CHAPTER 2

LITERATURE REVIEW

Air Flow Through Porous Media.

1. Flow of Gases at Low Density Through a Packed Bed.

Kanki, T. and Iuchi, S. (1982) investigated flow of gases at low density through a packed bed using the concept of equivalent diameter and tortuosity factor. They made use of the equivalent capillary model. Based on the mean free path concept, the equivalent diameter was defined for free molecular flow as the ratio of the molecular velocity to the frequency of collisions of molecules with the walls of the porous structure. Despite the assumption of free molecular flow, the equivalent diameter was shown to be identical to Blake's, $D_{eq} = 4\ \varepsilon / S_V\ (1 - \varepsilon)$, for continuum flow. In addition, a frequency distribution law of the radius of cross-sectioned spherical particles packed uniformly in the bed was deduced from statistical arguments and then applied to determine the tortuosity factor, which was given as a function of the porosity as $F_O = (2 - \varepsilon)^{3/4}$. Applying these results to the equivalent capillary model, expressions for permeability of gases through a packed bed were derived for the cases of free molecular, continuum and transition flows. The dependency of porosity on the Kozeny constant was also briefly discussed.

2. Analysis of Flow of Rarefied Gases Through Packed Beds by Monte Carlo Method.

Seze, M. et. al. (1977) studied the flow of rarefied gases through sphere-packed bed under free molecular region by the Monte Carlo method. In their analysis, the randomly packed bed was considered as a collective of regularly packed units and the permeability of this representative unit was calculated by the Monte Carlo method. For extension to the packed bed, Oatley's method was used to take account of the direction of flow, and proportional flow allotment according to the ratio of the unit area to the bed was adopted for the direction of the cross section. The calculated results were in good agreement with the observed values, suggesting that this analytical method offers easy calculation of flow through the packed bed.

3. Flow of a Rarefied Gas with Thermal Creep in a Circular Tube.

Channel flow of a rarefied gas at a uniform temperature has been studied both theoretically and experimentally by many investigators (Edmonds, T. et. al.. 1965 and Gross, E. P. et.al. 1957). However, any analytical solution demonstrating explicitly the behavior of the gas flow, especially in the transition flow region where the well-known Knudsen minimum occurs, has not yet been obtained because of the complexity of the momentum transport by molecular collisions. Nor has the gas flow induced by thermal stress been fully researched.

In this paper, Kanki, T. and Iuchi, S. (1973) studied the problem of rarefied gas flow with thermal creep in a circular tube, with special reference to the effect of thermal creep on the gas flow. The solution of the Boltzmann equation with the BGK model was obtained by use of an iterative procedure which uses the slip continuum solution as the first guess. The volumetric flow rate of the flow induced by the pressure gradient resulting from this analysis was in fair agreement with the experimental data in the whole range of the Knudsen number. The solution also gave a fairly good approximation for the thermal creep in consequence of the theoretical work.

Chemical and Physical Properties of Porous Ceramic Refractory.

1. Effects of Al_2O_3 -TiO_2 Contents on the Structure and Permeability of Porous Magnesia Ceramic.

Tsuchinari, A. et al. (1991) investigated the effects of Al_2O_3 - TiO_2 contents on the fractal characteristic of the pores. They studied the changes in the pore structure and in the permeability of porous magnesia ceramic with different matrix contents of TiO_2 - Al_2O_3 at a fixed TiO_2/Al_2O_3 molar ratio of 0.96. The pore shapes of became complicated and the pores tended to have a fractal nature as the matrix content increased. It was proposed that the change in pore shape was caused by the increase in the amount of the matrix and its reaction with MgO grains. Both the mean pore diameter and permeability showed a maximum at certain matrix contents, namely 10 wt. % and 15 wt. % respectively. On the other hand, the fractal dimension of the pore shape changed from 1.39 at 5 wt. % to 1.65 at 20 wt. % of matrix. The fractal dimension changed sharply between 10-15 wt. % and the observed permeability was found to agree well with that of a non-spherical particle system calculated with its pore size modified by its fractal dimension.

2. Influence of Grain Size and Firing Temperature on the Structure of Porous Magnesia Ceramic.

Tsuchinari, A. et. al. (1992a) studied the changes in the pore structure and physical properties of porous magnesia ceramic containing 15 wt. % TiO_2 - Al_2O_3 matrix with a fixed TiO_2/Al_2O_3 molar ratio 0.96. The grain size of the MgO aggregate and the firing temperature were varied to control the pore shape. The typical pore shape was complicated and depended on the grain size and the firing temperature. The pores were found to have a fractal nature. While the fractal dimension increased with the increasing firing temperature for small grains, it decreased with the increasing firing temperature for large grains. The fractal dimension for each MgO grain size occurred at a temperature which was close to that at which the $MgAl_2O_4$ - Mg_2TiO_4 solid solution was formed. Specimens with small grains were found to shrink during firing, but volume expansion was observed for large- grain specimens. These phenomena were explained as the densification and reduced molar volume of $MgAl_2O_4$ - Mg_2TiO_4 solid solution and $CaTiO_3$ formed. From the above facts, it was possible to control the pore shape by varying the grain size and firing temperature.

Tsuchinari, A. et. al. (1992b) investigated the effect of MgO powder addition into permeable Al_2O_3 refractory containing TiO_2 and Al_2O_3 as matrix on its corrosion, penetration and thermal shock resistance. $Al_2O_3 \cdot TiO_2$ was detected in all specimens. Via adding MgO, $Na_2O \cdot 4\,MgO \cdot 15\,Al_2O_3$ and $MgO \cdot Al_2O_3$ were produced. The amount of $MgO.Al_2O_3$ increased as MgO addition increased. Crack along the grain boundary crack decreased as MgO addition increased. This phenomena indicated that $Na_2O \cdot 4\,MgO \cdot 15\,Al_2O_3$ and $Mg \cdot Al_2O_3$, which were mainly produced around the aggregates prevented TiO_2 from penetrating into the grain boundary. Bulk density initially increased and apparent porosity decreased as MgO content increased, but they showed the opposite tendency above MgO content of 5 to 7 wt. %. Corrosion resistance increased as MgO addition increased and was superior by about two-fold compared with no MgO addition. Penetration thickness was also reduced by MgO addition and the thickness was halved compared with no MgO addition. MgO addition increased strength and fracture energy, and thus resulted in improved resistance against both thermal shock fracture and thermal shock damage. Particularly, the fact that the penetration thickness was decreased by MgO addition suggested that it would possible to operate stable bubbling without O_2 cleaning.

3. Effect of Addition of Titania and Alumina Powders into Permeable Magnesia Ceramic.

Tsuchinari, A. et. al. (1990) investigated the properties of permeable magnesia refractory containing titania and alumina powders in the matrix in order to produce permeable refractory with high thermal shock resistance, corrosion resistance and low penetration of molten steel. By adding titania and alumina powders in the matrix, bright glossy portion and dark glossy portion were observed in the matrix and around the grain boundary of magnesia. The bright glossy portion was identified as $CaTiO_3$ (Perovskite) via X-ray diffraction and EPMA analyses. The dark glossy portion was surmised to be Al_2TiO_5 (aluminum titanate) via EPMA analyses, although Al_2TiO_5 was not detected via X-ray diffraction. The collapse of magnesia grains was caused by the generation of $CaTiO_3$ and Al_2TiO_5 along the magnesia grain boundary. Apparent porosity, mean pore diameter and permeability became higher or larger as TiO_2/Al_2O_3 molar ratio decreased, and they reached their maximum values at the equivalent molar ratio. Above the equivalent molar ratio, these values became lower or smaller. Permeability was proportional to the product of the apparent porosity and the square of average pore diameter. Thermal shock resistance increased two-fold compared with no addition of TiO_2/Al_2O_3. Although corrosion resistance deteriorated with TiO_2/Al_2O_3 addition, it was still superior to the conventional porous alumina refractory. Penetration thickness by molten steel was not dependent on TiO_2/Al_2O_3 molar ratio addition, and was very small compared with conventional one. This permeable magnesia refractory will have a good possibility of being used on actual operation.

4. Effect of MgO Addition on the Properties of Porous Al_2O_3 Refractory Containing TiO_2 and Al_2O_3 in the Matrix.

Tsuchinari, A. et. al. (1992c) studied the properties of porous Al_2O_3 refractory containing TiO_2/Al_2O_3 at a molar ratio of 0.96 as the matrix and a different amount of MgO additive. Bright glossy areas were observed around and inside the Al_2O_3 particles. These were determined as $Al_2O_3 \cdot TiO_2$ via X-ray diffraction and EPMA analyses. The addition of MgO generated dark glossy areas, the occupant of which was $Na_2O \cdot 4\,MgO \cdot 15\,Al_2O_3$. But at high MgO contents, $Al_2O_3 \cdot TiO_2$-$MgO \cdot Al_2O_3$ and $Na_2O \cdot 4\,MgO \cdot 15\,Al_2O_3$ coexisted in the dark glossy areas. These compounds prevented TiO_2 from invading the grain boundary. Consequently grain-boundary cracks into the particles decreased and the physical properties, especially compressive and bending strength, were tremendously improved. Thermal shock resistance was also improved by the rise in strength and fracture energy due to the addition of MgO. Corrosion resistance increased as the content of MgO increased. This was considered to be generated by the occlusion of FeO within MgO. Particularly, the fact that the penetration thickness decreased with the addition of MgO should not only contribute to stable operation in actual use but also eliminate the procedure in which the porous plugs are cleaned by O_2 after every usage.

5. Solid Reaction in the MgO Excess Region of the System $MgO \cdot TiO_2 \cdot Al_2O_3$.

MgO refractories have high corrosion and penetration resistance to molten steel, but suffer from low thermal shock resistance (Davidge, R. W. et. al. 1967). There have been reports (Hayashi, Y. et.al. 1989 and Okamoto, T. et. al. 1989) on the methods of adding $ZrO_2 \cdot SiO_2$ or ZrO_2 in an attempt to improve the thermal shock resistance of MgO refractories, however, they are not yet in practical use. As a supplementary measure, Tsuchinari, A. et. al. (1992d) studied porous magnesia refractories containing TiO_2 and Al_2O_3 as matrix, using the concept that the formation of $Al_2O_3 \cdot TiO_2$ having low thermal expansion should improve thermal shock resistance.

In his report, the influence of firing temperature on $MgO \cdot TiO \cdot Al_2O_3$ solid solutions in an environment of excess MgO, as in the case of porous MgO refractories, was studied. The formation mechanism of MgO. $TiO_2 \cdot Al_2O_3$ solid solution was experimentally investigated on the basis of laminated solid-phase reactions of $MgO \cdot TiO_2$ and $MgO \cdot Al_2O_3$ systems.

The result showed that though $MgO \cdot Al_2O_3 \cdot 2MgO \cdot TiO_2$ solid solution was detected, no $Al_2O_3 \cdot TiO_2$ was observed in a permeable MgO ceramic containing TiO_2 and Al_2O_3 as matrix. The formation of $MgO \cdot Al_2O_3 \cdot 2MgO \cdot TiO_2$ solid solution resulted from interface reactions between $2MgO \cdot TiO_2$ and $MgO \cdot Al_2O_3$. Thus $MgO \cdot Al_2O_3 \cdot 2 MgO \cdot TiO_2$ solid solution was detected at 1,573-1,673 K and its amount increased with the firing temperature. $2MgO \cdot TiO_2$ was formed in the system $MgO \cdot TiO_2$ but was not produced in the system $MgO \cdot TiO_2 \cdot Al_2O_3$ because the amount of Mg diffusion at the interface between the aggregate and matrix additives was too little due to the large aggregate size of MgO and small amount of Mg diffusion. The laminated solid phase reaction between $MgO \cdot TiO_2$ and $MgO \cdot Al_2O_3$ system caused a decrease in the formation of $MgO \cdot Al_2O_3$ and $2 MgO \cdot TiO_2$ at the interface. On the other hand, $MgO \cdot Al_2O_3$-$2MgO \cdot TiO_2$ solid solution increased. Mg was detected in the matrix without addition of MgO as matrix. Al diffused in the layer of $MgO \cdot TiO_2$, and Ti diffused in the layer of $MgO \cdot Al_2O_3$, as found by EPMA analysis. The formation mechanism of the $MgO \cdot Al_2O_3$-$2MgO \cdot TiO_2$ solid solution consisted of the following steps:

1. The diffusion of Mg at the interfaces between MgO aggregate and matrix additives.
2. The formation of $MgO \cdot TiO_2$ and $MgO \cdot Al_2O_3$ during Mg diffusion.
3. The formation of $2 MgO \cdot TiO_2$ by a reaction between $MgO \cdot TiO_2$ and MgO.
4. A solid solution reaction between $MgO \cdot Al_2O_3$ and $2MgO \cdot TiO_2$ during Al diffusion in $2MgO \cdot TiO_2$.

The diffusion coefficient of Mg was 4.8×10^{-7} cm^2/s in the laminated solid phase reaction. The value showed good agreement with the reported value for the diffusion coefficient of Mg ($4.79 \times 10^{-7} cm^2/s$).

6. Permeable Ceramics Utilizing Spherical Particles.

Okawa, K. et. al. (1986) studied the effect of spherical alumina particles on the physical properties of the permeable ceramics and the results obtained through the actual application of a tundish upper nozzle utilizing spherical alumina particles. Spherical particles are superior to non-spherical particles in terms of fluidity and packing density. Compressive strength of the improved permeable refractories is less than that of normal permeable refractory but it can be improved by adding fine alumina powder and using higher forming pressure. If the multiplication products of [apparent porosity x (pore diameter)^2] are identical, permeability of the improved permeable refractory is greater than that of normal permeable refractory. If the permeability is identical, corrosion resistance of the improved permeable refractory is higher than that of the normal permeable refractory. The upper nozzle for a tundish was fabricated using the improved permeable refractory to inhibit the nozzle clogging and put in operation. The result of operation revealed that there was no problem with regards to permeability, durability and precipitates.

7. Corrosion Resistance of Permeable Refractory.

Tsuchinari, A. et. al. (1979) investigated the effects of the physical properties and chemical composition of the raw materials on the corrosion resistance to molten steel of Al_2O_3, $MgO{\cdot}Al_2O_3$ and MgO permeable refractory materials. The corrosion resistance of a permeable refractory depends largely on the low melting point material produced by the reaction between the molten steel and the permeable refractory. The corrosion resistance improves with decreasing apparent porosity and decreasing mean pore size, and with increasing compressive strength. The corrosion resistance of the MgO system is superior to that of the Al_2O_3 and the $MgO{\cdot}Al_2O_3$ systems.

8. Porous Plug Made of Spherical Particles for Bubbling from the Bottom of the Ladle.

Kochi, H. et. al. (1987) developed for bottom bubbling, a new type of porous refractory plug made of spherical alumina particles. When this type of plug was used at the ladle, it exhibited some characteristic features which could not be attained by conventional plugs. The porous plug made of spherical alumina particles was better than that made of non-spherical particles in terms of resistance to thermal shock and corrosion. The former contained certain pores into which molten steel did not penetrate. Such pores and the high thermal-shock resistance of the porous plug prevented the occurrence of bubbling troubles and contributed greatly to stable operation for steel making.

9. Application Results of Al_2O_3 Porous Plug Containing $TiO_2 \cdot Al_2O_3$ and MgO as Matrix in Actual Operation.

Al_2O_3 porous plugs containing TiO_2, Al_2O_3 and MgO in the matrix improved porous plug were applied to a 200 ton ladle. Although there occurred cracks in the longitudinal and transverse directions in the conventional porous plugs , no cracks were observed in the improved porous plugs. Therefore porous plug was superior to the conventional one in thermal shock resistance.

The average wear rate was 9.0 mm/heat for the improved plug and 9.8 mm/heat for the conventional one. The improved plug showed 8% higher corrosion resistance compared with the conventional one.

Although the conventional porous plug underwent O_2 cleaning after every heat in order to avoid bad gas blowing, the improved one underwent O_2 cleaning after every two heats because of higher penetration resistance. It was possible to obtain stable gas blowing even with less O_2 cleaning frequency. Penetration thickness of the improved plug was 5.9 mm on average, whereas it was 11.2 mm for the conventional plug. This fact agreed with the basic experimental results.