# APPLICATION OF MÖSSBAUER SPECTROSCOPY TO DEOXIDATION FROM LIQUID IRON BY ALUMINIUM

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# APPLICATION OF MÖSSBAUER SPECTROSCOPY TO DEOXIDATION FROM LIQUID IRON BY ALUMINIUM

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Résumé.- Cette étude a pour but d'étudier la désoxygénation du fer liquide par l'aluminium. L'hercynite $FeAl_2O_4$ et les formes γ, κ, θ et α de $Al_2O_3$ sont les formes d'oxydes produits pendant l'opération. Les résultats expérimentaux indiquent que le fer est sous forme de $Fe^{2+}$ dans l'hercynite et $\gamma$-$Al_2O_3$ et dans l'état $Fe^{3+}$ pour κ, θ et $\alpha$-$Al_2O_3$. On peut penser que les oxydes sont produits dans l'ordre suivant : d'abord l'hercynite, puis les formes γ, κ, θ et α de $Al_2O_3$ successivement, par réaction de l'hercynite avec Al dans le fer liquide.

Abstract.- This study was carried out to investigate the deoxidation mechanism from liquid iron by aluminium. Hercynite ($FeAl_2O_4$), γ-, κ-, θ- and $\alpha$-$Al_2O_3$ were the oxides produced during deoxidation. From the experimental results, it was thought that iron species in hercynite and $\gamma$-$Al_2O_3$ were in the state of $Fe^{2+}$, and those in κ-, θ- and $\alpha$-$Al_2O_3$ were in the state of $Fe^{3+}$. It was thought about the formation of the oxides as follows. Hercynite produced at first, and γ-, κ-, θ- and $\alpha$-$Al_2O_3$ in that order produced by reaction of hercynite with aluminium in liquid iron, because electrons of iron species leaned around aluminium species in Fe-Al alloy.

1. Introduction.- It is known that the oxides produced in molten iron with addition of small amount of aluminium (0.04-0.1wt%) during solidifying are hercynite, γ-, κ-, θ- and $\alpha$-$Al_2O_3$. As the mechanism of their formation was not clarified, this study was carried out to know the state of electron around iron species in the aluminous oxide by means of Mössbauer spectroscopy and to investigate the mechanism of formation of aluminous oxides.

2. Experimental.-

2.1. Apparatus.- The absorption of the 14.4 keV gamma ray of $^{57}Co$ diffused into chromium plate was measured at room temperature. A proportional counter was used to detect the 14.4 keV gamma ray. The sample was vibrated sinusoidally at 3 Hz. The width Γ was about 0.8 mm/s from the measurement of natural iron and $^{57}Co$ (Cr) at room temperature.

2.2. Sample.- Electrolytic iron with addition of small amount of aluminium (0.04-0.1wt%) was melted in the levitation furnace of purified Ar-gas atmosphere and kept at 2200°-2300°C for about 40 s. After that, the molten iron was quenched by a chill mould quenching method. The produced oxide during solidifying was extracted from the sample by iodine-alcohol method and identified by X-ray diffraction. The extracted oxides were used as the sample for Mössbauer effect measurement. The oxides were pasted in silicon grease and wrapped in aluminium foil.

3. Experimental results and discussion.- Figure 1 shows the spectrum of Mössbauer spectroscopy for the mixture of hercynite and wüstite (FeO).

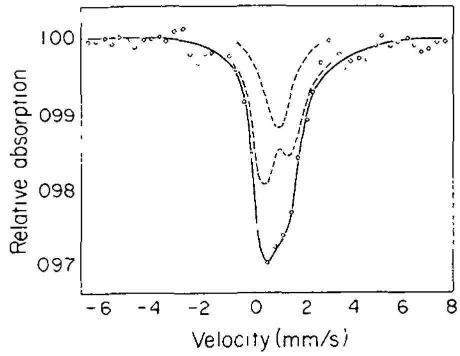


Fig. 1 : Mössbauer spectrum of the mixture of hercynite and wüstite. Doublet : wüstite, singlet : hercynite.

It is thought that this spectrum consists of the spectra of hercynite and wüstite /1,2/, and iron species in hercynite and wüstite are in the state of $Fe^{2+}$. Figure 2 shows the spectrum of Mössbauer spectroscopy for the mixture of γ- and $\kappa$-$Al_2O_3$.

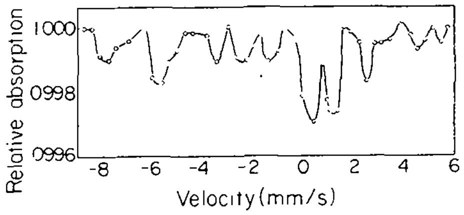


Fig. 2 : Mössbauer spectrum of the mixture of γ- and $\kappa$-$Al_2O_3$.

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Though the spectrum shown in figure 2 is complicated, it seems that there is the Zeeman splitting pattern in the spectrum.

Figure 3 shows the mechanism of formation of aluminous oxides. Isomer shift of Fe-Al alloy is + 0.165 -+ 0.425 mm/s from the standard absorber of α-Fe at room temperature /3-7/. This means that aluminium species works as the acceptor of electron in the case of Fe-Al alloy, in other words, electron of iron species leans around aluminium species.

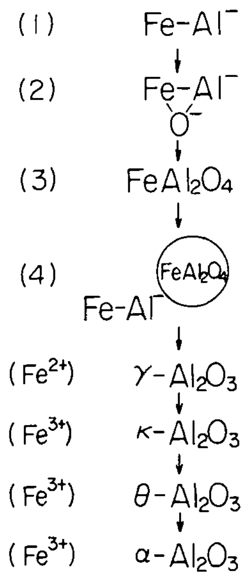


Fig. 3 : Mechanism of formation of aluminous oxide.
(1) Electron of iron species leans around aluminium species.
(2) Nucleation of oxide.
(3) Formation of hercynite.
(4) Reaction of hercynite with aluminium.

It is thought that this lean means to combine iron species with aluminium species strongly. On the other hand, this lean decreases the interaction between inner electron and nucleus of aluminium. But, if leaving the electron, which leans around aluminium species, around another species, iron binds more strongly with aluminium. In such a state, if there is oxygen at the neighbour site of iron and aluminium, the electron, which leans around aluminium, leaves around oxygen species. In this state, nucleus of oxide consisting of iron, aluminium and oxygen forms in liquid iron. After that, the nucleus of oxide grows as reacting with iron, aluminium and oxygen, and the oxide grows until it's chemical composition becomes to that of hercynite. If oxygen species is not around hercynite, hercynite cannot grow. In such a state, if aluminium species diffuse more around hercynite, in contrast with the formation of hercynite, the reaction of hercynite with aluminium occurs, maybe, because electron of iron species leans around aluminium species. By this reaction, iron species in hercynite go out to liquid iron. As, at the beginning step of the reaction, there is iron of fair amount in the oxide, spinel structure of hercynite does not break entirely. So the oxide becomes to $\gamma$-$Al_2O_3$ of spinel type structure. It is thought that iron species in $\gamma$-$Al_2O_3$ is in the state of $Fe^{2+}$. The reaction advances moreover, and amount of iron in the oxide becomes small until the chemical composition of the oxide becomes near to that of $Al_2O_3$, so κ-, θ- and $\alpha$-$Al_2O_3$ occur in that order. As it seems that iron species in $\kappa$-$Al_2O_3$ is in the state of $Fe^{3+}$ from the spectrum shown in figure 2, it is thought that iron species in θ- and $\alpha$-$Al_2O_3$ are in the state of $Fe^{3+}$.

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