Influence of Kiln Atmosphere on Chemical States of Iron in Red Clay

Mitsuru WAKAMATSU, Nobuyuki TAKEUCHI, Ohn MAUNG,
Gao-Chao LAI and Shingo ISHIDA*

(Department of Inorganic Materials, Faculty of Engineering and Design, Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto-shi 606
*Department of Industrial Chemistry, Chubu University)

赤色粘土中の鉄の化学状態に炉内雰囲気を与える影響

若松 盈・竹内信行・Ohn Maung・頼 高潮・石田信伍*

(京都工芸繊維大学 工芸学部 無機材料工学科)
(* 中部大学 工業化学科)

The chemical states of iron in fired red clay containing iron in high concentration and the phase transformation occurring during firing in various atmospheres were studied by X-ray diffraction, ESR and ESCA. It was pointed out that the reduction of Fe ions to metallic iron and the formation of hercynite (FeAl_2O_4) took place competitively during the firing of the clay at 1000°–1200°C under reducing conditions. The color of the clay fired below 1250°C in a reducing atmosphere was dependent only on the firing temperature, but not on the atmosphere.

[Received November 2, 1985]

Key-words : Furnace atmosphere, Red clay, Color of fired clay, FeAl_2O_4

1. Introduction

The mechanical and the optical properties of red clay fired at 1250°C under various atmospheric conditions has been described in the previous paper¹⁾. The bloating and the blackening of fired clay were observed to be prevalent when firing was performed in reducing atmosphere^{1)–5)}. Iron, under the mild reducing condition, was in the ferrous state and sometimes metallic iron was observed when the firing was carried out under strongly reducing conditions^{1), 6)–9)}. The presence of hercynite in the clay fired below 1250°C was briefly mentioned^{1), 10)}. In this paper, the stability of hercynite phase, namely, its formation and disappearance under various firing conditions is discussed in detail in connection with the chemical states of iron in the fired clay.

2. Experimental

The firing of the samples were performed in the same way as described in the previous paper¹⁾. The fired samples were measured with X-ray diffraction, ESR, ESCA and color spectrometers. In ESR measurements, the signals of manganese ion were taken as the standard signals for determining the magnetic field. For ESCA measurements, the peak of C1s was taken as the

standard peak for determining the binding energy which appears at 285.0 eV and then, the peak of Si 2p was again determined. The binding energy values of Fe 2p_{3/2} peaks for those samples were determined by the assuming that the binding energy of Si 2p did not change for all samples fired under any atmospheric condition. The argon etching treatment was performed for 5 min to remove the impurities covering the surface of the samples.

3. Results and discussion

3.1 X-ray diffraction analysis of red clay

Table 1 shows the components present in red clay fired at different temperatures and atmospheric conditions^{11), 12)}. Gas compositions of the kiln atmospheres are shown in Table 2¹⁾. In a strongly reducing atmosphere, that is at $m=0.7$ (m =air ratio), metallic iron was observed at low temperature (1000°C), but at 1100°C, the hercynite phase was present, and above 1200°C, the metallic iron phase was again observed. This fact strongly indicates that two competitive reactions occurred simultaneously, namely, the reduction to metallic iron and the hercynite formation. The hercynite must be formed at the expense of the decomposed products of clay minerals, such as

Table 1. The X-ray diffraction analysis of red clay fired in different temperatures and atmospheres.

Air ratio (-)	Keep temp. (°C)	α -Quartz	α -Cristobalite	Mullite	Iron	Hercynite	Hematite
0.7	1000	+			+	+	
	1100	+		+		+	
	1150	+		+		+	
	1200	+		+	+		
	1250	+	+	+	+		
0.8	1000	+			+	+	
	1100	+		+		+	
	1200	+	+	+	+		
	1250	+	+	+	+		
0.9	1000	+				+	
	1100	+	+	+		+	
	1200	+	+	+		+	
	1250	+	+	+			
1.0	1250	+		+			+
1.2	1250	+		+			+
1.4	1250	+		+			+
1.6	1250	+		+			+

Table 2. Gas compositions of the kiln atmosphere for various air ratios expressed in mole percent.

Air ratio <i>m</i>	Atmosphere				
	N ₂	CO ₂	O ₂	CO	H ₂
0.7	82.6	0.0	0.0	8.2	9.2
0.8	89.2	0.0	0.0	5.5	5.3
0.9	94.9	0.0	0.0	2.8	2.3
1.0	88.3	11.7	0.0	0.0	0.0
1.2	86.6	9.6	3.8	0.0	0.0
1.4	85.4	8.2	6.4	0.0	0.0
1.6	84.5	7.0	8.5	0.0	0.0

alumina. The decomposition of clay takes place at a high temperature and thus hercynite formation is slow at lower temperatures. Thus at 1000°C, the reduction to iron is considered to be faster than the formation of hercynite. Under the same reducing condition at 1100°C, decomposition of clay is rapid and thus it possibly leads to the formation of hercynite instead of the formation of metallic iron. At higher temperatures above 1200°C, diffusion of hercynite to the silica phase or glass phase is considered to occur, and alumina recombines with silica to form mullite and the remaining iron oxide is reduced to iron. This can happen because mullite occurs abundantly at high temperature, and the transformation of α -quartz to cristobalite in a reducing atmosphere supports above assumption of the diffusion of hercynite into the silica phase. The diffusion rate also depends on the amount of glass phase present in the clay. Thus hercynite was

readily decomposed in the case of the red clay sample fired at $m=0.8$.

The reactions which occurred at $m=0.8$, is quite the same as $m=0.7$, but only hercynite instead of iron was found at 1000°C. This may be due to the decrease in reducing power to compete with hercynite formation. At $m=0.9$, the reduction to metallic iron was so slow that hercynite formation was dominant below 1200°C. At 1200°C, hercynite seems to diffuse and dissociate in the silica phase, forming mullite and cristobalite. Under strongly reducing conditions, such as $m=0.7$ and 0.8, metallic iron was formed and, while under a mild reducing condition such as $m=0.9$, metallic iron could not be detected by X-ray diffraction analysis and consequently, iron oxide must be combined with silica to form a silicate which dissolved in glass. Sericite was stable up to 1000°C. At relatively low temperatures, the cristobalite phase was not observed because the transformation to cristobalite occurs at 1470°C^[13,14], but its presence in red clay fired at 1250°C may be caused by the ferrous ions which acts as a promotor or a catalyst for the transformation. The peaks of α -quartz are shown in Fig. 1. Here, the peaks are higher in the samples fired under oxidizing conditions than in those fired under reducing conditions which shows that ferrous ions act as a strong flux to attack the quartz structure. In a neutral or oxidizing atmosphere, the presence of hematite, confirmed by X-ray analysis, has no effect on the transformation of quartz to other forms^[15].

Fig. 1. The comparison of the X-ray diffraction peaks of α -quartz of the fired red clay bodies at 1250°C.

3.2 ESCA measurement of red clay fired at 1250°C

Figure 2 shows the ESCA of clay bodies fired at 1250°C under various atmospheric conditions. The vertical lines corresponding to the binding energies of Fe^{3+} and Fe^{2+} in an isolated state as well as those of Fe_2O_3 and metallic iron in a bulk state are shown at the bottom of the figure. For samples fired at $m=0.8$, that is, in a strongly reducing atmosphere, the two ESCA peaks are attributed to Fe^{2+} ions and the metallic iron. In the case of the firing in mild reducing atmosphere at $m=0.9$, the peak indicates only the presence of Fe^{2+} . The peaks of Fe^{2+} ions and fayalite are very similar and are very difficult to distinguish by means of ESCA¹⁶⁾. In the case of the firing in strongly oxidizing atmospheres, that is, at $m=1.4$, the ESCA spectrum shows a peak of Fe_2O_3 in the bulk state which confirms the presence of hematite detected by the X-ray diffraction analysis, but the presence of Fe^{3+} ions could not be detected as was observed by ESR analysis. This is possibly due to the presence of so small amounts of Fe^{3+} ions as to be undetectable by ESCA.

Fig. 2. The ESCA spectra of $\text{Fe } 2p_{3/2}$ region for fired red clay bodies.

3.3 ESR analysis of fired clay below 1250°C

The authors already revealed from the ESR analysis of the clay fired at 1250°C that in the clay fired under oxidizing conditions, the Fe^{3+} signal as well as the hematite signal were observed, and Fe^{3+} ions appeared to be trapped in the quartz structure or in the mullite structure¹⁷⁾. Hematite was thought to be formed from the degradation of alumina octahedrons in which some iron oxides were present as impurities. The ESR signal of metallic iron shows a slight rise at the low magnetic field and then the pattern falls to a low value at the high magnetic field¹⁾. Figure 3 shows the ESR spectra of red clay fired at various temperatures in the strongly reducing atmosphere of $m=0.7$. According to the X-ray diffraction data, Fe metal was found at all temperatures except at 1100°C where hercynite occurred abundantly. According to Ishida et al., the red clay fired in a reducing atmosphere produced a signal which corresponded to nonstoichiometric iron oxide but did not mention the presence of hercynite¹⁸⁾. Maniatis et al.¹⁰⁾ described that hercynite undergoes a magnetic transition at 8 K but did not mention the magnetic properties near room temperature. The ESR signal observed in the clay fired at 1100°C is prominent and is likely to be related to hercynite. The signal of hercynite is not known, and the data of ESR spectrum for hercynite is still lacking. The mutual interaction of various states of iron oxide makes it very difficult to explain the ESR spectra of the fired clay samples even qualitatively¹⁸⁾. As shown in Fig. 3, the intensity of the signal decreases as the iron phase develops. The patterns generally have

Fig. 3. The ESR spectra of red clay fired at various temperatures in strongly reducing atmosphere of $m=0.7$.

Fig. 4. The ESR spectra of red clay fired at various temperatures in reducing atmosphere of $m=0.8$.

Fig. 5. The ESR spectra of red clay fired at various temperatures in mild reducing atmosphere of $m=0.9$.

two signals, where one signal appears around 1 kG and the other is around 3 kG. The signal near 1 kG is similar to the signal of metallic iron, but the signal at the higher magnetic field is unknown. Figures 4 and 5 show the ESR spectra of red clay fired at various temperatures under the atmospheres of the air ratios of 0.8 and 0.9. The two series of spectra have the same trend as that of $m=0.7$. In Fig. 4, the spectra have two signals like Fig. 3. The signal at the low magnetic field seems to be caused by metallic iron, and the intensity of the signal at the high magnetic field decreases as the iron phase develops. At 1000°C, where hercynite appears, the peak of the signal is relatively high. In Fig. 5, where the ESR spectra of samples fired under mild reducing conditions are shown, the signal at about 1 kG is rather weak compared with the other figures. It could also be considered that the absence of an iron phase under these mild conditions reduces the interference of

the metallic iron signal; hence, the curves are flattened at the low field. Here, the presence of hercynite detected by X-ray diffraction analysis at temperatures below 1250°C also shows the appearance of a signal at a high field. Thus, the hercynite phase seems to be strongly responsible for the signal at the high field.

3.4 Color characteristic of the fired clay samples

It was described in the last paper that the atmosphere strongly affects the color of the fired clay samples¹⁾. That is, in a strongly reducing atmosphere, the color is black; whereas in a mild reducing atmosphere, the color becomes yellowish grey, and in oxidizing conditions, the color is iron red. The samples fired below 1250°C in reducing conditions usually obtain a dark grey color and their colors cannot be distinguished by the naked eye. In order to have a better understanding of the color, the color was measured by a color spectrum analyzer and was plotted in a Munsell diagram¹⁹⁾. Figure 6 shows the Munsell diagram of red clay fired in various temperatures and atmospheres. This figure as shown was determined at value equals 4 which is nearest to the values of samples varying from 3.44 to 4.64. In this figure, the circle, the square and the triangle stand for firing temperature of 1000°C, that of 1100°C and that of 1200°C, respectively. This diagram shows that the color of clay depends on the firing temperature irrespective of the firing atmosphere, because the sample colors are grouped separately with respect to the temper-

Fig. 6. The Munsell diagram on value=4, of the clay bodies fired in various atmospheres below 1250°C. ●: indicates the temperature 1000°C, ■: indicates the temperature 1100°C, and ▲: indicates the temperature 1200°C and air ratio from 0.7 to 0.9.

ature. At 1000°C, where the temperature is insufficient to start high temperature reactions, the color of the samples lie along the neighborhood of 5 YR as shown by circles. At 1100°C, where hercynite is dominant, the colors of the samples are clustered in the region between 10 PB and 5P, or in other words, the colors are purplish blue. At 1200°C, the colors of the fired samples are grouped between 10 RP and 5 R, or reddish purple.

Because the brightness is 4 and the chroma is less than 1 for every sample, the colors of all the samples are rather dull. It is also difficult to explain which component determines the color factor as the coloration is not only caused by iron compounds but also by carbon deposition which can blacken the wares fired in the reducing atmosphere²⁰⁾.

4. Concluding remarks

The reactions occurring in clay during firing under reducing conditions, have been explained mainly from the viewpoints of the breakdown of the clay structure and the reduction of iron oxide. Under strongly reducing conditions, metallic iron was formed even at low temperatures. The alumina octahedral structure of clay breaks down first and forms hercynite at relatively low temperatures, and at that time, the silica structure is thought to be intact. As the temperature is raised, hercynite seems to diffuse into the silica structure through the glass phase and forms iron silicate and mullite. The ferrous ions such as iron silicate again act as a promoter to transform the low temperature form of the silica structure to the high temperature form, that is, from quartz to cristobalite. The hercynite phase disappears between 1100° and 1200°C. The condition for the beginning of the hercynite phase is still unknown, and it seems to form at a temperature where the alumina octahedral structure starts to collapse. The papers describing the presence of hercynite in fired clay under reducing conditions are very

few, because the stability of hercynite is sensitive to temperature as well as atmosphere. Unless the atmosphere and temperature are accurately controlled, the results become complex. The atmosphere employed in each experiment was produced by mixing the specific gases, and the flow rate was maintained high enough so that the composition of gases was assumed to be constant. One of the objective of this paper was to investigate the behavior of red clay under various firing conditions.

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