§27. In-Situ Investigation for Microwave Reduction Process of Metal Oxides by High Vacuum Devices

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It is believed that reduction started from lower temperatures and proceeded faster by the effect of microwave than by the conventional heating. Takayama reported that copper powders, which were oxidized on the surface, were reduced in air by microwave heating[1]. Heated sample was sintered to a bulk metal copper. There is little difference between this sample and those sintered by the conventional heating in H_2 + N_2 gas. It is shown the possibility that the microwave promotes reduction. The goal of our work was to reveal the effect of microwave of the reduction of the metal oxides. Then, the authors have measured the partial pressure of oxygen during the microwave heating or the conventional heating.

In the experiment, we used the high vacuum device to measure partial pressure of oxygen. Details of devices showed in the annual report. The samples were heated by microwave and conventional method at about 1200℃.and kept 1000 seconds. We measured the temperature, pressure, and partial pressures of outgas. The rutile powder of the purity 99.9% from Kojundo chemical lab., Co., Ltd., Japan is molded like the column of 8mm in the diameter and 4mm in height. The amount of the sample is 0.01 mol. The molding supplementary agent has not been added. This sample is left by the vacuum for 12 hours, each sample holder is inserted in the maximum point of magnetic field or infrared oven with the vacuum maintained, and it heats it. After the experiment, we measured the structure of the samples by SEM.

Fig.1 shows the result of quadruple mass spectrometer analysis. From the measurement results in Fig.1, the amount of the oxygen discharge when microwave heating in the maximum point of magnetic field is 5 ~ 10 times larger than when conventional heating.

The expression concerning the rapidity of response by absolute kinetics is,

$$k=(k_B T/\hbar)\exp(-\Delta G^0/RT). \quad (1)$$

where k_B and ħ are the Boltzmann constant and the Plank constant. ΔG^0 is the activation energy. The plot of Fig.1 corresponds to the one that both sides taken in the logarithm. This plot is called as Arrhenius plot. From Fig.1 and (1), it is found that there is a possibility that the microwave heating promotes the reductive reaction. This result is being examined closely now.

Fig.2 shows the result of SEM. From Fig.2, the grain boundary has disappeared by the magnetic field heating at 1220℃, 1000s. However, a grain boundary of the departure raw material plainly remains as a comparison by the infrared oven heated up to 1200℃, 1000s.

In summary, it is guessed that the microwave heating promotes reduction reaction and changes the structure in non-equilibrium. In future, we will reveal these non-equilibrium reaction and non-equilibrium structure formation.

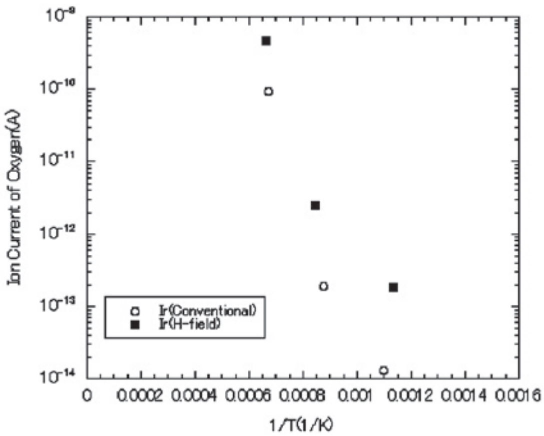
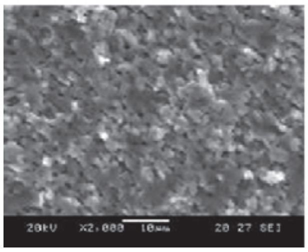
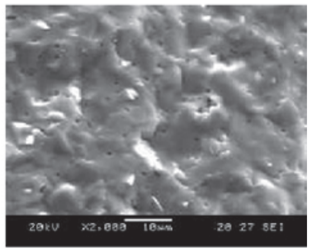


Fig. 1. Comparison of amounts of oxygen discharge in microwave and conventional heating.



Conventional heating at 1200℃, 1000s



Microwave heating in magnetic field at 1220℃,1000s

Fig. 2. SEM images of microwave heating and microwave heating at about 1200℃.

1) S.Takayama J.Powder Matallurgy vol.49 No.3 274-280 (2006)