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STUDY OF CALCIUM-IRON-SILICATE GLASSES BY MOSSBAUER SPECTROSCOPY

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Abstract.- The behavior of iron atoms in calcium-silicate glasses has been studied by the Mossbauer effect. The equilibrium concentration ratio, \( N_{Fe^3+}/N_{Fe^{2+}} \), increases as the CaO content or the partial oxygen pressure during heat treatments increases. In the glasses containing a large amount of Fe\(_2\)O\(_3\), Fe\(_{2^+}\) ions occupy octahedral sites, while Fe\(_{3^+}\) ions behave as amphoteric ions. For a small partial oxygen pressure, \( N_{Fe^3+}/N_{Fe^{2+}} \) increases slightly with increasing CaO/SiO\(_2\) ratio. In glasses containing a small amount of Fe\(_2\)O\(_3\), the coordination state of Fe\(_{3^+}\) ion has not been clearly determined, while the Fe\(_{2^+}\) ion occupies tetrahedral sites besides octahedral sites.

In steel-refinements and welding, it is important to investigate the slag of CaO-SiO\(_2\)-Fe\(_2\)O\(_3\) system. In this work, the redox reaction and coordination behavior of iron atoms in CaO-SiO\(_2\) slags containing 10 mol\% Fe\(_2\)O\(_3\) and 0.2 mol\% Fe\(_2\)O\(_3\) have been studied by the Mössbauer effect as a function of CaO/SiO\(_2\) ratio and partial oxygen pressure during heat treatments.

The glassy samples were prepared for Mössbauer measurements as follows. As starting materials, analytical grade reagents of CaCO\(_3\), SiO\(_2\) and Fe\(_2\)O\(_3\) were used. After being mixed, they were melted in a platinum or a molybdenum crucible at 1600°C for 8 h in atmospheres (pure oxygen, air or CO-CO\(_2\) mixed gas) with several partial oxygen pressures. The glass melt was quenched under that atmosphere, ground to be powdered and fixed on an aluminum thin film.

The γ-ray source, the \(^{57}\)Co in palladium, was driven with a constant velocity controlled by a laser interferometer. Every spectrum was analyzed by the iterative least square procedure on the assumption that the line shape is Lorentzian and two peaks indicating a quadrupole split have the same intensity and the same width.

Some of the Mössbauer spectra are shown in figure 1. The isomer shift and quadrupole splitting obtained in this study are shown in Table I. The coordinate states of ferrous and ferric ions were determined by comparing the observed isomer shift with those reported for crystalline /1-5/ and glassy materials /4-8/.
Table I: Isomer shift (i.s.) and quadrupole splitting (q.s.)

(\text{CaO-SiO}_2)\text{-0.2mol}\%\text{Fe}_2\text{O}_3 \text{ glasses}

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<th>\text{i.s}</th>
<th>\text{q.s}</th>
<th>\text{i.s}</th>
<th>\text{q.s}</th>
<th>\text{i.s}</th>
<th>\text{q.s}</th>
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<tbody>
<tr>
<td>obtained result</td>
<td>0.82-0.94</td>
<td>1.83-2.29</td>
<td>-0.07-0.1</td>
<td>1.05-1.61</td>
<td>0.25-0.34</td>
<td>1.03-1.25</td>
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<tr>
<td>estimated state of iron</td>
<td>\text{Fe}^{2+}_{\text{oct}}</td>
<td>\text{Fe}^{3+}_{\text{tet}}</td>
<td>\text{Fe}^{3+}_{\text{oct}}</td>
<td></td>
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</tbody>
</table>

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<th>\text{i.s}</th>
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<th>\text{q.s}</th>
<th>\text{i.s}</th>
<th>\text{q.s}</th>
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<tbody>
<tr>
<td>obtained result</td>
<td>0.22-0.30</td>
<td>0.8-1.1</td>
<td>0.6-0.74</td>
<td>1.8-2.1</td>
<td>0.9-1.1</td>
<td>1.9-2.1</td>
</tr>
<tr>
<td>estimated state of iron</td>
<td>\text{Fe}^{3+}</td>
<td>\text{Fe}^{2+}_{\text{tet}}</td>
<td>\text{Fe}^{2+}_{\text{oct}}</td>
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\text{Fe}^{3+} \text{ peak was too weak to estimate the coordinate state of ferric ions. On the other hand, the Mössbauer measurements indicate that \text{Fe}^{2+} \text{ occupies both octahedral and tetrahedral sites. The N}_{\text{Fe}^{3+}}/N_{\text{Fe}^{2+}} \text{ ratio shows similar dependence on CaO/SiO}_2 \text{ ratio and Po}_2 \text{ as that of N}_{\text{Fe}^{3+}}/N_{\text{Fe}^{2+}} \text{ in figure 2.}\

It has been reported that \text{Fe}^{3+} \text{ ions occupy tetrahedral sites and \text{Fe}^{2+} \text{ occupy octahedral one in alkali-silicate glasses. However, the present study shows that the calcium-silicate glasses containing a large amount of Fe}_2\text{O}_3 \text{ occupy octahedral ferric sites besides tetrahedral ones and glasses containing a small amount of Fe}_2\text{O}_3 \text{ occupy tetrahedral ferrous sites besides octahedral ones. Moreover, the phenomenon that the decreasing of Po}_2 \text{ or CaO content resulted in the reduction of N}_{\text{Fe}^{3+}}/N_{\text{Fe}^{2+}} \text{ ratio for both glasses containing a large and small amount of Fe}_2\text{O}_3 \text{ would suggest that the redox reaction would involve ferric and ferrous complex anions in consideration of Johnston's redox reaction 191.}\

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References

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