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Use of Slag Containing Water as a Lubricant in High Straining Rolling for Ultrafine-grained Steels

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We investigated the possibility of using waste slag as a lubricant in high straining rolling for ultrafine-grained steels. When slag is applied as a lubricant, it might satisfy the requirement for stable biting workpieces because slag is as stable as glass with high hardness at the biting temperatures in rolling (100–200°C). On the other hand, ordinary slag doesn't have the fluidity necessary to provide a lubricating effect at rolling temperatures of 300–400°C since its melting temperature is usually high. However, slag containing water has been targeted as a new lubricant, and we focused on lowering the glass transition temperature and the structural change of slag containing water with the aim of improving the lubricity of slag in rolling. The microstructures of slag containing water and slag that released water were observed in the present study, along with *in-situ* observation of water released from the surface of slag containing water were conducted after heating in a SiO_2–Na_2O–B_2O_3 slag system. We found that water was mainly contained in the phase formed by ions dissolved from the original slag under hydrothermal conditions, and the amount of water was dependent on the state of the phase, such as glass or crystal. It was confirmed that slag containing water could provide a lubricating effect when the water is released from the slag above the glass transition temperature because a porous structure is formed due to the water release.

KEY WORDS: lubricant; waste slag; high straining rolling; ultrafine-grained steel; slag containing water; glass transition temperature; hydrothermal condition; porous structure; water release.

1. Introduction

Iron and steelmaking slag have been used in civil engineering and architecture, for example as raw materials in cements, sub-bases and concrete aggregates.[1] However, with the enactment in May 2000 in Japan of "a basic law for establishing a recycling-based society" there is a need for the development of new uses for waste slag in various engineering fields.[2]

Further, ultrafine-grained steels are expected to satisfy the social demands for conservation of energy and resources[3] because they show high strength and high corrosion resistance, as well as having a good recycling ability from the reduction in alloying elements. Thus key technologies for high straining rolling for ultrafine-grained steels have been developed in the PROTEUS project (PROTEUS: production technologies for environment-conscious ultrafine-grained steels).[4] Technological innovation for controlling the lubricating, *i.e.* the friction between the roll and the workpiece, is urgently required to carry out high straining rolling in industrial applications. Although the main role of a lubricant is its lubricating effect (low friction) in rolling, it also should satisfy need for the stable bite of a workpiece (high friction) as an anti-slipping agent in high straining

rolling, which needs a high reduction of the workpiece. Ikeda and Inagaki[5] proposed that lubricants for high straining rolling should give high friction in the solid state at biting temperatures (100–200°C) to keep the bite of the workpiece stable, yet melt at rolling (300–400°C) to provide low friction against a large load. However, neither conventional oils nor solid lubricants satisfy the requirement of high friction to fulfill the stable bite of a workpiece in high straining rolling.

We have tried to use waste slag as a lubricant material in high straining rolling. Quenching molten slag forms slag in the glass state; this vitreous slag qualifies as a high friction material due to its characteristic hardness which is as high as glass.[6] On the other hand, slag is not expected to provide low friction at rolling since ordinary slag does not melt at 300–400°C. Thus, in a previous work, we studied slag containing water.[7] Slag has been reported to decrease the glass transition temperature, that at which solid glass is transformed into a supercooled liquid to indicate fluidity below the melting point, by containing water under hydrothermal conditions (high temperature and high vapor pressure).[8–12] Therefore, this slag is expected to show fluidity at a temperature lower than the melting temperature for the original slag and so provide lubricating effects at the temperature

range of the rolling. We have investigated the effect of various slag components on the glass transition temperature in an SiO_2–Na_2O based slag system that contained water under hydrothermal conditions.[7] We found that slag containing water demonstrated much lower glass transition temperatures than those of the original slag, and that lowering glass transition temperatures of slag containing water depended on the slag components. However, it is thought that a lubricating effect is not always given by a supercooled liquid above the glass transition temperature because solidification, *i.e.* crystallization or glassification, from the supercooled liquid may occur due to the water release from the slag.[7]

Therefore, in this study we have paid attention to the structural change of slag containing water with increasing temperature. We observed in a previous study that slag expanded above the glass transition temperature.[7] From this observation, it was predicted that the hardness or strength of the slag become low in comparison with the original slag containing water since a lacunose structure was formed in the slag. That is, even if a supercooled liquid is transformed into a solid accompanying the water release, it is expected that the slag can provide low friction at rolling if a brittle structure is formed after the release of the water. In the present work, to gain fundamental knowledge for improving the lubricity of slag, the water release caused change of the slag microstructure has been examined, and water release from the surface of the slag containing water has been observed upon heating in an SiO_2–Na_2O–B_2O_3 slag system.

2. Experimental

2.1. Sample

Slag samples were prepared from reagent grade SiO_2, Na_2CO_3 and H_3BO_3. A mixture (5 g) of these powders, which correspond to a given composition (63mass%SiO_2–27mass%Na_2O–10mass% B_2O_3), was fed into a 20%Rh–Pt crucible. The mixture was melted at 1 200°C for 3 h in air, followed by air-cooling.

The schematic of the autoclave, composed of a stainless tube, pistons, packing and an electric heater, for hydrothermal hotpressing[13–15] is shown in **Fig. 1**. The sample can be heated by an electric heater while applying pressure to keep the sample under hydrothermal conditions.

The above pre-melted sample was ground and sieved to under 125 μm. This powder (2 g) and distilled water (0.4 g) were then mixed thoroughly and the mixture set in a stainless tube (inside diameter 2 cm) in the autoclave. The mixture ratio of water to powder was determined in a preliminary experiment. This mixture was pressed at 40 MPa at room temperature and heated to 250°C in 20 min at the same pressure to keep the sample under hydrothermal conditions. Without any holding time at 250°C, it was then cooled to room temperature in 20 min. The experimental conditions were chosen to have the maximum ionic product of water in the hydrothermal solution[16] since it is considered that slag tends to contain water due to the increase of active H^+ and OH^-.

Water release from the slag was carried out by keeping the slag containing water at 400°C for 3 h under an argon atmosphere (200 cc/min (s.t.p.)). Slag that did not com-
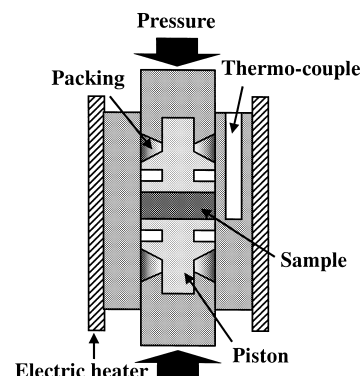

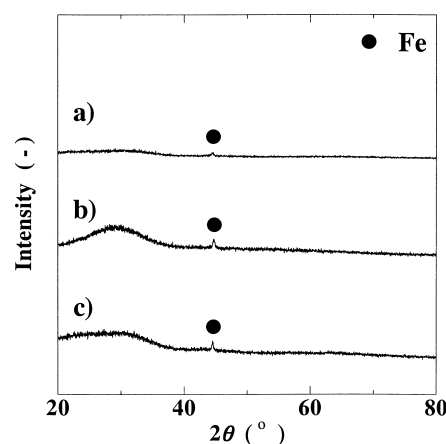**Fig. 1.** Schematic of the autoclave for hydrothermal hotpressing.

Fig. 2. XRD patterns of samples (a) before, (b) after hydrothermal hotpressing and (c) after water release for SiO_2–Na_2O–B_2O_3 system.

pletely release water was obtained by keeping the slag containing water at 400°C for 5 s under an argon atmosphere (200 cc/min (s.t.p.)).

Figure 2 shows the results of X-ray diffractometry (XRD) for the samples before and after hydrothermal hotpressing, as well as after water release. No samples had any noticeable peaks, showing the glass state. A weak peak found near $2\theta=45°$ for each sample was caused by entrapped iron from the iron mill used for grinding or crushing the sample.

2.2. *In-situ* Observation of the Water Release from the Sample

We observed the behavior of water released from the surface of the sample after hydrothermal hotpressing. A sample, set in an Al_2O_3 crucible, was heated at a rate of 50°C/min under an argon atmosphere (70 cc/min (s.t.p.)).

3. Results and Discussion

3.1. Lowering the Glass Transition Temperature of Slag Containing Water

Figure 3 shows the results of TG-DTA for samples before and after hydrothermal hotpressing.[7] A piece of sample (0.0130 g) was loaded in an Al sample holder and heated at 10°C/min under an argon atmosphere (100 cc/min (s.t.p.)). α-Al_2O_3 was used as the standard material. In both the TG and DTA curves, the broken lines and solid lines in-
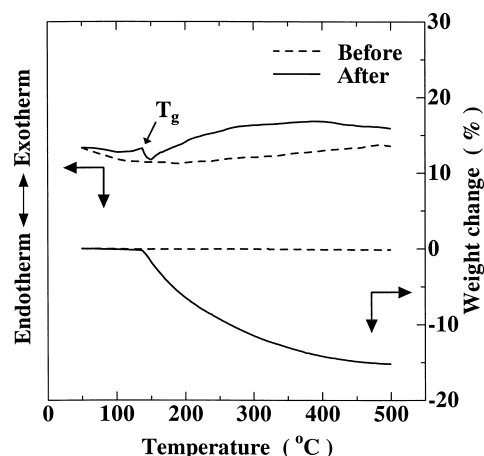
Fig. 3. TG-DTA of the samples before and after hydrothermal hotpressing for the SiO_2–Na_2O–B_2O_3 system.

Fig. 4. Relationship between the glass transition temperature and water content in samples after hydrothermal hotpressing for SiO_2–Na_2O–M_xO_y systems (M_xO_y=0 (SN), Al_2O_3 (SNA), B_2O_3 (SNB), CaO (SNC), K_2O (SNK), Li_2O (SNL), MgO (SNM), V_2O_5 (SNV)).

Fig. 5. XRD patterns of samples (I) before and (II) after hydrothermal hotpressing for (a) SiO_2–Na_2O–Al_2O_3 and (b) SiO_2–Na_2O-Li_2O systems.

dicate the samples before and after hydrothermal hotpressing, respectively. No phase transformation occurred in the sample before hydrothermal hotpressing because exothermic or endothermic peaks were not found until 500°C. This result shows that the glass transition temperature of the sample before hydrothermal hotpressing was above 500°C. On the other hand, the DTA curve of the sample after hydrothermal hotpressing indicated an endothermic peak, that is to say, glass transition temperature at about 150°C. It was found that the sample after hydrothermal hotpressing showed a glass transition temperature, such as 150°C, which is much lower than that of the original slag before hydrothermal hotpressing.

The weight of the sample before hydrothermal hotpressing showed no change, whereas weight loss occurred from the glass transition temperature for the sample after hydrothermal hotpressing, as shown in Fig. 3. It is thought that water began to be released from the sample when the sample was transformed to a supercooled liquid at the glass transition temperature; indicating that water contained in the sample contributed to the lowering of the glass transition temperature.

The relationship between the glass transition temperature and the water content in the sample obtained form TG-DTA for 63mass%SiO_2–27mass%Na_2O–10mass%M_xO_y(M_xO_y=0, Al_2O_3, B_2O_3, CaO, K_2O, Li_2O, MgO, V_2O_5) systems[7] is shown in **Fig. 4**. The glass transition temperature decreased with increasing water content, which depended on the additive components in the slag. Samples containing Al_2O_3 or V_2O_5, which are classified as intermediate oxides or network formers like B_2O_3 from the viewpoint of their glass-forming ability based on the single bond energy of the additive oxides,[17] tended to gain more water than samples containing network modifiers such as Li_2O, K_2O, CaO or MgO. The results of XRD in samples containing Al_2O_3 and Li_2O before and after hydrothermal hotpressing are shown in **Fig. 5**. The sample containing Al_2O_3 as well as B_2O_3, which tended to gain a lot of water, indicates a glass state was achieved before and after hydrothermal hotpressing, while noticeable peaks occurred in the samples containing Li_2O after hydrothermal hotpressing. Thus, we also postulated that the formation of crystals during hydrothermal hotpressing caused a decrease of water content in samples in com-
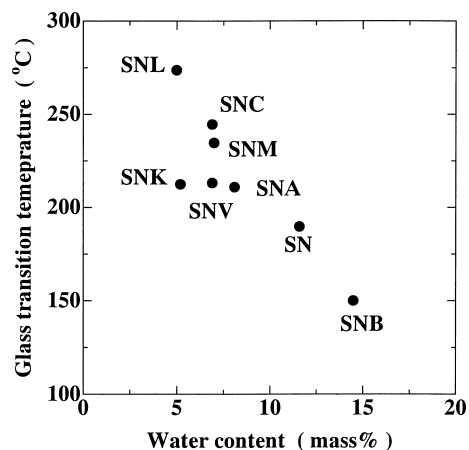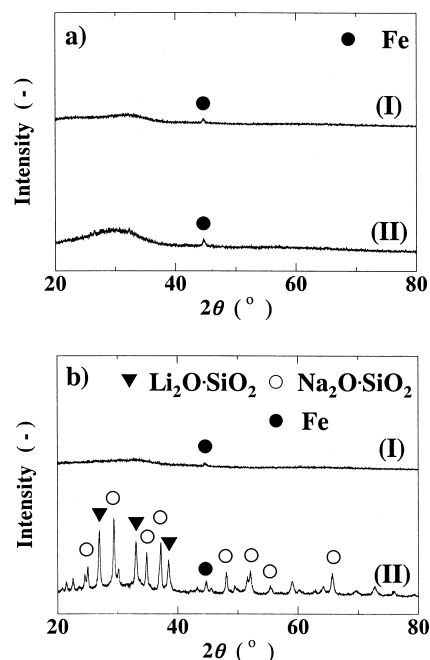
parison with that of glass.

3.2. Change of the Microstructure of Slag Containing Water

It is considered that the transformation of solid glass into a supercooled liquid at the glass transition temperature gives a lubricating effect due to the fluidity. However, the DTA curve of a sample after hydrothermal hotpressing provides a gradual exothermic above the glass transition temperature, showing solidification from the supercooled liquid accompanying the release of water contained in the sample (Fig. 3). This solidification may lower lubricity.

Here, we focused on the structural change of the slag during and after water releasing above the glass transition temperature to investigate the possibility of the lubricity of slag. The results of the *in-situ* observations of the shape of
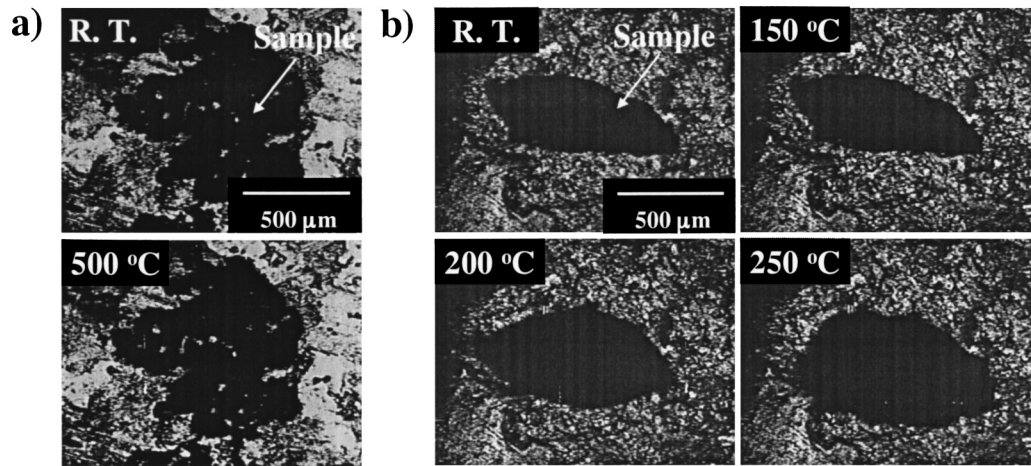
Fig. 6. *In-situ* observation of melting and softening behavior of samples (a) before and (b) after hydrothermal hotpressing by a laser microscope for the SiO_2–Na_2O–B_2O_3 system.
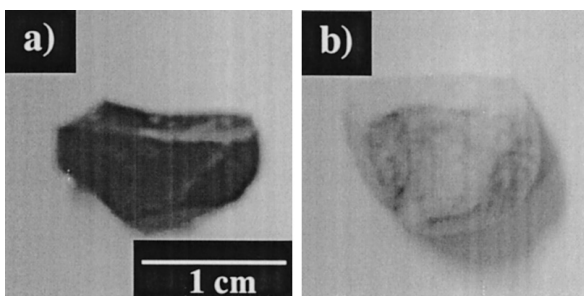

Fig. 7. Appearance of samples (a) after hydrothermal hotpressing and (b) after the release of water for the SiO_2–Na_2O–B_2O_3 system.

Fig. 8. SEM micrographs of a sample (a) after hydrothermal hotpressing and (b) after water release for the SiO_2–Na_2O–B_2O_3 system.

the samples before and after hydrothermal hotpressing[7] are shown in **Fig. 6**. The black and white parts are the silhouette of the sample and a Pt substrate, respectively. The shape of the sample before hydrothermal hotpressing did not change from room temperature to 500°C. On the other hand, it is found that the sample after hydrothermal hotpressing expanded gradually 150°C, *i.e.* glass transition temperature. Comparisons between the appearance of the sample after hydrothermal hotpressing and that of the sample after water release are shown in **Fig. 7**. The size of the sample after water release is larger than that of the sample after hydrothermal hotpressing. **Figure 8** shows the SEM images of slag after hydrothermal hotpressing and slag after water release. In the sample after hydrothermal hotpressing, ions dissolved from the surface of glass particles into the hydrothermal solution form a reaction layer around the particles. On the other hand, the sample after water release has a porous structure; as a result, Fig. 8, a porous structure is formed in the slag when water is released from the slag containing water above glass transition temperature. It is expected that after water release the slag is crushed by the rolling load because of the brittle structure and so provides lower friction than the original solid slag containing water.

The behavior of the water released from the surface of slag containing water after hydrothermal hotpressing was observed upon heating using a laser microscope to examine the process of the porous formation. As shown in **Figs. 9** (c)–**9**(f), water was released from the slag surface above the glass transition temperature determined by DTA like
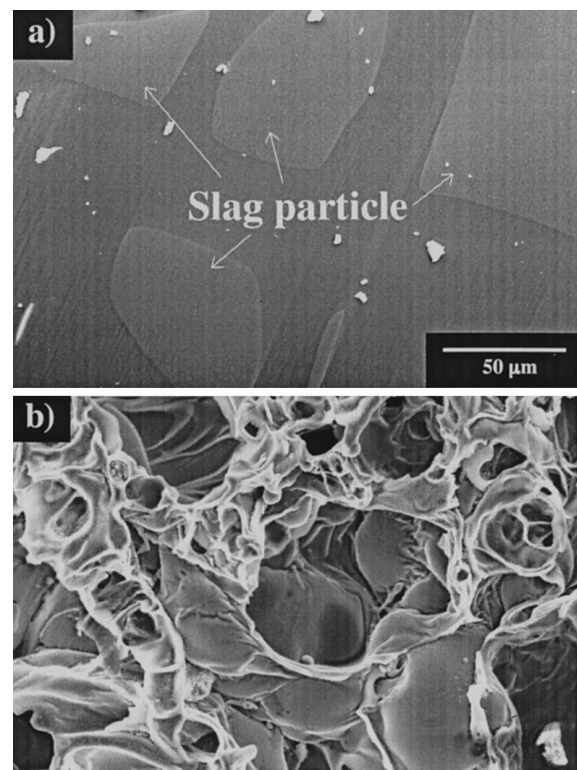
bubble leaving a liquid surface. This indicates that the spot releasing water becomes a supercooled liquid at the moment of water releasing. The number of the spots and the frequency of water releases increased with increasing temperature (Figs. 9(g)–9(h)). The places where water was released remained as pores. Therefore, it was confirmed that the porous structure shown in Fig. 8 was formed by the water release. **Figure 10** shows an SEM image of slag that did not completely release water. Pores due to the water release exist in the region except for slag particles, while slag particles maintain their shape. This suggested that water is mainly contained in the phase formed under hydrothermal conditions.[14]

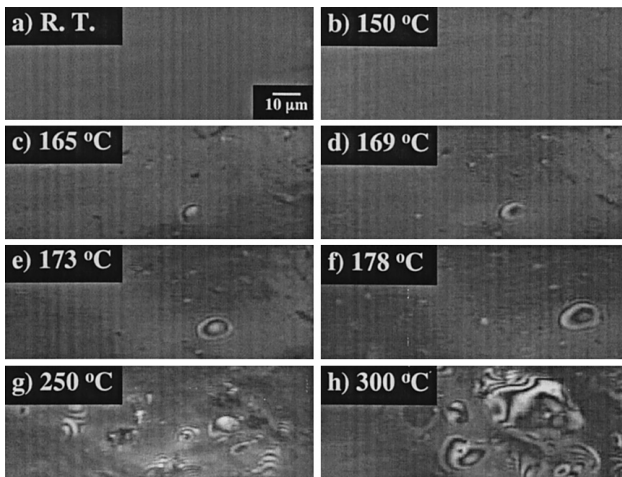From the above results, we found that it is necessary to

Fig. 9. Observation of the release of water from the surface of a sample after hydrothermal hotpressing and heating with a laser microscope for the SiO_2–Na_2O–B_2O_3 system.

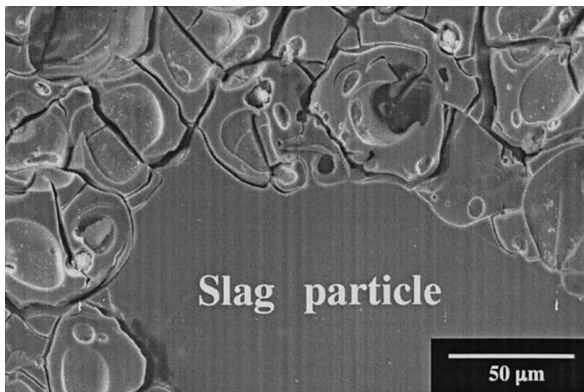**Fig. 10.** SEM micrograph of the sample during water release for the; SiO_2–Na_2O–B_2O_3 system.

increase the amount of water contained in slag by preventing the formation of the crystal phase under hydrothermal conditions in order to form the porous structure, *i.e.* brittle structure, of slag after water release above the glass transition temperature, as well as to lower the glass transition temperature of slag.

In order to use slag containing water as a lubricant in high straining rolling for ultrafine-grained steels, it is necessary to understand more deeply not only a reaction between slag and H_2O under hydrothermal conditions but also the state of H_2O existed in the microscopic structure of slag containing water. The authors are planning to produce slag containing water with general slag compositions on the basis of the above new information as well as the results obtained in the present work, and then to accumulate the information on frictional characteristics of the slag containing water when the slag containing water is applied as a lubricant in a friction test of roll materials with steels.

4. Conclusion

We considered slag containing water as a lubricant in high straining rolling for ultrafine-grained steels by focusing on lowering the glass transition temperature and the structure change of slag containing water. We examined the structures of slag containing water and slag that released water above the glass transition temperature, and conducted *in-situ* observations of water released from the surface of slag containing water upon heating in an SiO_2–Na_2O–B_2O_3 system.

It was found that water is mainly contained in the phase formed under hydrothermal conditions; and that the glass phase formed under hydrothermal conditions tended to contain more water than did the crystal phase. We confirmed that a porous structure was formed by water released from slag containing water. Thus, it is expected that slag is crushed by the rolling load after water is release due to the brittle structure of this slag, and so will provide lower friction than the original slag containing water.

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