Phase Composition and Coloration of Hidasuki on Bizen-yaki

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The formation of Hidasuki,a characteristic red-colored pattern on the surface of Bizen-yaki, was investigated from the viewpoints of its mineral composition and coloration. Hematite,corundum and quartz were found in Hidasuki. The same phase composition as that of Hidasuki was obtained when a sample, mixture of Bizen-clay and 8 or 10 wt% potassium chloride, was cooled down at the rate of 0.2 or 0.5 ℃/min in air after it was heated at 1300 ℃ for 3 hours. It was also clarified that hematite in Hidasuki,crystallizing as the glassy phase was cooled down, could cause its red coloring peculiar to Hidasuki.

Introduction

Bizen-yaki, a characteristic pottery produced in the Okayama area, is made from high iron content clay called Bizen-clay. Its in the clay is 2-3 wt% as hematite.[1] The clay is heated at relativelty high temperature without glaze. Some characteristic patterns are found on the surface of Bizen-yaki. Hidasuki is a typical pattern among them. Before greenweares are heated, straw ropes are used to prevent their mutual contact and it is only where straw ropes are used that Hidasuki appeares.

There are many papers concerning the coloration of the surface of pottary and its mineral composition.[2] Indeed they investigated the relation among coloration, its mineral comoposition and heating condition in the cases of glazed pottery, but rarely did they deal with pottery without glaze such as Bizen-yaki. The coloring formation of Hidasuki has not been clarified, so, in this papar, we hope to report some new findings concerning its coloring through the investigation of the relation between mineral composition of Hidasuki and its coloration.

Experimental

Bizen-clay was sieved through a 100-mesh screen after powdering. The powder was left for one week in a desiccater.The relative humidity in the desiccator was 50%. Various amounts of chemical grade potassium chloride were added to the clay and heated at the scheduled temperatures in an electric furnace. Atmosphere was not controlled. Heating time was fixed to 3 hours following a previous paper.[3] Cooling rates were varied from quenched to 0.1℃/min in an atmosphere of air or N_2. Phase identification was performed by X-ray powder diffraction (XRD) and a spectro colori meter was used to distinguish the differences in color among samples. Each surface of the samples was examined by scanning electron microscope (SEM) and electron probe micro analyzer(EPMA).

Results and Discussion

It is recognized by XRD that corundum,hematite and quartz are present in addition to glassy phase in Hidasuki on Bizen-yaki on the market.[3] And that, mineral composition similar to Hidasuki except hematite could be obtained when the mixture of Bizen-clay and 8wt% KCl were quenched after heat treatment at 1300℃ for 3 hours.[3] Hematite was formed when the mixture of Bizen-clay and 8wt% KCl was heated at 600℃ to 1200℃, though it was disappeared at higher than 1300℃. [4]

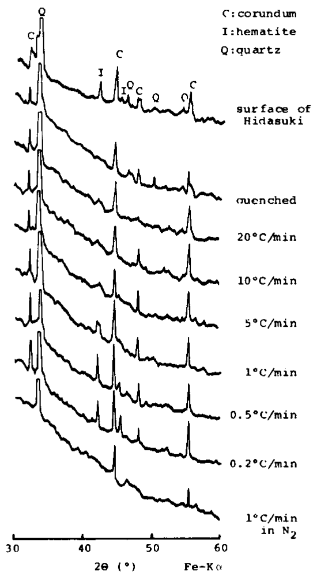

Fig.1 X-ray diffraction patterns of the surface of Hidasuki and Bizen-clay 8wt% KCl added cooled down at various rates after heated at 1300° for 3 hr. (C:corundum,Q:quartz,I:hematite)

In this study, we observed the changes of mineral compositions and coloration under the above-mentioned experimental conditions varying cooling conditions and KCl amount. Fig.1 shows each XRD result of Hidasuki and Bizen-clay 8wt% KCl added when they were cooled down at various conditions. According to these results, at rapid cooling rates, corundum and quartz are formed in addition to glassy phase. However, reducing the cooling rate below 5℃/min, the formation of hematite can be recognized besides the above-mentioned substances, and mineral composition of samples become similar to that of Hidasuki. The amount of hematite decreases with lowering the cooling rates. Hematite was not formed in every case where the sample was cooled down in an atmosphere of N_2. These results suggest that iron components in glassy phase[4] are crystallized as the samples are cooled down in air and they reappeare as the form of hematite.

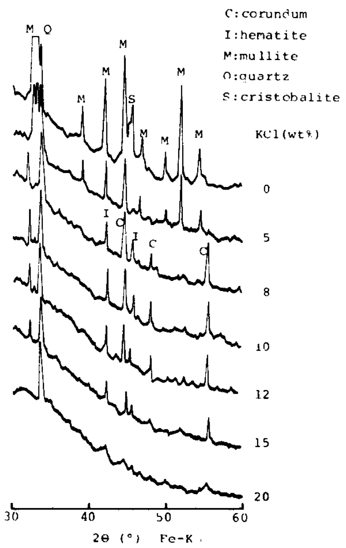

Fig.2 X-ray diffraction patterns of Bizen-clay containing various amount of KCl. All samples were heated at 1300℃ for 3 hr and cooled down at 0.2℃/min. (M:mullite,Q:quartz,S: α —crystoballite,C:corundum I:hematite)

Fig.2 illustrates the XRD results when the amount of KCl added to the clay are varied at a fixed cooling rate of 0.2℃/min. According to Fig.2, the formation of mullite is shown when 0 or 5wt% KCl was added to the clay. However, mullite is not found in both of Hidasuki and the clay containing KCl more than 8wt%. Simultaneously, the amount of hematite increases with the amount of KCl and the maximum amount of hematite is formed when 8 or 10wt% KCl added. And then, the amount of hematite reduces with the amount of KCl. The formation of corundum is also shown when 8,10,12 and 15wt% KCl were added. The forming process of corundum was reported by authors. [3] As for mineral composition of Hidasuki, a similar composition to Hidasuki is obtained when the samples 8 or 10wt% KCl added are cooled down at the rate of 0.2 or 0.5℃/min in air.

It is considered that the fomation of hematite is responsible for the red coloring of heated bodies containing high iron components.[5] We also considered the relation between the coloration and the relative amount of hematite formed varying cooling rates.

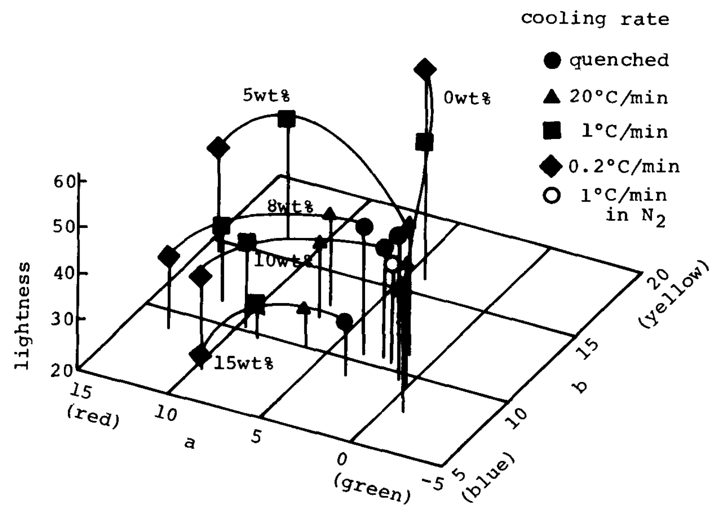

Fig.3 Effect of the amount of KCl added and cooling rate on the coloration of heated Bizen-clay.

Fig.3 shows the selected data of the samples used in the above-mentioned experiments in the form of Lab chromaticity diagram. According to Fig.3, it is found that the sample becomes more reddish with lowering the cooling rate in spite of the different amount of KCl added. Without KCl, the color of heated samples becomes yellowish rather than red with the decrease of the cooling rate. The sample of 8wt% KCl added cooled down at the rate of 1℃/min in N_2 has a coloration similar to that of the heated body cooled down at the rate of 10 or 20℃/min without KCl. It is also found in Fig.3 that the less amount of KCl added makes the color of samples more reddish at the cooling rate of 0.2℃/min.

In this study, we could not make a quantitative analysis of hematite, but the degree of red coloring is in good agreement with the changes of relative X-ray intensity of hematite shown in Fig.1. The a,b values of Hidasuki are also shown in Fig.3. Similar values are obtained when the samples, 8 or 10wt% KCl added, are cooled down at the rate of 0.2℃/min in air. This result is also in good accordance with the results of mineral composition of Hidasuki shown in Fig.2. Fig.4 shows SEM photographs of Hidasuki and samples 8wt% KCl added cooled down at various rates. The hexagonal plate like substances seen on the surfaces of Hidasuki and samples cooled down below 1℃/min seems to be hematite because of their richness of iron proved by EPMA and their shape.[6] The surface of Hidasuki is also similar to that of the sample cooled down at a rate of 0.2℃/min.

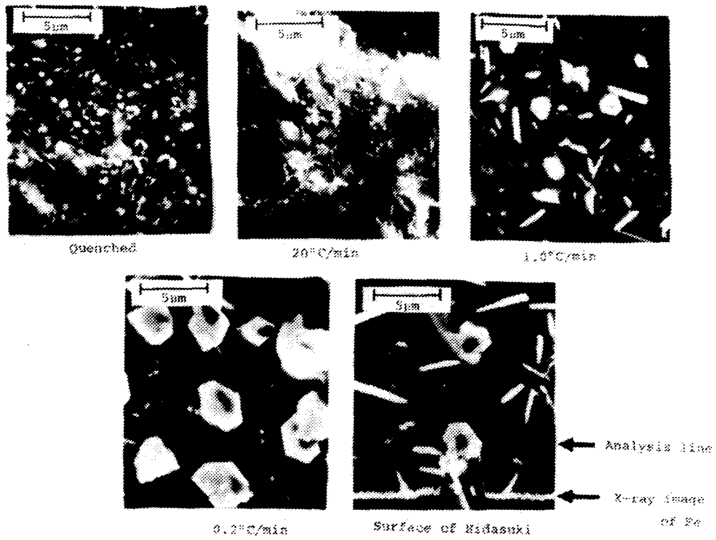

Fig.4 EPMA result and SEM photographs of the surface of samples. Each samples except Hidasuki is a mixture of Bizen-clay and 8wt% KCl.

It is concluded from these results that hematite formed in Hidasuki with glassy phase was responsible for the red coloring of Hidasuki. Hematite could be crystallized when the glassy phase formed through the reaction of Bizen-clay and potassium was cooled down. The same phase composition and colorification as those of Hidasuki was obtained when a mixture of Bizen-clay and 8 or 10wt% KCl was cooled down at the rate of 0.2 or 0.5℃/min in air after heating at 1300℃ for 3 hours.

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