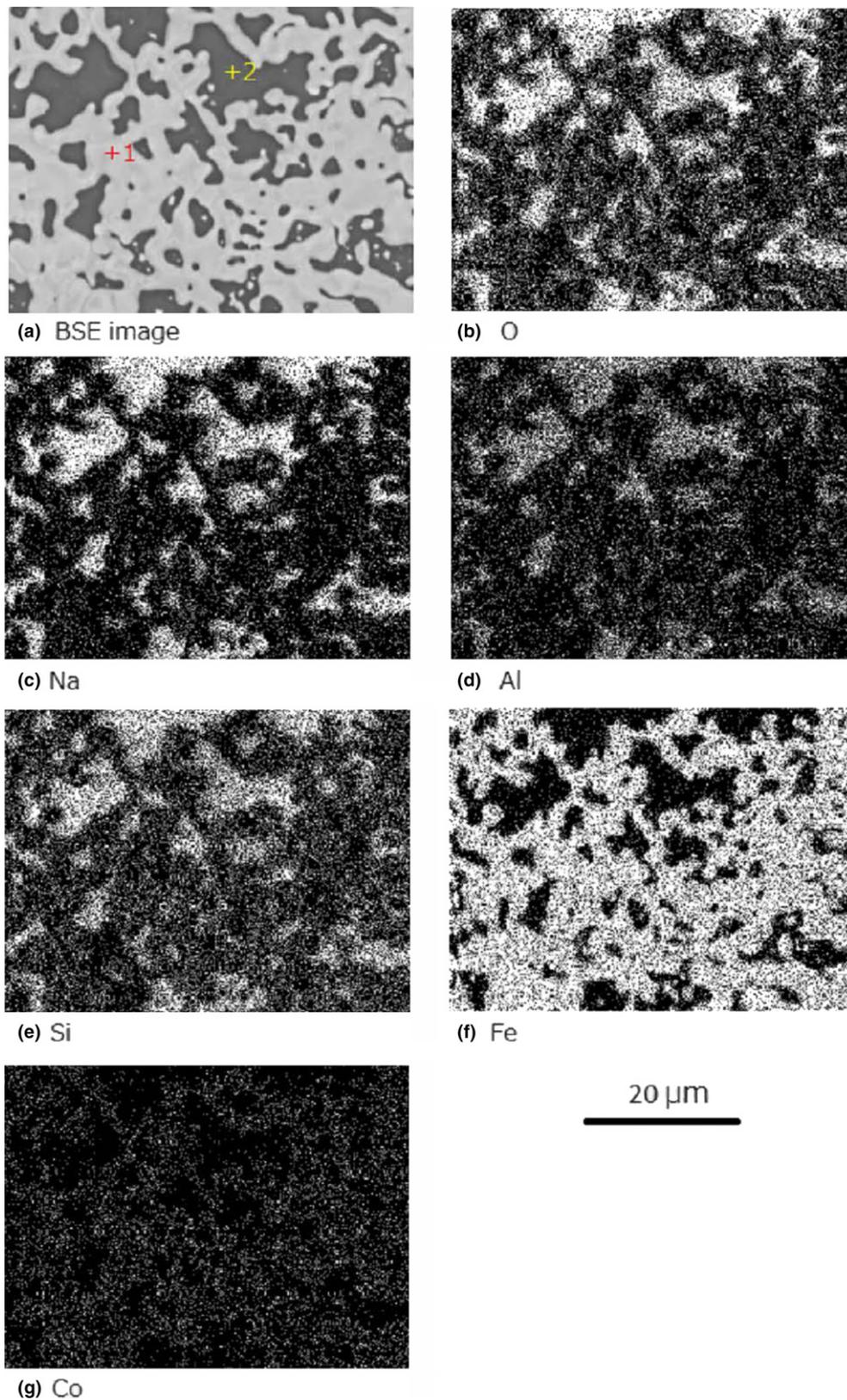


Fig. 3. EDX element distribution maps of the conductive deposit for O (b), Na (c), Al (d), Si (e), Fe (f), and Co (g), along with the BSE image (a).

eral that the refining temperatures can be reduced by using the borate flux. It can be expected that the technique will be applied to the other metal elements by controlling temperature and gas concentration based on Ellingham diagrams, which show the temperature dependence of ΔG of metals and metal oxides. Our findings will be useful for the separation of valuable or hazardous metals in a

recycling process as well as the reduction in the refining temperatures.

IV. Summary

A small amount of iron oxide existing as a solid solution in aluminosilicate or OPC was found to deposit as metallic iron

Table II. EDX Point Analysis of the Deposit. Point 1 is Located at the Conductive Area and Point 2 at the Nonconductive Base Material. Both Points are Marked in Fig. 3(a)

Element	Point 1 (wt%)	Point 2 (wt%)
C	4.4	3.2
O	0	53.1
Na	1.2	18.4
Al	0.4	8.2
Si	0.1	14.5
Fe	87.1	1.5
Co	0.4	0
W	6.3	0.2

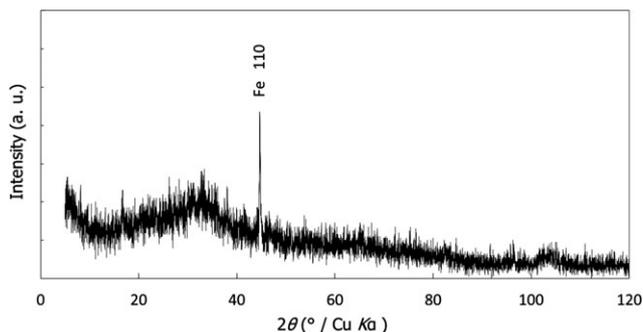


Fig. 4. Powder XRD pattern of the conductive deposit formed on the glass phase.

by heating with sodium borate (Na/B molar ratio = 3) at 950°C in 100% H₂ for 2 h, while such deposition was not observed without the addition of sodium borate. The deposit with metallic luster showed a low resistance. The SEM, EDX, and XRD analyses confirmed the deposition of iron and cobalt from aluminosilicate containing trace amounts of iron and cobalt. This is the first observation of the enhancement of the reduction deposition of metals by the addition of

sodium borate flux. We expect that this technique will be applied to the ore refining processes at lower temperatures, e. g., at 950°C for iron, and to the separation of trace metals in various processes such as recycling, purification, and materials synthesis based on the thermodynamic control of the deposition process.

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