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EFFECTS OF Fe_2O_3 ADDITION ON THE NITRIDATION OF SILICON POWDER

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16. Abstract

The reaction of silicon powder and nitrogen was studied in the range of 1300-1400°C. When an addition of Fe_2O_3 was more than 0.8wt%, the reaction was linear and compared to samples with no Fe_2O_3, the reaction velocity increased 5-?0 times. The reactions were mediated by the process of peeling and cracking in a thin layer of Si_2N_4 formed on the silicon particles or on the surface of the Fe-Si melts. As the addition of Fe_2O_3 increased, the rection activation energy for highly pure samples decreased. Fe_2O_3 which exceeded the Si_3N_4 solubility limits was finally converted to d-Fe.

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The reaction of silicon powder (purity: 99%, average particle /45*
size 15 μm) and nitrogen (O_2<0.5 ppm, dew point<-60°C) was studied
in the range of 1300-1400°C. When the addition of Fe_2O_3 to the
silicon was more than 0.8 wt%, the progress of the reaction was
linear and compared to samples with no addition the reaction veloc-
ity increased 5-10 times.

The reactions were mediated by the process of peeling and
cracking in the thin layer of Si_2N_4 formed either on the silicon
particles or on the surface of the Fe-Si melts or by the process
of dissolution eduction from the Fe-Si solution. As the addition
of Fe_2O_3 to the silicon increased, the reaction activation energy
for highly pure samples decreased from about 160 kcal/mol to about
133 kcal/mol. Fe_2O_3 which exceeded the Si_3N_4 solubility limits
was finally converted to α-Fe. The solubility limit of Fe in
Si_3N_4 was in the range of 0.24-0.49 at% at 1400°C.

1. Background   /46

There has been much research carried out concerning the re-
reaction of silicon powder and nitrogen. It is known that certain
impurities inside the silicon powder used for nitridation acceler-
ate the nitridation reaction. Among these impurities, iron
compounds are very effective [1, 2]. This kind of research is
being conducted continuously, but there has been no research dis-
cussing the velocity of the reaction [3, 4].

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* Numbers in the margin indicate pagination in the foreign text.

Factors other than impurities in the silicon have been reported as affecting speed of nitridation, for example minute quantities of oxygen in the nitrogen atmosphere [5-10]. For this experiment we established a comparatively pure nitrogen atmosphere (O_2<0.5 ppm, dew point<-60°C), and studied the effects of Fe_2O_3 addition, chiefly in respect to velocity [11-14]. The results have been integrated and reported below.

Many additives have been reported effective in the acceleration of nitridation. The reason we have chosen iron, which is easy to combine by a silicon pulverization process, is that it is the most universal of powders for industrial use, and an oxide, because minute amounts of powder are easy to procure as reagents.

2. Experiments

2.1 Materials

The silicon powder used in the experiments was 99.99% pure and was from the Takajundo Chemical Co., Ltd. Lump silicon was pulverized with a stainless steel ball mill. The powder from which impurities had been removed by acid treatment had average particle size of about 15 µm, and the chief impurity was iron. 0.007 wt% was detected by X-ray fluorescence analysis. The powder was also analyzed for aluminum and calcium, but none was detected. The powder was not analyzed for oxygen content. The particle distribution was measured by the Omnicon Pattern Analysis System of the Shimazu Manufacturing Co., Ltd. The results are shown in table 1.

The nitrogen used for the reactions was obtained from a gun of highly pure liquid oxygen by evaporation (O_2<0.5 ppm, dew point<-60°C). The Fe_2O_3 used as additive was of special quality with particle size below 0.5 µm.

2.2 Nitridation

One gram of the silicon powder and Fe_2O_3 was precision weighed and placed in an agate mortar. The mixture was moistened with 1 or 2 drops of distilled water and after mixing with care so as not to pulverize further, was shaped into a disc using a 15 mm steel mold. After drying a day and a night, the disc was reweighed and the experiments carried out. The packing rate of the powder was about 60%, and the thickness of the sample was about 4 mm.

TABLE 1. SIZE DISTRIBUTION OF SILICON POWDER USED IN THE EXPERIMENTS

Diameter of particle (/mm)	Number of oversize particle	Percent (wt%)
Total	8288	100.0
0.5	5739	100.0
1.0	4821	99.97
2.0	2948	99.56
3.0	2056	98.7
4.0	1474	97.0
5.0	1046	94.5
6.0	811	92.0
7.0	616	88.5
8.0	442	83.8
9.0	354	80.3
10	288	76.6
12	192	68.4
14	127	59.1
16.	83	49.5
18	56	41.6
20	40	34.6
22	30	28.5
24	22	22.2

After drying, the sample was placed in an alumina ($Al_2O_3 > 99\%$) crucible and lowered into a vertical tubular furnace, the core of which is an alumina tube. A thermobalance was applied continuously. After the atmospheric nitrogen had been displaced, the temperature was raised about 150°C/h until the determined temperature had been reached while injecting 500 cc of nitrogen per minute. When the temperature was reached, it was maintained, and the increase in weight and the temperature

was recorded. The experimental temperatures were near 1300, 1350, /47 and 1400°C. The amount of additive was chosen after consulting Suzuki's results [2], and were by wt% of the unreacted mixture 0, 0.8, 1.6, 3.2 and 6.2.
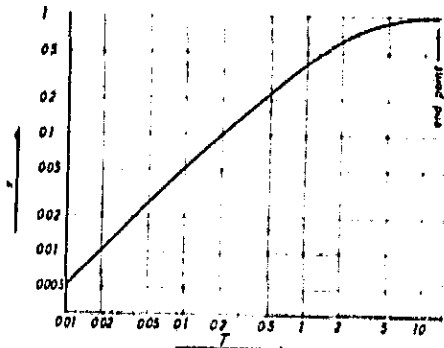
3. Results

3.1 Rection Velocity

The results concerning temperature and reaction velocity are in tables 2-1 through 2-5 for each Fe_2O_3 addition. The items concerning the reaction are not from the beginning because the data are from after the temperature inside the furnace had become regular. The reaction velocity A (μm/h) is from the increase in weight measured by the thermobalance, which is the change in the speed of decrease in the size of silicon particles. This was done as previously reported [12], but this time, dead time was not calculated. $\Delta T/\Delta t$ were claculated separetely for 5% reaction range units for the value of A. The relationship formula necessary for this conversion is 12

Fig. 1. Calculated relation between x and T in Eq. (1) for the silicon powder in Table 1. End point shows the end of the reaction.

$$x = \sum_{n=1}^{m}\{1-(1-T/R_n)^3\}\alpha_n \qquad (1)$$

x: silicon after reaction, the weight as opposed to the amount initial silicon

m: number of particle layers

T: decrease in size of silicon particles, the thickness of silicon after reaction

R_n: the average size of particles n

n: the weight of particles n

The relationship between x and T according to this formula are shown in figure 1.

The value of A in table 2, i.e. the calculation of $\Delta T/\Delta t$, was calculated by contrasting the amount of silicon in the sample

TABLE 2-1. CALCULATED REACTION RATE, A m/h.   ADDED Fe_2O_3: 0%

Reaction temperature (°C)		Range of reaction (%)	JT (μm)	Jt (h)	A (μm/h)
1350	1357	10-15	0.114	6.82	0.017
1400	1408	10-15	0.114	0.24	0.475
	1408	15-20	0.125	0.16	0.781
	1408	20-25	0.136	0.20	0.523
	1408	25-30	0.147	2.00	0.074
	1408	30-35	0.159	5.50	0.029

Table 2-2. Calculated reaction rate, A μm/h. Added Fe_2O_3: 0.8 wt%

Reaction temperature (°C)		Range of reaction (%)	JT (μm)	Jt (h)	A (μm/h)
1300	1309	10-15	0.114	2.44	0.047
	1310	15-20	0.125	1.34	0.093
	1310	20-25	0.136	1.60	0.085
	1310	25-30	0.147	1.78	0.083
	1310	30-35	0.159	1.21	0.131
1350	1359	10-15	0.114	0.67	0.170
	1361	15-20	0.125	1.08	0.116
	1362	20-25	0.136	0.40	0.340
	1363	25-30	0.147	0.37	0.397
	1363	30-35	0.159	0.38	0.418
	1363	35-40	0.173	0.39	0.444
	1363	40-45	0.187	0.54	0.346
	1363	45-50	0.207	0.62	0.334
	1363	50-55	0.230	1.02	0.225
1400	1400	10-15	0.114	0.31	0.368
	1401	15-20	0.125	0.37	0.338
	1401	20-25	0.136	0.26	0.523
	1401	25-30	0.147	0.17	0.865
	1401	30-35	0.159	0.11	1.45
	1401	35-40	0.173	0.12	1.44
	1401	40-45	0.187	0.12	1.56
	1401	45-50	0.207	0.14	1.48
	1401	50-55	0.230	0.10	2.30
	1401	55-60	0.256	0.17	1.51
	1401	60-65	0.287	0.17	1.69
	1401	65-70	0.319	0.24	1.33
	1401	70-75	0.357	0.36	0.992

(sample weight-amount of Fe_2O_3) with the detected increase in weight. Strictly speaking, since the reaction system was an open one, there were identical reactions with silicon and the alumina crucible and between silicon and the oxygen in the silicon, the oxygen in the atmosphere, and the oxygen in the Fe_2O_3 [4, 9, 15, 16] with the result that the increase in weight did not always correspond to the reaction rate. However, as will be explained later, the scattering was very slight and has been ignored in the calculations of table 2.

3.2   The Condition of the Silicon Nitride Formed

The mineral composition of the nitrided samples as determined by the X-ray diffraction method were investigated [17], and the results arb shown in table 3. X-ray fluorescence analysis indicated that the iron additive did not scatter outside the system, but remained inside the nitrided sample. In samples with more than 3.2 wt% Fe_2O_3 added, all of it remained as metallic iron. The addition of Fe_2O_3 in large quantities caused the generationof Si_2N_2O. The amount of β phase material in the nitride, in general, was greater at high temperatures.

TABLE 2-3. CALCULATED REACTION
RATE. A m/h. ADDED Fe_2O_3: 1.6wt%

Reaction temperature (°C)		Range of reaction (%)	ΔT (μm)	Δt (h)	Λ (μm/h)
1300	1307	10-15	0.114	2.04	0.056
	1307	15-20	0.125	1.80	0.069
	1307	20-25	0.136	1.18	0.115
	1307	25-30	0.147	1.22	0.120
	1307	30-35	0.159	1.32	0.120
	1307	35-40	0.173	1.40	0.124
	1307	40-45	0.187	1.60	0.117
	1307	45-50	0.207	1.96	0.106
	1307	50-55	0.230	3.04	0.076
	1307	55-60	0.256	6.86	0.037
1350	1363	15-20	0.125	0.74	0.169
	1365	20-25	0.136	0.68	0.200
	1365	25-30	0.147	0.44	0.334
	1365	30-35	0.159	0.35	0.454
	1365	35-40	0.173	0.37	0.468
	1365	40-45	0.187	0.32	0.584
	1365	45-50	0.207	0.40	0.518
	1365	50-55	0.230	0.40	0.575
	1365	55-60	0.256	0.45	0.569
	1365	60-65	0.287	0.56	0.513
	1365	65-70	0.319	0.71	0.449
	1365	70-75	0.357	0.90	0.397
1400	1398	15-20	0.125	0.20	0.625
	1399	20-25	0.136	0.20	0.680
	1400	25-30	0.147	0.24	0.613
	1400	30-35	0.159	0.16	0.994
	1400	35-40	0.173	0.14	1.24
	1400	40-45	0.187	0.08	2.34
	1400	45-50	0.207	0.12	1.73
	1404	50-55	0.230	0.08	2.88
	1407	55-60	0.256	0.08	3.20
	1407	60-65	0.287	0.12	2.39
	1407	65-70	0.319	0.18	1.77
	1407	70-75	0.357	0.10	3.57

Parts of samples with different amounts of Fe_2O_3 additive nitrided at 1400°C were lightly pulverized in an agate mortar and the resultant powde observed by electronic microscope. The results are shown in figure 2. In all cases, minute rectangular crystals were observed. There was no special relation between the differences in the amounts of Fe_2O_3 added and the configuration of the Si_2N_4 formed.

4. Observations

4.1 Reaction Velocity

Figure 3 is an Arrhenius plot of table 2. In table 2, hyperbolic reactions were noted in systems with no Fe_2O_3 added, but linear reactions were noted when there were additions ex-cept got the initial period of the reaction. This tendency can be seen in figure 3. When different amounts of Fe_2O_3 are compared in figure 3, the addition of Fe_2O_3 to the silicon powder accelerated nitridation, but addition of Fe_2O_3 above 1.6 wt% was not always effective. Except for low temperatures, the speed of nitridation accompanied the increase of additive but there was a tendency for saturation. The nitridation speed at 1400°C with an additive of Fe_2O_3 of more than 1.6 wt% was 5-10 times higher than when there was no additive. This effectiveness at acceleration was remarkable at low temperatures.

Table 3. Mineral composition calculated from X-ray data and the amounts of free silicon calculated from T.G.A results for the nitrided samples

Fe$_2$O$_3$ added (wt%)	Reaction temperature (°C)	Results from X-ray diffraction			T.G.A results	
		100·β/(α+β) (%)*	Free Si (wt%)	Si$_2$N$_2$O	Reacted Si (%)	Free Si (wt%)
0	1300	8.7	—	—	9.0	85.8
	1350	9.3	—	—	17.6	73.8
	1400	14.4		—	33.4	54.5
0.8	1300	10.8	—	—	40.7	47.1
	1350	12.9	—	—	60.3	28.6
	1400	12.9	9.2	—	81.8	11.9
1.6	1300	10.8	—	—	62.4	27.9
	1350	12.2	4.7	—	84.9	9.8
	1400	14.4	0.8	—	94.3	3.6
3.0***	1300	12.7	10.7		82.3	11.8
	1350	12.2	1.4	—	94.6	3.4
	1400	14.4	0	detected	97.7	1.4
6.2***	1300	12.9	1.0	detected	98.4	1.0
	1350	13.7	0.6	detected	100.0**	0.6
	1400	16.7	0	detected	101.5**	0

* Contents of β type in total Si$_3$N$_4$ formed by the reaction.
** Caused by the formation of Si$_2$N$_2$O.
*** α-Fe was detected in all samples nitrided with 3.2 and 6.2 wt% Fe$_2$O$_3$ addition.
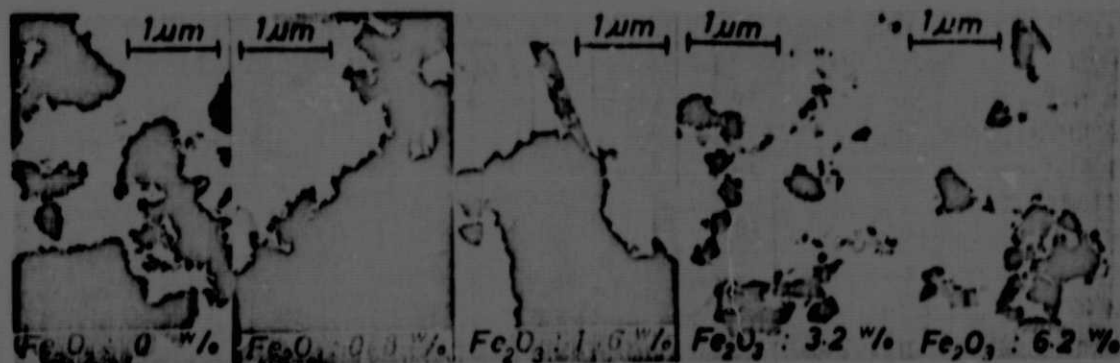

Fig. 2. Electron micrographs of powdered sample nitrided at about 1400°C. Mineralogical data of those samples are shown in Table 3.
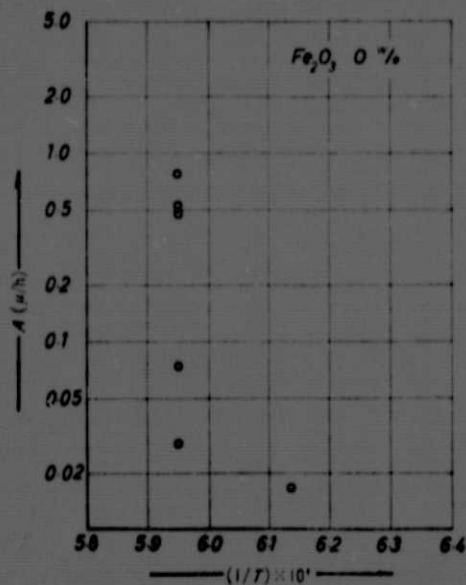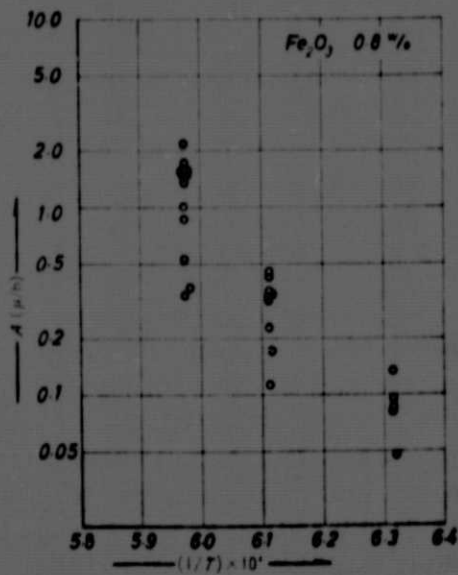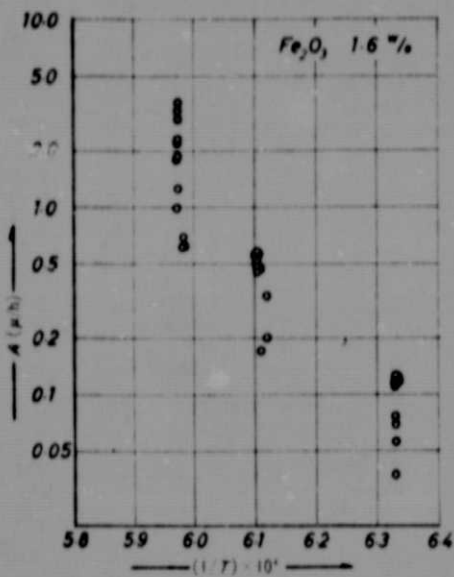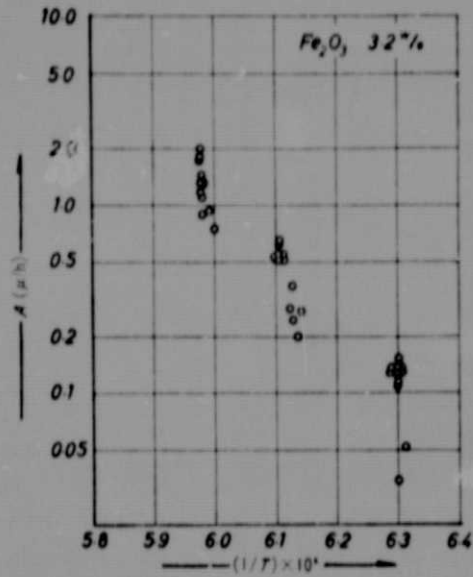

Fig. 3(1)

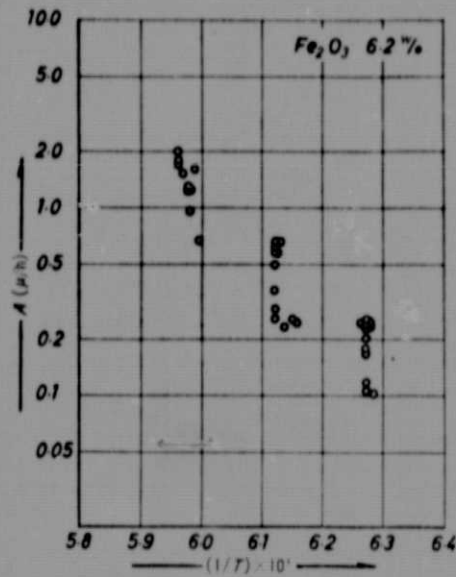Fig. 3(2)

fig³ (3) fig. ³ (4)

fig. 3 (5)

Fig. 3. Arrhenius plot of calculated reaction rate, A μ/h in Table 2-1~2-5.

Table 4. Activation energy calculated from Fig. 3.

Added Fe_2O_3 (wt%)	Activation energy (kcal/mol)
0	—*
0.8	153
1.6	165
3.2	150
6.2	133

* 156[1] and 158[2] kcal/mol were reported.

Table 4 shows the reaction activation energy found from figure 3. The average values between 1300-1400°C are recorded in the table. The values could not be recorded when there was no additive, but in the range where the addition of Fe_2O_3 was small, the values of /51 highly pure reactions which were 156 kcal/mol [11], and 158 kcal/mol [12], agree very closely. As the Fe_2O_3 additive increased the values tended to become lower. This was obvious in reaction with an additive of 6.2 wt%, and it is possible that when the additive is large, the rate of reaction is determined by a different mechanism.

4.2 The State of the Iron During Nitridation and Fugacity

When Fe_2O_3 coexists with a sufficient quantity of silicon, as in the present experiment, it is estimated that reactions such as the following take place during nitridation.

Table 2-4. Calculated reacton rate, A μm/h. Added Fe_2O_3: 3.2 wt%

Reaction temprature (°C)	Range of reaction (%)	ΔT (μm)	Δt (h)	A (μm/h)
1300	1312	10-15	0.114	2.26	0.051
	1314	15-20	0.125	0.88	0.142
	1314	20-25	0.136	1.04	0.131
	1314	25-30	0.147	1.14	0.129
	1314	30-35	0.159	1.06	0.150
	1314	35-40	0.173	1.34	0.129
	1314	40-45	0.187	1.42	0.132
	1314	45-50	0.207	1.64	0.126
	1314	50-55	0.230	2.14	0.107
	1314	55-60	0.256	2.00	0.128
	1314	60-65	0.287	2.50	0.115
	1314	65-70	0.319	4.10	0.034
1350	1355	15-20	0.125	0.46	0.272
	1357	20-25	0.136	0.69	0.197
	1359	25-30	0.147	0.61	0.241
	1360	30-35	0.159	0.58	0.274
	1362	35-40	0.173	0.46	0.376
	1364	40-45	0.187	0.39	0.479
	1365	45-50	0.207	0.41	0.505
	1365	50-55	0.230	0.42	0.548
	1365	55-60	0.256	0.42	0.610
	1365	60-65	0.287	0.46	0.624
	1365	65-70	0.319	0.58	0.550

Reaction temperature (°C)	Range of reaction (%)	ΔT (μm)	Δt (h)	A (μm/h)
	1365	70-75	0.357	0.72	0.496
1400	1396	20-25	0.136	0.18	0.756
	1397	25-30	0.147	0.16	0.919
	1399	30-35	0.159	0.18	0.883
	1401	35-40	0.173	0.16	1.08
	1401	40-45	0.187	0.16	1.17
	1401	45-50	0.207	0.16	1.29
	1401	50-55	0.230	0.18	1.28
	1401	55-60	0.256	0.18	1.42
	1401	60-65	0.287	0.16	1.79
	1401	65-70	0.319	0.18	1.77
	1401	70-75	0.357	0.18	1.98

Table 2-5. Calculated reaction rate, A μm/h. Added Fe$_2$O$_3$: 6.2 wt%

Reaction temperature (°C)		Range of reaction (%)	ΔT (μm)	Δt (h)	A (μm/h)
1300	1318	15-20	0.125	1.22	0.102
	1321	20-25	0.136	1.30	0.105
	1321	25-30	0.147	1.24	0.119
	1321	30-35	0.159	0.96	0.166
	1321	35-40	0.173	0.86	0.201
	1321	40-45	0.187	0.76	0.246
	1321	45-50	0.207	0.88	0.235
	1321	50-55	0.230	1.00	0.230
	1321	55-60	0.256	1.10	0.233
	1321	60-65	0.287	1.22	0.235
	1321	65-70	0.319	1.34	0.238
	1321	70-75	0.357	2.00	0.179
1350	1350	15-20	0.125	0.52	0.240
	1352	20-25	0.136	0.54	0.252
	1356	25-30	0.147	0.64	0.230
	1360	30-35	0.159	0.62	0.256
	1360	35-40	0.173	0.60	0.288
	1360	40-45	0.187	0.52	0.360
	1360	45-50	0.207	0.42	0.493
	1360	50-55	0.230	0.41	0.561
	1360	55-60	0.256	0.41	0.624
	1360	60-65	0.287	0.44	0.652
	1360	65-70	0.319	0.49	0.651
	1360	70-75	0.357	0.63	0.567
1400	1395	25-30	0.147	0.22	0.668
	1397	30-35	0.159	0.10	1.59
	1399	35-40	0.173	0.18	0.961
	1399	40-45	0.187	0.16	1.17
	1400	45-50	0.207	0.16	1.29
	1400	50-55	0.230	0.18	1.28
	1402	55-60	0.256	0.17	1.51
	1404	60-65	0.287	0.17	1.69
	1404	65-70	0.319	0.18	1.77
	1405	70-75	0.357	0.18	1.98

The similar reactions Si$_3$N$_4$-Fe$_2$O$_3$ and Si-Si$_3$N$_4$-Al$_2$O$_3$ are also thought possible [15, 16]. In any case, when the reaction system is open as in this experiment, SiO is transferred out of the reaction system during the reaction period because it is volatile [15,16], and isolated iron or silicide such as FeSi$_2$ is generated. It is believed that when the temperature is above 1208°C, the common melting point of FeSi$_2$-Si [18], a silicon solution of iron is generated. If the reaction proceeds sufficiently, the solution limit of Si$_3$N$_4$ is exceeded, and the iron additive, as shown in table 3, exists as metallic iron which retains its equilibrium with Si$_3$N$_4$ at less than one atmosphere of nitrogen [19].

For example, in table three, for the sample which was nitrided at 1300°C with a Fe$_2$O$_3$ additive of 3.2 wt%, a 10% residue of silicon was noted in the sample after nitridation. In spite of this, the generation of metallic iron was noted. This can probably be explained by lack of uniformity of reactions in the samples. According to tagle 3, when more than 3.2 wt% of Fe$_2$O$_3$ (corresponding to 0.49 at% Fe in the Si$_3$N$_4$ when nitridation was completed) was added, metallic iron was generated. Consequently, we can say that in the present experiment, the solubility of iron into Si$_3$N$_4$ at near 1400°C was in the range of 0.24-0.49 at%. This value is

almost in agreement with that of another experiment [19] in which the solubility of iron synthesized in Si_3N_4 with the same starting materials was in the range of 0.4-0.6 at%.

The amount of disassociated silicon noted by X-ray diffraction and recorde in table 3 is, in general, smaller than that calculated from the results from the thermobalance. This is possibly due to the fugacity of SiO mentioned earlier. When Fe_2O_3 was added at 6.2 wt%, there was more than 100% nitridation of the sample at near 1400°C. This is thought to have some connection with the fact that Si_2N_2O was noted in the sample.

4.3 Structure and Shape of the Silicon Nitride Formed

The Si_3N_4 generated by nitridation of silicon in these experiments was, as shown by table 3, largely α phase. As the temperature became higher and the Fe_2O_3 was increased, there was a slight tendency for β phase to increase, but not markedly.

The relation of temperature to the amount of β phase is probably due to the fact that β phase is rather stable at high temperatures [17]. It is believed that first α phase is generated, and this by going through a process of sublimation, recrystallization is converted into β phase. The increase of β phase which accompanies an increase in Fe_2O_3 addition is probably dur to the acceleration of the recrystallization in the solution [13, 17]. In Figure 2 can be seen some idiomorphic clear minute crystals thought to have been formed by crystal frowth.

4.4 Reaction Mechanism

It is believed that the reactions of table 2 in which Fe_2O_3 was added proceeded almost linearly. This fact must be satisfied by the reaction mechanism. One corroboration is the process of

peeling and cracking of the thin layer of Si_3N_4 formed by the reaction on the silicon or on the surface of the solution containing iron [12]. However, in the case of Fe_2O_3 additive, the melt participates in the reaction; thus the Si_3N_4 thin layer can possibly be attributed, for example, to the V.L.S. mechanism [4,20], or to the dissolution eduction process recorded as S.L.S. [21, 22].

The average activation energy 130-160 kcal/mol (table 4) between 1300-1400°C is comparatively near the diffusion barrier, 186 kcal/mol [14], of nitrogen in Si_3N_4 synthesized under almost the same conditions using identical silicon powder. It was noted that for additions of above 1.6 wt% of Fe_2O_3 (0.57 at% in silicon as an Fe additive, 0.24 at% in completely nitride silicon) the amount of increase in reaction velocity hardly changes, and the velocity of nitridation was five to tenfold. This fact is in accord with separate results [19] where the solubility limits of iron in Si_3N_4 near 1400°C and in silicon at 1400°C were 0.4-0.6 at%. It also agrees closely with the fact that the autodiffusion rate of hydrogen in Si_3N_4 raises one unit when the addition of iron is above the solubility limits [14].

The significance of the above is that the reaction proceeds according to the diffusion rate. The progress of the reaction is linear because, as mentioned before, there is an intervention of peelong and cracking of the Si_3N_4 skin formed on the silicon or on the surface of the solution containing iron or an intervention of a dissolution eduction process. Hyperbolic reactions were noted in highly pure powder with no iron additive. The reason for this is not clear, but compared with previous research [12], particle size was coarse and it is possible that minute quantities of oxygen in the atmosphere participated in the reactions.

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5. Summary

The effects of the addition of Fe_2O_3 on the reaction of silicon (purity: 99.99%, average particle size: 15 μm) and nitrogen (O_2<0.5 ppm, dew point<-60°C) were studied at temperatures in the vicinity of 1300-1400°C. When there was no Fe_2O_3 added, the reactions proceeded hyperbolically, because the particles were coarse. When 0.8 wt% of Fe_2O_3 was added to the mixture, linear reactions were noted. In the range above 0.8 wt%, the reaction velocity was raised five to ten times. The Fe_2O_3 added in excess of the solubility limits of Si_3N_4 remained as metallic iron after nitridation. /52 The solubility limits of iron in Si_3N_4 are believed to be in the range of 0.24-0.49 at% at near 1400°C. A tendency was seen for the reaction activation energy to decrease as the amount of iron additive was increased. In cases when the addition of iron was small, the value was about 160 kcal/mol, and when the addition was 6.2 wt%, the value was 133 kcal/mol.

It is believed that the reactions were determined by the diffusion rate of nitrogen in the Si_3N_4. With the addition of Fe_2O_3, the reactions became linear. This was thought to be due to the intervention of peeling and cracking of the Si_3N_4 skin formed on the silicon or on the surface of the solution containing iron, or that it is mediated by a dissolution eduction process.

REFERENCES

1. Popper, P. and S. Ruddlesden, <u>Trans. Brit. Ceram. Soc.</u> <u>60</u>, 603-26 (1961).

2. Suzuki, H., <u>Bulletin of Tokyo Institute of Technology</u> <u>54</u>, 163-77 (1963).

3. Gribkov, V., V.A. Silaev, B.V. Schchetanov, E.L. Umantsev and A.S. Isaikin, <u>Sov. Phys.-Crystallogy.</u> <u>16</u>, 852-54 (1972).

4. Messier, D.R. and P. Wong, <u>J. Am. Ceram. Soc.</u> <u>58</u>, 480-85 (1973).

5. Naruse, W., M. Nojiri and M. Tada, <u>Nihon-kinzokugakkai-Shi</u> <u>35</u>, 731-38 (1971).

6. Mangels, J.H., <u>J. Am. Ceram. Soc.</u> <u>58</u>, 354-55 (1975).

7. Blegen, K., "Special Ceramins No. 6," edited by P. Popper. The British Ceramin Research Association, Stoke-on Trent, 1975, pp. 223-244.

8. Wild, S., P. Grieveson and K.H. Jack, "Special Ceramins No. 5," <u>ibid.</u>, 1972, pp. 223-244.

9. Sin-Shong-Lin, <u>J. Am. Ceram. Soc.</u> <u>58</u>, 271-273 (1975).

10. Mitomo, M., <u>J Am. Ceram. Soc.</u> <u>58</u>, 527 (1975).

11. Huettinger, K.J., <u>High Temp.-High Pressures</u> <u>1</u>, 221-230 (1969).

12. Inomata, Y., and Y. Uemura, <u>Yogyo-kyokai-Shi</u> 83, 244-248 (1975).

13. Inomata, Y., <u>ibid.</u> <u>83</u>, 497-500 (1975).

14. Kijima, K. et al., to be published.

15. Messier, D.R. and G.E. Gazza, <u>J. Am. Ceram. Soc.</u> <u>58</u>, 538-40 (1975).

16. Inomata, Y., K. Yukino and T. Wada, <u>Yogyo-kyokai-Shi</u> <u>84</u>, 254 (1976).

17. Inomata, Y., <u>Yogyo-Kyokai-Shi</u> 82, 522-526 (1974).

18. Hansen, M. <u>Constitution of Binary Alloys</u>, McGraw-Hill, Inc., 1958, pp. 711-717.

19. Yamamura, H., K. Kijima, S. Shirasaki, Y. Inomata and H. Suzuki, <u>J. Mat Soc.</u> <u>11</u>, 1754-1755 (1976).

20. Wagner, R.S. and Ellis, W.C., <u>Trans. AIME.</u> <u>233</u>, 1053-1064 (1965).

21. Kaiser, W., and C.D. Thurmond, <u>J. Appl. Phys.</u> <u>30</u>, 427-431 (1959).

22. Inomata, Y., and T. Yamane, <u>J. Crystal Growth</u> <u>21</u>, 317-318 (1974).

REFERENCES

1. Popper, P. and S. Ruddlesden, Trans. Brit. Ceram. Soc. 60, 603-26 (1961).

2. Suzuki, H., Bulletin of Tokyo Institute of Technology 54, 163-77 (1963).

3. Gribkov, V., V.A. Silaev, B.V. Schchetanov, E.L. Umantsev and A.S. Isaikin, Sov. Phys.-Crystallogy. 16, 852-54 (1972).

4. Messier, D.R. and P. Wong, J. Am. Ceram. Soc. 58, 480-85 (1973).

5. Naruse, W., M. Nojiri and M. Tada, Nihon-kinzokugakkai-Shi 35, 731-38 (1971).

6. Mangels, J.H., J. Am. Ceram. Soc. 58, 354-55 (1975).

7. Blegen, K., "Special Ceramins No. 6," edited by P. Popper. The British Ceramin Research Association, Stoke-on Trent, 1975, pp. 223-244.

8. Wild, S., P. Grieveson and K.H. Jack, "Special Ceramins No. 5," ibid., 1972, pp. 223-244.

9. Sin-Shong-Lin, J. Am. Ceram. Soc. 58, 271-273 (1975).

10. Mitomo, M., J Am. Ceram. Soc. 58, 527 (1975).

11. Huettinger, K.J., High Temp.-High Pressures 1, 221-230 (1969).

12. Inomata, Y., and Y. Uemura, Yogyo-kyokai-Shi 83, 244-248 (1975).

13. Inomata, Y., ibid. 83, 497-500 (1975).

14. Kijima, K. et al., to be published.

15. Messier, D.R. and G.E. Gazza, J. Am. Ceram. Soc. 58, 538-40 (1975).

16. Inomata, Y., K. Yukino and T. Wada, Yogyo-kyokai-Shi 84, 254 (1976).

17. Inomata, Y., Yogyo-Kyokai-Shi 82, 522-526 (1974).

18. Hansen, M. Constitution of Binary Alloys, McGraw-Hill, Inc., 1958, pp. 711-717.

19. Yamamura, H., K. Kijima, S. Shirasaki, Y. Inomata and H. Suzuki, J. Mat Soc. 11, 1754-1755 (1976).

20. Wagner, R.S. and Ellis, W.C., Trans. AIME. 233, 1053-1064 (1965).

21. Kaiser, W., and C.D. Thurmond, J. Appl. Phys. 30, 427-431 (1959).

22. Inomata, Y., and T. Yamane, J. Crystal Growth 21, 317-318 (1974).

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