In-situ high temperature X-ray diffraction study of Fe/Al$_2$O$_3$ interface reactions

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In-situ experiments on the Fe/Al$_2$O$_3$ interface reaction were carried out with a high temperature X-ray diffractometer capable of measuring the X-ray diffraction pattern in 1–4s, using an imaging plate. The kinetic formation processes of the interface reaction layer were measured in short-period exposure experiments using the apparatus. The time-temperature phase diagram of Fe/Al$_2$O$_3$ in air was determined. FeAl$_2$O$_4$ was formed at the Fe/Al$_2$O$_3$ interface between 1595 K and 1675 K in air. The formation of FeAl$_2$O$_4$ obeyed the parabolic rate law. The value of the activation energy suggests that the diffusion of Al into FeAl$_2$O$_4$ controls the rate of formation. The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, compressive strain caused by FeAl$_2$O$_4$ occurs on Al$_2$O$_3$. © *1999 Kluwer Academic Publishers*

1. Introduction

It is important that the properties of the metal-oxide interface for the production of MOS devices are investigated. Al$_2$O$_3$ is a typical oxide ceramic, and it is expected that Fe exhibits strong activity at the metal-oxide interface [1]. Therefore, particular attention is paid to the Fe/Al$_2$O$_3$ system.

The interface reactions of Fe/Al$_2$O$_3$ have been investigated by several researchers [1–5]. The investigations have concentrated on carrying out measurements of microstructures and phases after the reaction. However, *in-situ* experiments are necessary to reveal the elementary reaction processes in detail. In such experiments, X-ray diffraction methods have the advantage of being able to observe crystal structure changes during the Fe/Al$_2$O$_3$ interface reaction.

In this paper, *in-situ* experiments on the Fe/Al$_2$O$_3$ interface reaction are described. These experiments were carried out with a high temperature X-ray diffractometer [6, 7], which is capable of measuring the X-ray diffraction pattern in 1–4s using an imaging plate to elucidate (1) the elementary formation processes of the reaction layer, (2) the relationship between time and temperature during phase transformation, (3) the reaction control factor based on the activation energy of the reaction layer, and (4) the thermal stress relationship between the reaction layer and the substrate (Al$_2$O$_3$).

2. Experimental procedure

Polycrystalline α-Al$_2$O$_3$ (purity 99.5%; Toshiba Corporation) was cut into pieces measuring 20 mm $\times$ 10 mm $\times$ 0.5 mm. These were polished with a diamond whetstone and cleaned in acetone for use as substrates. An Fe (purity 99.99%) thin film was deposited on the substrate by means of vacuum deposition at 1×10^{-3} Pa. The thickness of the thin film was 0.2 μm.

Fig. 1 shows the schematic of a high temperature X-ray diffractometer [6, 7], which consists of a Seemann-Bohlin camera [8] and an imaging plate (IP) [9]. Because the Seemann-Bohlin camera is a parafocusing camera that produces high intensity diffraction lines and because the two-dimensional IP has good X-ray sensitivity, this high temperature system can record complete diffraction patterns in 1–4s [6, 7]. Using Co X-rays at 50 kV and 160 mA filtered by an Fe filter, a peak intensity of approximately 5000 counts is obtained from the (104) reflection of Al$_2$O$_3$, using a 4s exposure.

The samples were heated from room temperature to between 1574 K and 1675 K at a rate of 60 K/min, held at that temperature for 1 h, and then cooled to room temperature. This heating process was performed in air. The *in-situ* measurements were carried out with repeated exposures (exposure time: 4s) during the heating process.

3. Results and discussion
3.1. Formation of reaction layer

Fe (α-Fe) changed to Fe$_2$O$_3$ (α-Fe$_2$O$_3$) during heating in air and only Fe$_2$O$_3$ existed at 1574 K. Fig. 2 shows the X-ray diffraction patterns of Fe/Al$_2$O$_3$ held at 1595 K for 1 h in air. There are dead angles at the center of the diffraction patterns because the apparatus uses two sheets of IP. Fe$_2$O$_3$ was found at the middle of heating, and FeAl$_2$O$_4$ was formed in approximately 40 min at this temperature. Fig. 3 shows the X-ray diffraction patterns of Fe/Al$_2$O$_3$ held at 1675 K for 1 h in air. The intensity of the Fe$_2$O$_3$ diffraction peaks diminished with time, and all Fe$_2$O$_3$ changed to FeAl$_2$O$_4$ after about 1 h.
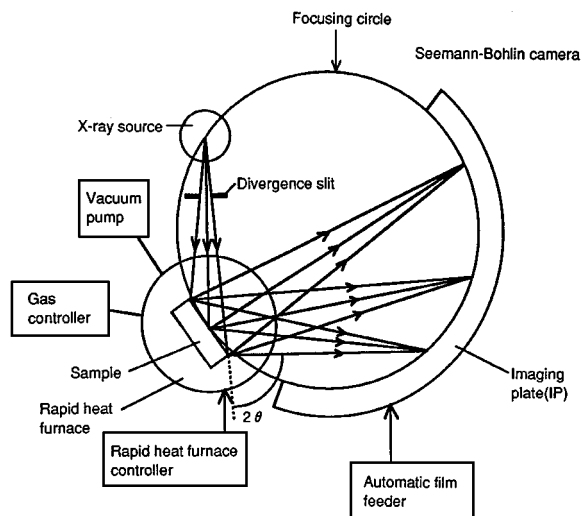
Figure 1 Schematic of the high temperature X-ray diffractometer [6, 7].

In-situ experiments were carried out at 1634 K and 1656 K in air. Fe_2O_3 and $FeAl_2O_4$ were formed in the same way as above. Fig. 4 shows a time-temperature phase diagram of Fe/Al_2O_3 in air. Note that these results were obtained under the experimental conditions in this work.

The above observations suggest that Fe_2O_3 is formed by the reaction and bonding between Fe and oxygen in air, while $FeAl_2O_4$ is formed by the reaction between Fe_2O_3 and Al_2O_3 at the interface, and the reaction formulas are $Fe + (3/4)O_2$ (in air) $\rightarrow (1/2)Fe_2O_3$ and $(1/2)Fe_2O_3 + Al_2O_3 \rightarrow FeAl_2O_4 + (1/4)O_2$ (in air). A model of these reactions is shown in Fig. 5. The diffusion path from Al_2O_3 to Fe_2O_3 is thought to be $Al_2O_3 \rightarrow FeAl_2O_4 \rightarrow Fe_2O_3$ on the basis of the phase diagram of Fe-Al-O reported by Trumble [10], where Fe_2O_3 is formed by the reaction between Fe and $(3/4)O_2$ (in air).

Table I shows a comparison of the experimental results obtained by us and by others. There are differences in the formed phases, such as whether an interlayer is formed or not, whether a high or a low vacuum is used, and whether pressing is used or not. When the interlayer was FeO or Fe + FeO compound, $Fe(Fe, Al)_2O_4$ was formed, according to Sakata *et al.* [5]. In this work, Fe that was oxidized in air changed to Fe_2O_3, which reacted with Al_2O_3 to form $FeAl_2O_4$. Therefore, it is possible that the diffusion path of this work is different from that of the work by Sakata *et al*. The interlayer depends on the atmosphere and the presence of FeO in the reaction system.

3.2. Activation energy of $FeAl_2O_4$ growth

In order to determine the growth rate of the $FeAl_2O_4$ layer at 1634 K, 1656 K, and 1675 K from the time history of the integrated intensity of (220) reflection of $FeAl_2O_4$, the time history of the thickness of the $FeAl_2O_4$ layer at each temperature was calculated. It was assumed that the thickness of the $FeAl_2O_4$ layer, formed from all of the deposited Fe, corresponds to the integrated intensity of (220) reflection of $FeAl_2O_4$ when the reaction layer of $FeAl_2O_4$ was completely formed. However, in this calculation, the effects of thermal expansion were ignored because the values were compared with those obtained in thermal treatment experiments performed by other researchers. The relationship between the square of the thickness (x) of $FeAl_2O_4$ layers at each temperature and time (t) is shown in Fig. 6. It is apparent that the parabolic rate law ($x^2 = Kt$; K: rate constant) [11] is upheld.

Because K is proportional to the diffusion coefficient,

$$\log K = 0.4343\,(-Q/RT) + A$$

where 0.4343 is the conversion constant from natural logarithm to common logarithm, Q is the activation energy, R is the gas constant, T is the temperature, and A
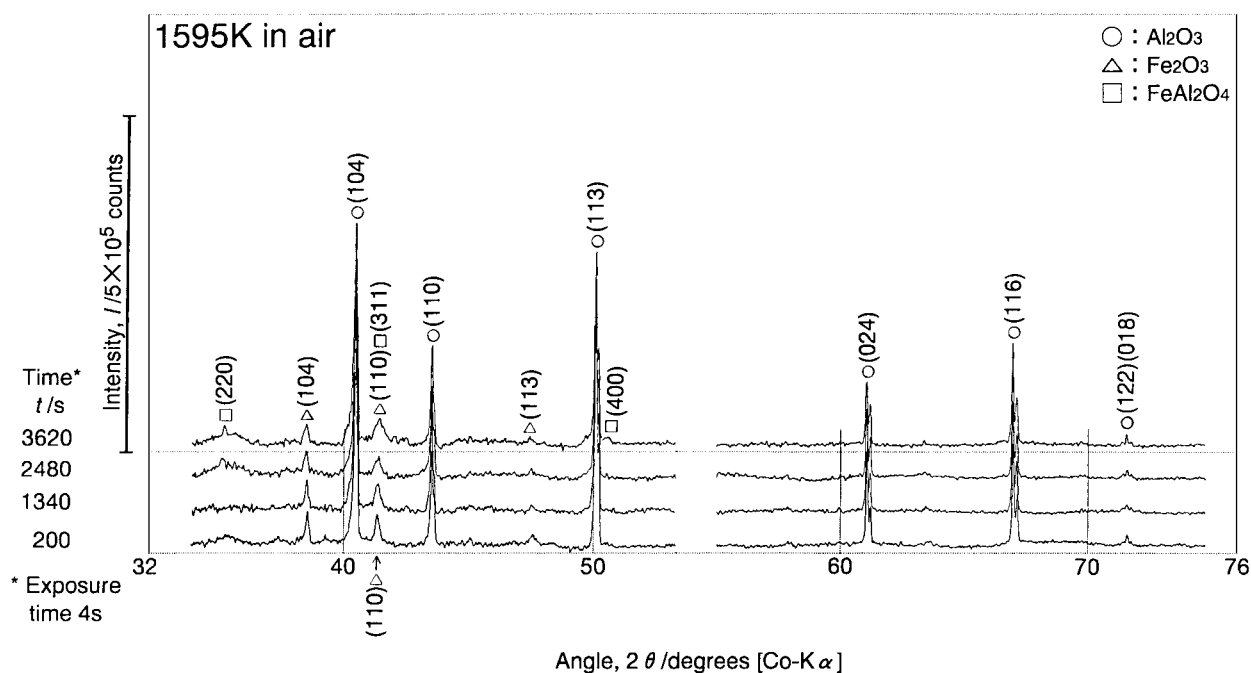

Figure 2 X-ray diffraction patterns of Fe/Al_2O_3 held at 1595 K for 1 h in air. Fe_2O_3 was present at the beginning, and $FeAl_2O_4$ was formed in approximately 40 min.

TABLE I Comparison of the experimental results obtained from this work and other works

Researcher	System	Experimental condition	Phase	Reference
Okamoto et al.	Steel/Cu/Al$_2$O$_3$	1.3 kPa (low vacuum) 1473 K 30 min	FeAl$_2$O$_4$	[2]
Suganuma et al.	Fe/(60 vol% Fe + 40 vol% Al$_2$O$_3$)/Al$_2$O$_3$	1573 K 2.1 GPa (press) 30 min	Fe + Al$_2$O$_3$	[3]
Naka and Okamoto	Steel/Cu/Al$_2$O$_3$	0.4–6.7 kPa (low vacuum) 1393–1573 K 30 min	FeAl$_2$O$_4$	[4]
Sakata et al.	Fe/FeO/Al$_2$O$_3$ Fe/(Fe + FeO)/Al$_2$O$_3$	1×10^{-3} Pa (vacuum) 1450 K 29.3 MPa (press) 10 h	Fe (Fe, Al)$_2$O$_4$	[5]
Colaianni et al.	Fe/Al$_2$O$_3$/Mo (110)	1×10^{-8} Pa (vacuum) 900–1200 K 1 s	Fe + Al$_2$O$_3$	[1]
		1×10^{-8} Pa (vacuum) 900–1200 K 1 s [after exposure of oxigen at 90 K]	Fe oxide + Al$_2$O$_3$	
This work	Fe/Al$_2$O$_3$	Air 1595–1675 K 1 h	FeAl$_2$O$_4$	
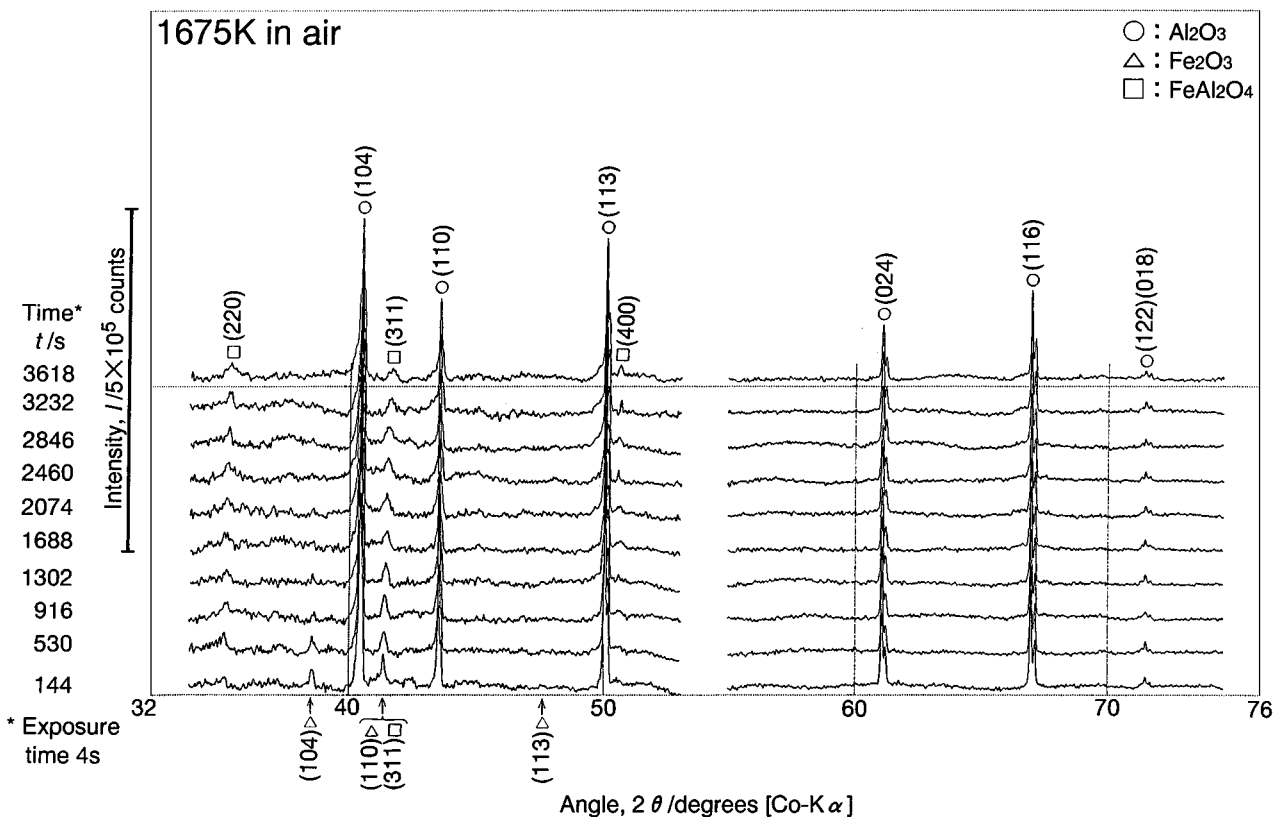
Figure 3 X-ray diffraction patterns of Fe/Al$_2$O$_3$ held at 1675 K for 1 h in air. All Fe$_2$O$_3$ changed to FeAl$_2$O$_4$ after about 1 h.

is a constant. Q is obtained from the gradient of log K and $1/T$. Fig. 7 shows the relationship between log K and $1/T$ for the growth of FeAl$_2$O$_4$ in our experiments. The value of Q was 458 kJ/mol. According to the experiments of Halloran and Bowen [12], the Q value for Fe diffusion in FeAl$_2$O$_4$ in an atmosphere of CO$_2$/CO = 0.1 was 273 kJ/mol. The Q value for FeAl$_2$O$_4$ layer growth in experiments of carbon steel/Cu/Al$_2$O$_3$ in an atmosphere of 400 Pa conducted by Naka and Okamoto [4] was 269 kJ/mol. These previously reported Q values differ from our value, because our work was performed in air. When Paladino and Kingery [13] measured Al diffusion into Al$_2$O$_3$ in air, the Q value was 477 kJ/mol, which is close to our value. It can therefore be inferred that Al diffusion into FeAl$_2$O$_4$ controls the reaction rate when the sample is held at a high temperature in air.
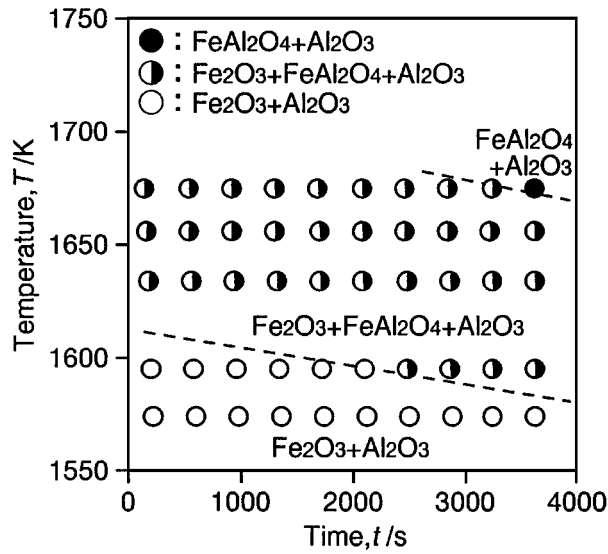
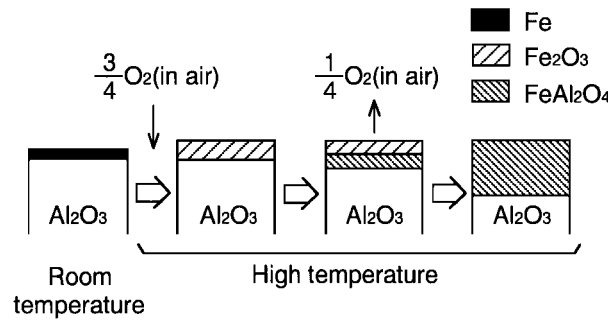*Figure 4* Time-temperature phase diagram of Fe/Al_2O_3 in air obtained in this work.

Figure 5 Formation model of $FeAl_2O_4$ at Fe/Al_2O_3 interface in air. The reaction formulas are Fe + (3/4)O_2 (in air) $\rightarrow$ (1/2)Fe_2O_3 and (1/2)Fe_2O_3 + Al_2O_3 $\rightarrow$ $FeAl_2O_4$ + (1/4)O_2 (in air).
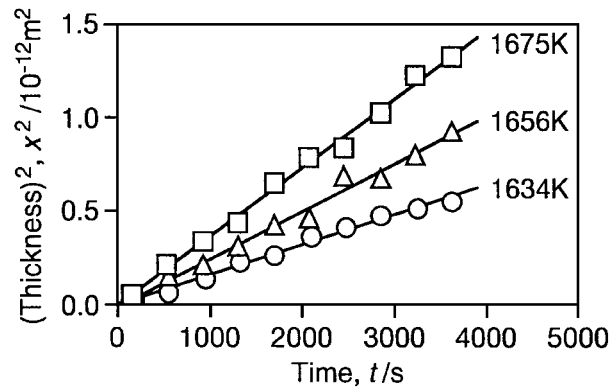

Figure 6 Relationship between the square of thickness (x) of $FeAl_2O_4$ layers at each temperature and time (t). The parabolic rate law is upheld.

3.3. Strain at interfaces

The average strains around the interfaces were verified, taking into account the reported values of the thermal expansion coefficients. Table II shows the thermal expansion coefficients evaluated from the lattice constants of Al_2O_3, Fe, Fe_2O_3, and $FeAl_2O_4$, which were calculated from the X-ray diffraction angles at different temperatures. The reference values [14–17] are shown for comparison. The value for $FeAl_2O_4$ is close to those for Fe and Fe_2O_3 and is larger than that for Al_2O_3.

TABLE II Thermal expansion coefficients evaluated from the lattice constants of Al_2O_3, Fe, Fe_2O_3 and $FeAl_2O_4$, which were calculated from the X-ray diffraction patterns at different temperatures. Reference values [14–17] are shown for comparison

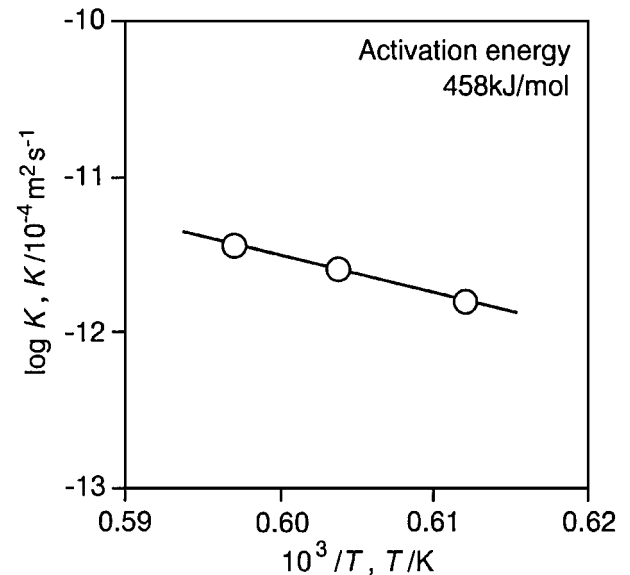| Material (system)	Thermal expansion coefficient ($\times 10^{-4}$ /K)		
	a	c	Reference
α-Al_2O_3 (Hexagonal)	0.08	0.09	a:0.08, c:0.09 [14]
α-Fe (Cubic)	0.14	—	a:0.12 [15]
α-Fe_2O_3 (Rhombohedral)	0.12	0.10	a:0.12, c:0.07 [16]
$FeAl_2O_4$ (Cubic)	0.13	—	a:0.09 [17]

Figure 7 Relationship between log K and $1/T$ for the growth of $FeAl_2O_4$. Activation energy was estimated as 458 kJ/mol.

It is thought that as a sample cools to room temperature, compressive strain caused by $FeAl_2O_4$ occurs on Al_2O_3.

4. Conclusions

In-situ high temperature X-ray diffraction experiments were carried out on the Fe/Al_2O_3 interface reaction. The following conclusions were reached:

1. The kinetic formation processes of the interface reaction layer were measured by short-period exposure experiments using a high temperature X-ray diffractometer.

2. The time-temperature phase diagram of Fe/Al_2O_3 in air was determined. $FeAl_2O_4$ was formed at the Fe/Al_2O_3 interface between 1595 K and 1675 K in air. The elementary reaction processes were Fe + (3/4)O_2 (in air) $\rightarrow$ (1/2)Fe_2O_3 and (1/2)Fe_2O_3 + Al_2O_3 $\rightarrow$ $FeAl_2O_4$ + (1/4)O_2 (in air). Note that these results were obtained under the experimental conditions in this work.

3. The formation of $FeAl_2O_4$ obeyed the parabolic rate law. The activation energy was 458 kJ/mol. This

value suggests that the diffusion of Al into $FeAl_2O_4$ controls the rate of formation.

4. The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, Al_2O_3 is compressed by $FeAl_2O_4$ at the interface.

Acknowledgements

References

1. M. L. COLAIANNI, P. J. CHEN and J. T. YATES, JR., *Surf. Sci.* **238** (1990) 13.
2. I. OKAMOTO, M. NAKA, K. ASAMI and K. HASHIMOTO, *Trans. JWRI* **11** (1982) 131.
3. K. SUGANUMA, T. OKAMOTO, M. SHIMADA and M. KOIZUMI, *J. Am. Ceram. Soc.* **66** (1983) C-117.
4. M. NAKA and I. OKAMOTO, Quart. *J. Jpn. Welding Soc.* **3** (1985) 702.
5. K. SAKATA, K. HONMA, K. OGAWA, O. WATANABE and K. NII, *J. Mater. Sci.* **21** (1986) 4463.
6. T. FUJIMURA and S.-I. TANAKA, *Acta Mater.* **45** (1997) 4917.
7. *Idem*. *Acta Mater.* **46** (1998) 3057.
8. H. P. KLUG and L. E. ALEXANDER, in "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" (John Wiley & Sons, Inc., New York, 1954) p. 211.
9. Y. AMEMIYA, S. KISHIMOTO, T. MATSUSHITA, Y. SATOW and M. ANDO, *Rev. Sci. Instrum.* **60** (1989) 1552.
10. K. P. TRUMBLE, *Acta Metall. Mater.* **40** (1992) S105.
11. F. S. PETTIT, E. H. RANDKLEV and E. J. FELTEN, *J. Am. Ceram. Soc.* **49** (1966) 199.
12. J. W. HALLORAN and H. K. BOWEN, *J. Am. Ceram. Soc.* **63** (1980) 58.
13. A. E. PALADINO and W. D. KINGERY, *J. Chem. Phys.* **37** (1962) 957.
14. I. E. REIMANIS, K. P. TRUMBLE, K. A. ROGERS and B. J. DALGLEISH, *J. Am. Ceram. Soc.* **80** (1997) 424.
15. Y. ISHIDA, J. WANG and T. SUGA, *Acta Metall. Mater.* **40** (1992) S289.
16. L. PETRAS, A. PREISINGER and K. MEREITER, *Mater. Sci. Forum* **228–231** (1996) 393.
17. D. TAYLOR, *Br. Ceram. Trans. J.* **84** (1985) 121.