Phase stability under high pressure gas and material processing by hot isostatic press.

（高圧ガス下での相平衡と熱間等方加圧(HIP)装置による材料処理）

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March 1994

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Acknowledgements

My parents Kunio Sawai and Takako Sawai let me be free to enter a school of a higher grade. They spend money freely for me for 27 years. Thanks to my parents, I could enjoy studying, enjoy sports, enjoy hobby and so on. My mother, Takako Sawai, settled my private trouble and I can not express enough gratitude to her. My grandmother Tonae Yoshida is 81 years old. She is an unusual aged lady who can understand young people, and she was the only woman to whom I could obey when I was in the period of rebelliousness. I do hope all of them to keep healthy and to live to age. And I do be filial to them forever. I do hope my little sister Mie Sawai to be the happiest woman in the world.

This research has been carried out under the guidance of Dr. Kozo Ishizaki of Department of Mechanical Engineering in Nagaoka University of Technology. Sometimes I had quarrels with professor, however, I believe he is a good educator. He provided most helpful guidance during the morning seminars, and in many other occasions. He gave me chances to present my research at Canada, Boston (2 times) and Newark. Thanks to professor, I can present and discuss in English, I can carry out research, I could study patents, and I have great confidence in myself. Students of Ishizaki's laboratory also provided helpful insights during the morning seminars.

The author would like to express his gratitude to "Mon–busho" (Ministry of Education and Culture), as well as to Kobe Steel Co., Ltd. (Kobelco) for providing an excellent support to the present work through the cooperative program. The author is also in debt to Osaka Sanso Kogyo Co., Ltd. (OSK) for helping the design of the experimental system for the superconducting filter.

Thanks to H. Ninomiya, my dear person, I could live a useful life, be excited, and forget all unpleasants. Everyday's call refreshed me, and I could exert myself for studying. I do hope we will go together forever.

Finally, the author can not express enough thanks to all members of Nagaoka body–building club for guiding me in my weight lifting, and giving advice to me about my anguish of heart, money and school life.

Yuichi Sawai,
March, 1994
Nagaoka

Abstract

New materials are produced to create new technologies, and the new technologies are also useful to produce new materials. A hot isostatic process (HIP) is an established method to densify materials, but is also an advanced new technology to synthesize new materials. HIP equipments have been developed for more than 20 years, but phase diagrams for HIPing have not been developed well. Almost all HIP users have been producing new materials by try and error efforts. If any new advanced technologies are developed, a phase diagram is one of the first requirements to obtain new materials. The first part of this thesis treats thermodynamical evaluation of phase equilibria under HIPing condition (chapters 1 to 3). Applications of HIPing to produce new functional materials (chapters 4 and 5) are followed.

HIP is a process which can control total gas pressure, P_{tot}, and temperature, T, independently. One more independent variable, oxygen partial pressure, P_{O2}, is added in oxygen hot isostatic process (O_2–HIP). In chapter 1, although HIP process are normally conducted under a closed chamber, it is shown that the chemical reactions take place to minimize the total Gibbs energy of the system during HIPing. Thus if a solid–gas reaction is progressed under high total gas pressure at a certain temperature, equilibrium partial pressure of a gas involving the chemical reaction is different from that under ambient pressure at the same temperature. Dependence of the reactant gas Gibbs energy on the inert gas pressure is derived theoretically by applying thermodynamics and statistical mechanics. Ellingham diagram is a famous diagram which shows an equilibrium partial pressure of a gas involving a solid–gas reaction at a given temperature. The Ellingham diagram can not be modified under high P_{tot}, and a new phase diagram in $RT\ln P_{O2}$–P_{tot}–T space (called HIP phase diagram) is established. Four dimensional HIP phase diagram is also established for a system which involves two reactant gases.

A concrete example, phase diagrams in Y–Ba–Cu–O superconducting system under various P_{tot}, is given in chapter 2. Phase diagrams of two variables, i.e., $RT\ln P_{O2}$ and T under constant P_{tot} of 50 or 200 MPa, and another phase diagram of two variables P_{tot} and T under 10 MPa of P_{O2} have been obtained for Y–Ba–Cu–O system. A HIP phase diagram of three variables ($RT\ln P_{O2}$–P_{tot}–T phase diagram) is established from those data. HIP phase diagrams can facilitate to distinguish effects of P_{O2} and P_{tot}. Increasing P_{tot} has an effect to increase oxygen fugacity, even under constant P_{O2}. By using those phase diagrams, phase transitions from $2(YBa_2Cu_3O_{7-x})$ containing CuO to $Y_2Ba_4Cu_7O_{15-y}$, and also from $Y_2Ba_4Cu_7O_{15-y}$ containing CuO to

2($YBa_2Cu_4O_8$) are proved to be oxidation reactions. Oxygen contents of $YBa_2Cu_3O_{7-x}$ and $Y_2Ba_4Cu_7O_{15-y}$ are less than their stoichiometric values, i.e., both of x and y are positive. These values of x and y are estimated by the HIP phase diagrams. The method to calculate x and y is also presented.

The HIP phase diagram can be extended to four variables case, using T, P_{tot}, P_{O2} and nitrogen partial pressure, P_{N2}, as variables. The HIP phase diagram of Si–N–C–O system involving oxidation and nitridation, is given in chapter 3. It is confirmed experimentally that the phase transition temperature from SiC to Si_3N_4+C increases with increasing P_{tot} under 0.1 MPa of P_{N2}. Inert gas pressure effects (up to P_{tot}=100 MPa) on nitridation and oxidation are discussed. Four dimensional HIP phase diagram in Si–C–N–O system is estimated by applying the theory developed in chapter 1.

Applications of O_2–HIP are given in chapters 4 and 5. New materials can be synthesized under high P_{O2} in O_2–HIP. It is possible to produce oxides which can not synthesized under ambient oxygen pressure. To oxidize silver is difficult under ambient oxygen pressure. Thus, silver replacement into the lattice of superconducting oxide is also difficult, because the reaction formula of silver replacement includes oxygen as the reactant gas. $YBa_2(Cu_{1-x}Ag_x)_4O_8$ (x is about 0.01) superconductor is synthesized at 1000 °C under 40 MPa of P_{O2} and 200 MPa of P_{tot} by O_2–HIP. Evidences of silver replacement into Cu(1) site in $YBa_2Cu_4O_8$ are presented by Raman scattering method and infrared absorption method. Raman scattering spectroscopy shows that the phonon frequency of O(4)–Cu(1) stretching vibration increases and that of O(1)–Cu(1) vibration decreases by doping silver, where O(4) and Cu(1) are the particular oxygen and copper atoms in an $YBa_2Cu_4O_8$ unit cell (defined in chapter 4). Increase in the phonon frequency is due to an increase in the force constant of O(4)–Cu(1) bond and decease in that of O(1)–Cu(1) bond by a silver replacement into the Cu(1) site. This proves that silver atoms replaced copper site. Ag–O bonding is detected in the 124 phase by an infrared absorption method also.

Another application of a HIP process is to produce porous materials. In chapter 5, an unique usage of a superconducting material is presented. A porous superconducting material is employed to separate a mixture of paramagnetic and diamagnetic gases, fluids and powders. Oxygen and argon are paramagnetic and diamagnetic materials, respectively. A mixture of oxygen and argon can be separated in a high magnetic gradient (BdB/dx), where B is the magnetic flux density and dB/dx is its gradient. Such a high BdB/dx can be obtained by a superconducting filter. It is based on the Meissner effect. The applied magnetic flux to the porous superconducting filter passes through penetrating pores only, it means that magnetic

flux density and its gradient becomes very high on the surface close to pores of the filter. The mixture of paramagnetic and diamagnetic gases can be separated there. Experimental results showed that a 50% oxygen and 50% argon mixture became a 61% oxygen and 39% argon mixture after passing through the filter in the external magnetic field B=0.033 T. A 90% oxygen and 10% argon mixture became 100% oxygen in the external field B=0.03 T and 0.015 T.

Summing up the present thesis, the following is clarified. It is shown that Gibbs energy is useful to discuss equilibrium in HIPing condition. The equilibrium condition in HIPing is derived. Molar volume of oxygen, v_{O2}, in the gas mixture is determined to depend on not only P_{O2} but also P_{tot}. HIP phase diagrams of Y–Ba–Cu–O superconducting system and Si–C–N–O system have been obtained and those are good guides for the researchers and O_2–HIP users to synthesize new materials. It has been proved by using HIP phase diagrams that the equilibrium partial pressure of the gas involving the chemical reactions changes with changing P_{tot}. The method to calculate the value of oxygen nonstoichiometry of Y–Ba–Cu–O superconducting phase by using HIP phase diagram is also presented. A new oxide material $YBa_2(Cu_{1-x}Ag_x)_4O_8$ (x is about 0.01) is synthesized by using O_2–HIP. Also O_2–HIP process is useful to produce porous materials and the porous $YBa_2Cu_3O_7$ is produced. A mixture of paramagnetic and diamagnetic gases is separated using the porous $YBa_2Cu_3O_7$ by applying Meissner effect.