NML Technical Journal
Vol. 34, Jan. – June, 1992, pp. 27 - 34

Short Review

OXIDATION PHENOMENA IN CARBON CONTAINING REFRACTORIES AND THEIR PROTECTION

B. CHATTERJEE & K. K. SINGH

National Metallurgical Laboratory, Jamshedpur-831 007, India

This paper highlights the various mechanisms of oxidation reaction of the carbon-bearing refractories in different atmospheres with special emphasis to MgO-C and Al_2O_3-C refractory composites. Kinetics of oxidation of the graphite phase in alumina-carbon refractories have been discussed in detail along with various models. In case of MgO-C refractories, besides oxidation reaction, reduction of MgO by carbon present in the composite and the effect of various atmospheres/gases thereupon have also been discussed.

This paper also discusses the effects of pore-structure, service-temperature, graphite-content, flake-size and purity of graphite and binders used (tar, pitch, resin etc.) on the oxidation behaviour of alumina-carbon and magnesia-carbon refractories. The reaction kinetics at lower temperatures are controlled largely by chemical rate and partly by pore diffusion, while at higher temperature the reaction kinetic is controlled by diffusion of oxidising gases, initially through the stationary surface gas film and then through the pore-structure of the decarbonized layer. The protective measures to be taken to reduce the oxidation of carbon-bearing refractory composites in different atmospheres have also been dealt with. The addition of silicon, magnesium, aluminium, silicon-aluminium alloy, silicon carbide, boron carbide etc. has been found to increase the oxidation resistance and thus resulting in longer lining lives. The paper thus contributes to the understanding of the effects of various parameters on the oxidation reaction in carbon containing refractories and also the remedial measures to be taken to enhance the oxidation resistance.

INTRODUCTION

With the rapid advancement in iron and steel making technologies during the last three decades, carbon containing oxide refractories are finding increased applications for the lining of various furnaces and vessels. This is due to the fact[1] that presence of carbon/graphite makes the refractories highly conducting and thermal shock resistant in addition to its non-wetability towards molten metal and slag. The new generation of carbon containing oxide refractories[2] includes Al_2O_3-C, Al_2O_3-SiC-C, MgO-C, ZrO_2-C etc. Al_2O_3-C refractories find greater use now-a-days in flow control devices i.e. nozzle, stopper, sliding plate, ladle and tundish, shroud etc. for continuous casting of steel. Al_2O_3-SiC-C refractories are used as runners in blast furnaces, slag-line of hot metal, ladles for pretreatment in iron-making, tapping trough of electric arc furnaces, slag-line (EAF) of ladle and top-pouring bricks for continuous casting in steel-making process. MgO-C refractories are used in slag line of L.D. converter, electric arc furnace, secondary refining furnace and ladle for pouring. ZrO_2-C has its limited use only in tundish, shroud and stopper for continuous casting of steel.

In different processes, different atmospheres varying in partial gaseous pressures prevail thereby behaving differently towards the graphite present in the refractories so far the reaction is concerned. The pore-structure and pore-size distribution in the bricks which are functions of the graphite flake-size, compaction and binder-quality play important role in the oxidation of carbon of the refractory body thus weakening the structure. This paper describes the kinetics of reaction of carbon-bearing oxide refractories under the various atmospheric conditions prevailing in the furnaces. It also deals with the mechanisms of inhibition of carbon-oxidation with the introduction of various additions. This helps in understanding the subject and undertaking necessary R&D work for improvements in protection devices so as to enhance lining lives and productivity.

MECHANISM OF OXIDATION

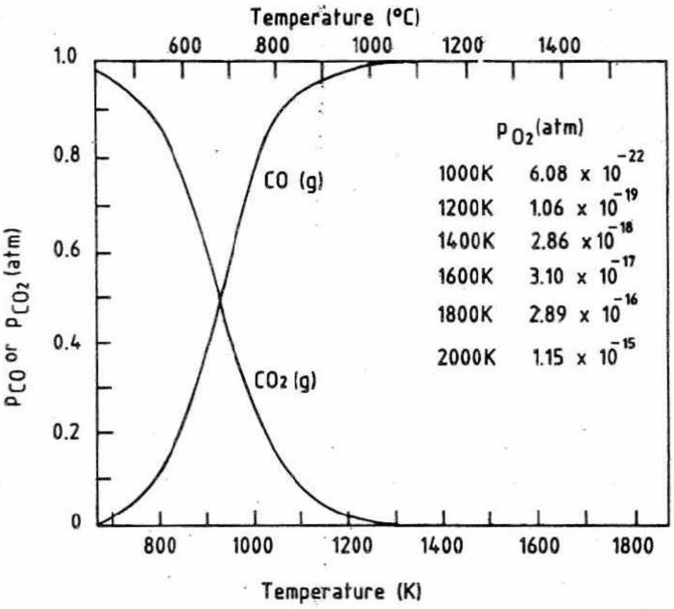

Fig. 1: Change of Partial Pressures of CO (g), CO_2 (g) and O_2 (g) Coexisting with Carbon (Total Pressure is 1 atm)

On being heated in air carbon starts oxidising between 600^0 C and 700^0 C forming CO(g) and CO_2(g). Yamaguchi[3,4] conducted experiments under varying partial pressures of CO, CO_2 & O_2 in co-existence with carbon (Fig. 1) so that the total of the three partial pressures (P_{CO}, P_{CO_2} & P_{O_2}) was 1 atmosphere. Observations made by him reveals that P_{O_2} is insignificant as compared to P_{CO} & P_{CO_2}. With the increase in temperature, P_{CO} increases and above 1000^0C, CO(g) occupies almost the major proportion, P_{CO_2} and P_{O_2} becoming negligibly small. In the presence of carbon, P_{CO} and P_{O_2} are related by the following expression

$$\log P_{CO} = 1/2 \log P_{O_2} + \log K_p \qquad \ldots (1)$$

The value of $\log K_p$ being 9.5 to 7.5 at temperatures between 950^0C and 1750^0C, P_{CO} is expected to become very high along the hot face of refractories when oxygen is injected into the bath. Increased CO gas diffuses around the hot face and fills up the adjacent open pores in the refractories fully, thus making the pressure almost equal to the furnace pressure. It, therefore, leaves the surface of the refractories only to be oxidised.

Consequently, the oxidation of refractories on the back side of the hot face has been observed[4] to proceed with repeated temperature changes. When there is a fall in temperature from $1500/1600^0$C to

600/700^{0}C on the reverse side, there will be an appreciable change in the mass of the gas in the open pores.

Refractories with open pores inhale the air during cooling and exhale the CO gas during heating. This is mainly caused by cyclic changes in temperature. In a study on the effect of pitch and resin binders on the development of porosity in MgO-graphite refractories, Lubaba *et al*[5] showed that the overall porosity of the carbonized composite product for the pitch and resin-bonded systems (2-6%) containing graphite does not vary much, because the decrease in volume due to carbonization does not increase the fired porosity substantially. For the resin-bonded specimens, there is a general tendency for the expansion to decrease from 3.5% to 1% with increasing binder content, the difference in behaviour has been explained by Rand & Mcenaney[6-8]. In the unbonded condition of MgO-C, the composites show a gradual decrease in porosity on heating at 1500^{0}C upto a certain graphite content, after which an increase in porosity occurs.

KINETICS OF OXIDATION

Al_2O_3-C Refractories

Ozgen *et al*[9]. in a study up to 1200^{0}C on the kinetics of oxidation of the graphite phase of alumina/graphite composite bodies with ceramic (clay) bond and fixed graphite content (30% by wt) reported that at low temperature i.e. up to 950^{0}C the kinetics are considered to be controlled partly by gaseous diffusion through the pore-structure and largely by chemical reaction at the active surface of the graphite flakes, whilst at temperatures higher than 950^{0}C the transport of oxygen through the pore-structure of the decarbonised layer controls the rate of reaction. In the high temperature region the reaction kinetics can be expressed by the following equation[10]

$$f(\alpha) = 2k \frac{I}{F} \left(\frac{A}{V}\right)^2 .t \qquad \text{......} (2)$$

where, F is a geometric factor, A, the external surface area of the material and V, the volume of the material. Further study by Ozgen[11] revealed the effects of varying graphite-content (10-50% by wt) by changing the size of the graphite flakes (coarse/fine) and using carbon bond (pitch/PFA) rather than ceramic bond. It has been observed that at a lower temperature i.e. at 750^{0}C the most reactive of all the above materials is the pitch-bonded one although by 800^{0}C the difference in reactivity between this and the 10% clay-bonded fine graphite material is considerably reduced. The order of reactivity at 750^{0}C is summarized below :-

Pitch Carbon Bonded 16% Fine Graphite	Clay-Bonded 10% Fine Graphite	Clay-Bonded 30% & 50% Fine Graphite	PFA Carbon bonded 35.4% Fine Graphite	Clay-Bonded 10% & 30% Coarse Graphite

It is thus established that increasing graphite flake-size greatly decreases the oxidation rate. At high temperature, the reaction is observed to be fully controlled by gaseous diffusion of reactant oxygen across the stagnant gas film at the outside of the sample, and then through the pore-structure of the decarbonised layer. The order of reactivity is found to be maintained for all the above materials except the clay-bonded 10% fine graphite containing material which becomes the most reactive.

MgO-C Refractories

During use at high temperatures in oxidising atmosphere or in vacuum Magnesia-carbon refractories lose weight by oxidation-reduction reaction which causes the deterioration of the refractories[12].

$$MgO(s) + C(s) = Mg(g) + CO(g) \qquad \text{....}(3)$$

Yamaguchi[13] discussed the reaction giving thermodynamic treatment. Tabata *et al*[14] have attempted to give a kinetic treatment by applying a heterogeneous reaction model to oxidation reaction for specimens exposed to the conditions under which MgO reacts with carbon and at temperatures up to 1600°C under a furnace pressure of 0.001 atm. Leonard & Herron[15], in order to measure the reactions between MgO & graphite, concluded that MgO(s) dissociated into Mg(g) and O_2(g).

$$MgO(s) = Mg(g) + 1/2\ O_2(g)$$
$$\text{and } MgO(g) + C(s) = Mg(g) + CO(g) \qquad \dots (4)$$

Cárniglia[16] concluded that the rate-determining step is the diffusion of Mg(g) and CO(g) as product gas through the specimen body to the surface and proposed a diffusion model. Tabata[14], however concluded that the above reaction proceeds very slowly when magnesia does not come into direct contact with carbon. The reaction comprises of two steps (a) chemical reaction at the MgO-C interface and (b) diffusion of Mg(g) and CO(g) as the product gas from inside the specimen to the surface. A simplified reaction model is shown in Fig. 2. Based on this model, the reaction is considered to be of the first order.

Tabata *et al*[14], based on the assumed reaction model and their test results, had drawn a model as given in Fig 3. They concluded from their experiments that under a constant pressure of 0.001 atm, the weight-loss and the texture (change moving inward from the hot surface) of the specimens changed rapidly at 1300°C and above with the increase in heating temperature and the holding-time of the specimen as well. The effects of Mg and O self-diffusion in the MgO crystals for the overall reaction were considered necessary.

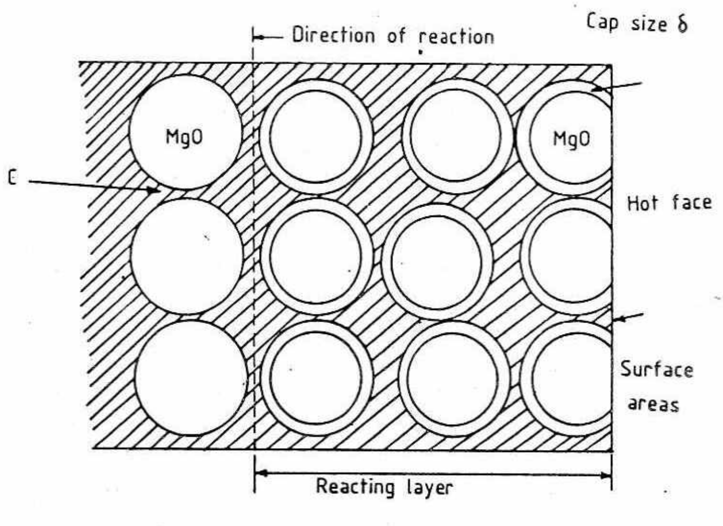

Fig. 2: Reaction Model

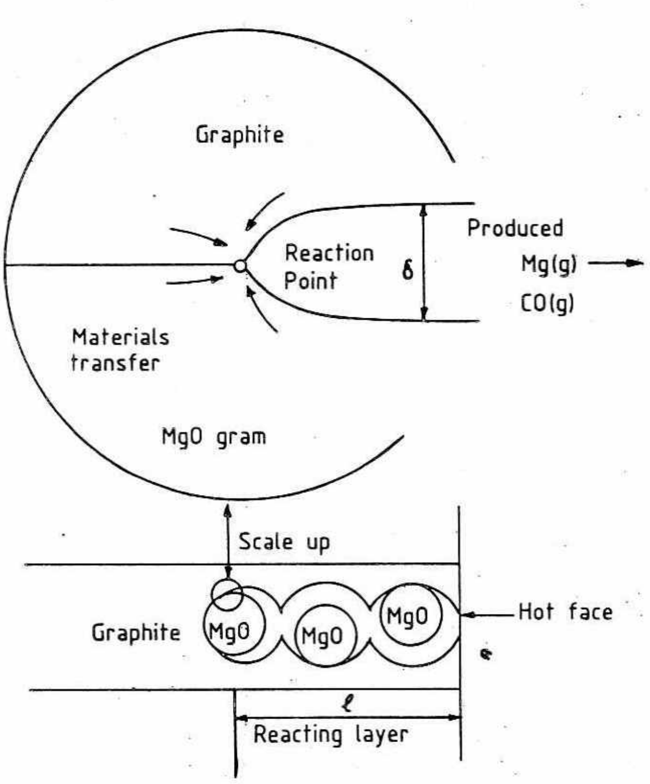

Fig. 3: Model of MgO - C Reaction

ZrO_2-C Refractories

Although very little information is available regarding oxidation behaviour of ZrO_2-C refractories, Yamaguchi[4] made a thermo-chemical study on ZrO_2-C refractories investigating the stability of different condensed phases co-existing with carbon under different O_2, N_2 & CO partial pressures. It has been observed that $ZrO_2(s)$ is stable at temperatures lower than 1520^0C, ZrN(s) being stable in a temperature range from 1520^0C to 1600^0C and ZrC(s) is stable over 1690^0C.

OXIDATION PROTECTION

The principal draw back of carbon-bearing refractories is the susceptibility towards oxidation of the graphite present forming decarbonised layer and thereby making the refractories weak. Several attempts have therefore been made to inhibit the oxidation of carbon by way of adding metals[17] such as Al, Si, Mg or their alloys and carbides[18] such as silicon carbide and boron carbide. These additions were originally considered[19] as oxygen getters but of late these are regarded to react with both oxygen and nitrogen present in the furnace gases and also with carbon, thereby resulting in a decreased permeability at high temperatures and thus reducing oxidation. Laboratory studies indicate that in the case of MgO-C, phase combinations include SiC + Si_2N_2O[20] when Si is added and SiC + Al_4C_3 followed by Mg. Al_2O_4 and Mg_2SiO[20-22] when both Si and Al are added. Most of the additives are meant for high temperature use. Low temperature oxidation which is a problem for the opposite side of the hot face has also been studied by Matsumura *et al*[23] using low melting point mixtures (silicate and borate of sodium).

Oxidation Inhibiting Mechanism

When Al is added to carbon containing refractories[21,24] at each stage, it reacts with the co-existing carbon, CO & N_2 through $Al_4C_3(s)$ & AlN(s) to form $Al_2O_3(s)$

$$\begin{aligned} &2Al(1) + 3CO(g) = Al_2O_3(s) + 3C(s) \\ &2AlN(s) + 3CO(g) = Al_2O_3(s) + N_2(g) + 3C(s) \\ &Al_4C_3(s) + 6CO(g) = 2Al_2O_3(s) + 9C(s) \qquad ...(5) \end{aligned}$$

Therefore, in the above reactions Al, AlN & Al_4C_3 are reduced by CO(g) to C(s) and the carbon-oxidation is thus being inhibited.

Alumina-Carbon Refractories

To prevent oxidation of alumina-carbon refractories, several workers [25,26] reported the additions of metals such as Al, Si or carbides such as SiC and B_4C. Kawakami *et al*[27] investigated the effects of particle size and amount of silicon content on the improvement of oxidation resistance of Al_2O_3-C refractories and compared the effect with SiC addition. It has been observed that the silicon added to Al_2O_3-C composite forms SiC whisker during carbonization which fills up the pores improving the oxidation resistance. Fine grained silicon powder has been found to be more effective than the coarser one. SiC addition has shown improvement in oxidation resistance but not to that extent as compared to silicon addition. Georges *et al*[28-29], Hiroki[30] and Maeda[31] studied the effect of SiC or Si or a mixture of both on oxidation at temperatures upto 1500^0C under O_2, air or CO-CO_2 mixtures between 1 atmosphere and 10-10.5 atmospheres. It has been observed that whether the Al_2O_3-SiC-C composite contains silicon or not, the refractories are moderately protected by silicon carbide against a gas phase, where oxygen pressure is equal to or higher than 10^{-1} atm at 1400°C. For improvement a temperature higher than 1400°C (i.e. about 1500°C) or a lower oxygen pressure will be beneficial. When SiC and Si are simultaneously present, two types of oxidation usually take place.

(a) Passive oxidation after formation of silicon covering layer, through which O_2 must diffuse for the reaction to confirm

(b) Active oxidation[32] with production of SiO which leaves the surface free to continue the reaction. At all gas compositions, the mixture of SiC and Si are found to be effective whereas only SiC proves to be a poor oxidation resistant material

MgO-C Refractories

Several researchers[25,33-37] have worked on the effect of metal addition on the oxidation behaviour of MgO-C bricks. Watanabe *et al*[38] in a detailed study on the effect of addition of some selected metals (Al,Mg) and alloys (Al-Mg-Ca-Si) observed the behaviour in graphite-metal and graphite-metal-MgO systems in Ar and CO atmospheres. It has been found that in Ar atmosphere[39], the crystal phases of Al and Si change to Al_4C_3 and SiC while Mg and Ca have no change in crystal phase, easily remaining in the vapour phase. Mg volatility is less with Ca-Si-Mg alloy than with Al-Mg alloy. Considering that the inside of the composite has a CO atmosphere, Al and Si form Al_4C_3 and SiC at lower temperatures. The change in crystal phases is thought to be from carbides into oxides i.e. Al_2O_3 and SiO_2. In case of Mg and Ca, the change takes place directly into the oxides i.e. MgO and CaO. The addition of the metals is considered to act as a reducing agent towards CO thus inhibiting carbon oxidation. Oxidation resistance is said to be improved by the addition of Al and Si by way of compacting the structure by crystal size expansion. Mg and Ca are found to form a secondary dense layer and thus improving the oxidation resistance. Matsumura *et al*[40] in a study to find out the suitability of Al, Al-Mg and Al-Si as additives for low temperature use, have found that oxidation resistance of Al-Mg containing bricks at 700°C is better than the other two, while they do not find any appreciable difference in oxidation resistance amongst the three kinds of metal containing bricks at 1000°C. They thought that this behaviour of Al-Mg may be due to its melting at 450°C and penetrating into the voids of a brick, where Mg vapour is generated, thereby preventing the oxidation of carbon. Al melts at 660°C and becomes Al_2O_3 at 700°C as per Yamaguchi[41] according to the reaction

$$Al_4C_3 + 6CO = 2Al_2O_3 + 9C \quad .... \ (6)$$

where oxidation is prevented by precipitation of carbon and the formation of Al_2O_3 prevents the penetration of Al liquid into the voids of a brick.

Yamaguchi[41], Kyoden *et al*[42] and Watanabe *et al*[17,37] state that these metals become Al_4C_3 and finally MgO. Al_2O_3.

Nagai *et al*[43] while studying the effect of Al addition under vacuum (0.2 torr) observed that magnesia-carbon bricks start to lose weight appreciably with the increase in Al content from about 900°C due to the reduction of MgO by Al where Al is transformed into MgO. Al_2O_3 spinel and is thought to cause the weight loss above 900°C with the resultant Mg vapour being liberated. However, Matsumura *et al*[29, 44] and Kiryu *et al* [45] observed that under vacuum and while in use in R.H. degassing vessel, the addition of Al alloys in increased amount upto a certain limit reduces the oxidation of MgO-C bricks.

The effect of impurities on the content of Al in MgO-C bricks was studied by Ishi *et al*[46] where it has been found that precipitation of metals, transfer of impurities towards the surface of magnesia grains and densification of grains occur as a result of the decrease of P_{O_2} at the surface of magnesia grains thus reducing the oxidation of carbon.

CONCLUSIONS

The following conclusions can be drawn :-

- The kinetics of oxidation of carbon-bearing oxide refractories at less than 950°C are controlled partly by the gaseous diffusion through the pore-structure of the refractory composite and mostly by the chemical reaction at the active surface of graphite flakes, whereas at temperatures higher than this, the reaction rate is controlled by the transport of oxygen through the pore-structure of the decarbonised layer.
- Oxidation depends on the nature of the atmosphere prevailing in the furnace.

- The pore-structure of the refractory oxide-graphite composite is dependent on the size of the graphite flake, graphite content and the binder content as well as on the nature of the binder.
- Oxidation of carbon containing refractories is controlled by the condensed phases present in the composite body.
- It is possible to inhibit the oxidation rate by adding metals like Al, Si & carbides like SiC & B_4C. Out of all these, alloys of Al & Mg are considered to be more effective than the others.

ACKNOWLEDGEMENT

The authors wish to thank the Director, National Metallurgical Laboratory for his kind permission to publish this paper. They also express their gratitude to Mr. K.N.Gupta, Head of FRP Division for showing keen interest in this work.

REFERENCES

1. **C.F. Cooper**, Refractories Journal, **6**, 11, 1980.
2. **K.K. Singh, K.C. Ray, M.K. Paria, B. Chatterjee** and **M.R.K. Rao**, Proc. of Int. Sem. on "Recent trends in refractories for steel making", Jamshedpur, India, pp 165-175, 1986.
3. **A. Yamaguchi**, Taikabutsu (Japanese), **35(7)**, 365, 1983.
4. **A. Yamaguchi**, Taikabutsu Overseas, **7(1)**, 4, 1987.
5. **N.C. Lubaba, B. Rand** and **N.H. Brett**, Br. Ceram. Trans. & Journal, **87**, 164, 1988.
6. **B. Rand** and **B. Mcenaney**, Br. Ceram. Trans. & Journal, **84**, 157, 1985.
7. **B. Mcenaney** and **B. Rand**, Br. Ceram. Trans. & Journal, **84**, 193, 1985.
8. **N.C. Lubaba, B. Rand** and **N.H. Brett**, Br. Ceram. Trans. & Journal, **87**, 158, 1988.
9. **O.S. Ozgen** and **B.Rand**, Br. Ceram. Trans. & Journal, **84**, 70, 1985.
10. **J. Szekeley, J.W. Evans and S.V. Sohn**, Academic Press, N.Y., 1976.
11. **O.S. Ozgen** and **B. Rand**, Br. Ceram. Trans. & Journal, **84**, 213, 1985.
12. **H.M. Mikami** and **J.R. Martinet**, Refractories Journal, **5**, 25, 1979.
13. **A. Yamaguchi**, Taikabutsu Overseas, **4**, 32, 1986.
14. **K. Tabata, H. Nishio** and **K. Itoh**, Taikabutsu Overseas, **8(4)**, 3, 1988.
15. **R.J. Leonard** and **R.H. Herron**, J. Amer. Ceram. Soc., **55(1)**, 16, 1972.
16. **S.C. Carniglia**, Ceramic Bulletin, **52(2)**, 160, 1973.
17. **A. Watanabe, H. Takahashi, T. Matumoto** and **M. Takahashi**, Taikabutsu, **36(2)**, 83, 1984.
18. **F. Kitani, T. Takahashi, M. Hanmyou, H. Ogura, S. Yoshino** and **T. Fujiwara**, Taikabutsu, **35(1)**, 3, 1983.
19. **P.L. Smith, J. Liddle** and **J. White**, Br. Ceram. Trans. & Journal, **84**, 62, 1985.
20. **H. Naefe, M. Seeger** and **D. Stosser**, 27th Int. Conf. on Refractories, Aachen, pp. 193, 1984.
21. **A. Watanabe, H. Takahashi, T. Matsuki** and **M. Takahashi**, 1st Int. Conf. on Refractories, Tokyo, pp. 125, 1984.
22. **J. Leveque, P. Mairesse** and **R.D. Whiteley**, 27th Int. Conf. on Refractories, Aachen, pp. 109, 1984.
23. **T. Matsumura, T. Kitani** and **T. Hokii**, Taikabutsu Overseas, **8(4)**, 27, 1988.
24. **A. Yamaguchi**, Taikabutsu Overseas, **7(2)**, 11, 1987.
25. **A. Yamaguchi**, Taikabutsu, **35(11)**, 617, 1983.
26. **T. Takahashi**, Taikabutsu, **35(4)**, 157, 1983.
27. **T. Kawakami, K. Aratani, S. Hasegawa** and **T. Sato**, Taikabutsu Overseas, **8(3)**, 18, 1988.
28. **A. Georges, B. Courrier** and **C. Gleitzerl**, Br. Ceram. Trans. & Journal, **86**, 124, 1987.
29. Ibid, Br. Ceram. Trans. & Journal, **86**, 146, 1987.
30. **N. Hiroki** and **A. Takahashi**, Taikabutsu Overseas, **7(2)**, 37, 1987.
31. **M. Maeda, K. Nakamura** and **M. Yamada**, J. Amer. Ceram. Soc., **72(3)**, 512, 1989.
32. **C. Wagner**, J. Applied Physics, **29**, 1295, 1958.
33. **Y. Miyagawa, F. Hoshi, K. Fuji, D. Katase, K. Hiragushi** and **H. Yamamoto**, Taikabutsu Overseas, **6(1)**, 16, 1986.
34. **A. Yamaguchi**, Taikabutsu, **38(4)**, 232, 1986.

35. **H. Kyoden, H. Nishio, K. Itoh** and **S. Hotta**, Taikabutsu, **38(4)**, 242, 1986.

36. **H. Endo**, Taikabutsu, **38(3)**, 178, 1986.

37. **A. Watanabe, H. Takahashi, T. Matumoto** and **M. Takahashi**, Taikabutsu, **36(12)**, 680, 1984.

38. **A. Watanabe, H. Takahashi, S. Takanaga, N. Goto, K. Anan** and **M. Uchida**, Taikabutsu Overseas, **7(2)**, 17, 1987.

39. **T. Tada, Y. Kakimoto, M. Isomoto** and **M. Matsushima**, Taikabutsu Overseas, **10(3)**, 148, 1990.

40. **T. Matsumura, S. Uto, K. Hosokawa** and **N. Geji**, Taikabutsu Overseas, **8(4)**, 24, 1988.

41. **A. Yamaguchi**, Taikabutsu, **38(8)**, 506, 1986.

42. **H. Kyoden, H. Mishio, K. Itoh** and **S. Hotta**, Taikabutsu, **38(4)**, 284, 1986.

43. **B. Nagai, T. Matsumura, S. Uto, T. Isobe** and **H. Ohsaki**, Taikabutsu Overseas, **6(2)**, 51, 1986.

44. **T. Matsumura, S. Uto, H. Osaki** and **T. Isobe**, Taikabutsu Overseas, **7(4)**, 46, 1987.

45. **Y. Kiryu, H. Yay, S. Aso, S. Uto, T. Isobe** and **T. Matsumura**, Taikabutsu Overseas, **7(4)**, 50, 1987.

46. **H. Ishi, I. Tsuchiya, Y. Oguchi, T. Kawakami** and **H. Takahashi**, Taikabutsu Overseas, **10(1)**, 3, 1990.