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OXIDATION RESISTANCE OF SILICON CERAMICS

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16. Abstract The article provides a review with eight references on the oxidation resistance, and examples of oxidation of SiC, Si ₃ N ₄ and sialon. A description is given of the oxidation mechanism, including the oxidation product, oxidation reaction and the bubble size. The oxidation reactions are represented graphically. An assessment is made of the oxidation process, and an oxidation example of silicon ceramics is given.			
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OXIDATION RESISTANCE OF SILICON CERAMICS

Hasegawa Yasutoshi and Kazushi Hirota**

1. PREFACE

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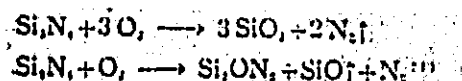
The development of scientific technology demands increasingly high standards for basic materials. Fire-resistant materials composed mainly of metallic oxides have been used widely in various high-temperature industries. Recent research has focussed on nitride, carbide, silicide and boride as a fire-resistant material. Much research has been done especially on nitride, carbide and acid nitride as high-temperature-resistant structural materials. From the energy conservation perspective, these materials are expected to be improved. These materials possess superior characteristics that other oxidized substances do not have. However, they tend to oxidize easily in a high-temperature environment. Unless a solution to this problem characteristic of the materials can be found, the economical use of these materials as a pyrogenic heat-resistant structural material in an oxidizing environment cannot be realized. Among the substances that are being discussed, Si_3N_4 , SiC and sialon are the first to be used as a superior fire-resistant material or partial heat-resistant structural material because of their relatively cheap prices and comparatively high purity. Their defects caused by oxidation during their usage, however, are the major obstacles hindering their further improvement. In this article, Si_3N_4 , SiC and sialon are all considered as silicon ceramics and their oxidation process at a high temperature is discussed.

* Numbers in margin indicate foreign pagination.

** (National Institute for Research in Inorganic Materials);
On the Oxidation Properties of Silicon Ceramics

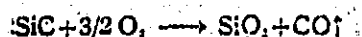
2. OXIDATION MECHANISM

(a) The oxidation of Si_3N_4 proceeds in a reaction as indicated below.

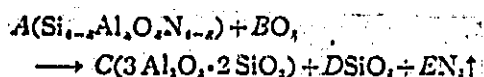


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(b) Similarly, oxidation of SiC takes place as follows:

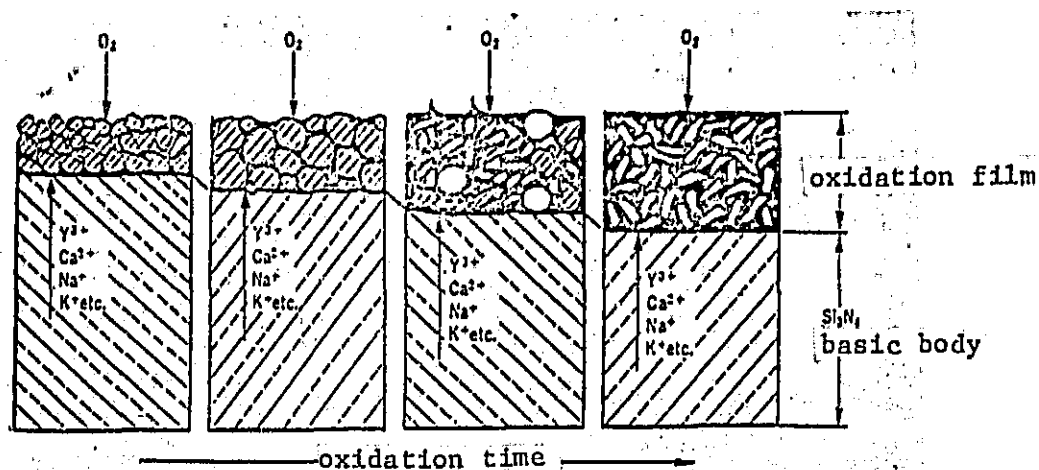


(c) Sialon's oxidation goes through the following reaction.



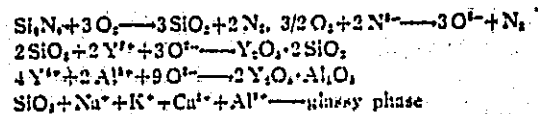
As shown in the above formulas, all of the materials increase in weight as the reaction proceeds. Generally, weight increase is the basis for an oxidation resistance assessment which will be discussed in detail in the following chapter. To give an example, sintered Si_3N_4 's (Y_2O_3 and Al_2O_3 are added as sintering auxiliary agents) oxidation process is shown in Figure 1. An analysis on the surface oxidation product by X-ray diffraction indicates that the strength of crystalline barite increases drastically at an early stage of oxidation, but as oxidation progresses, the strength decreases. After many hours of oxidation, the strength of crystalline barite drops to a point when it is no longer measurable. In inverse proportion to decreasing strength of crystalline barite, the glassy phase increases its strength. Y_2O_3 that was added as sintering agent together with Al_2O_3 reacts to SiO_2 which is produced by oxidation and forms $\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$ with gradually increasing strength. Similarly, after a long period of oxidation, Al_2O_3 can be found in the form $2\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$. These oxidation product actions are easy to understand when you look at them as surface accumulations of impurities in a sinter by pyrogenic oxidation.

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- 1) Oxidation product (comparison of intensity of diffracted X-ray) crystalline barite < crystalline barite >
crystalline barite > N.D.
Y2S < Y2S < Y2S < Y2S
N.D. N.D. N.D. (3YA)
sinter < sinter < sinter < sinter

- 2) Oxidation reaction



- 3) Bubble size (μm) (AME sample, 1300°C oxidation):
— 10-30 200-500

Figure 1. Oxidation reaction and oxidation chart of pressurized sinter Si_3N_4 (sintering agent, Y_2O_3); 5, Al_2O_3 : 3 wt %)

In a similar manner, Figure 2 shows the oxidation process of pressurized Si_3N_4 sinter. (Sinter agent, MgO : 5 wt % added). A scanning electron microscope shows an aggregate of crystals in the post oxidation surface, which looks like a porous oxidation film. However, further analysis of the section by a scanning electron microscope and an optical microscope reveal that the closer the oxidation layer gets to the surface, the more porous it gets. The part of the layer close to the basis is very fine. This is because impurities in the base accumulate on the surface during the oxidation process, forming a layer of fine glassy phase near the base and a porous layer as it goes to the top due to the on-going crystallization process [3].

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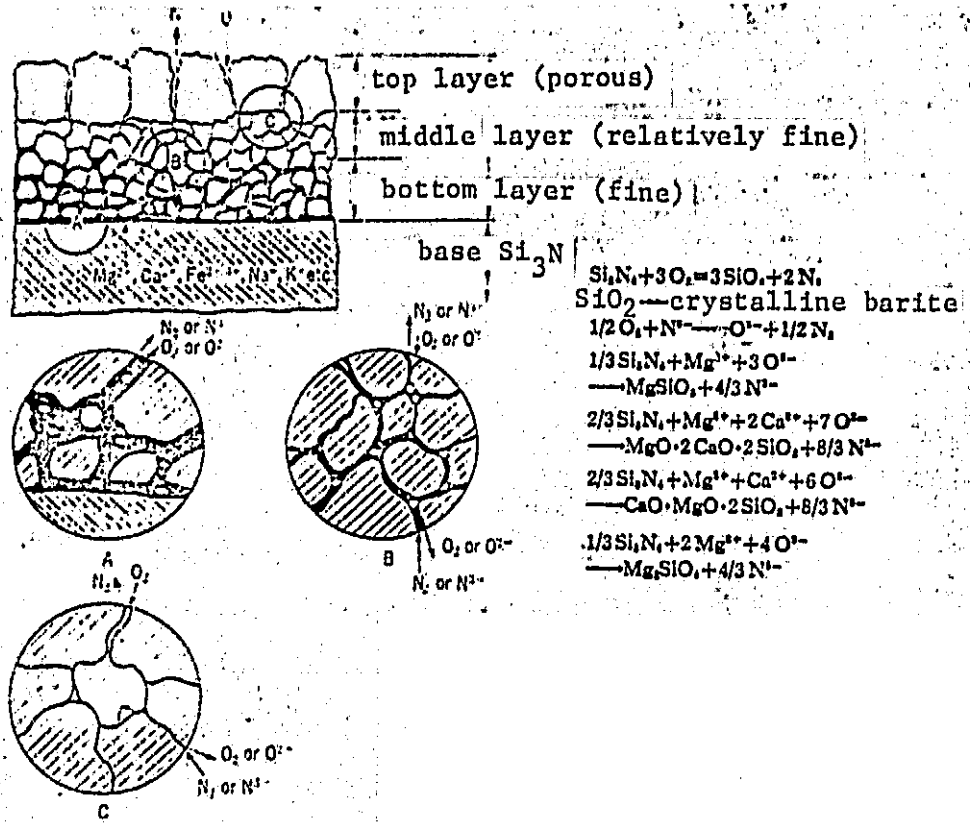


Figure 2. Oxidation reaction and chart of Si_3N_4 pressurized sinter (sinter agent MgO): 5 wt % added, $1300^\circ C$, 30d

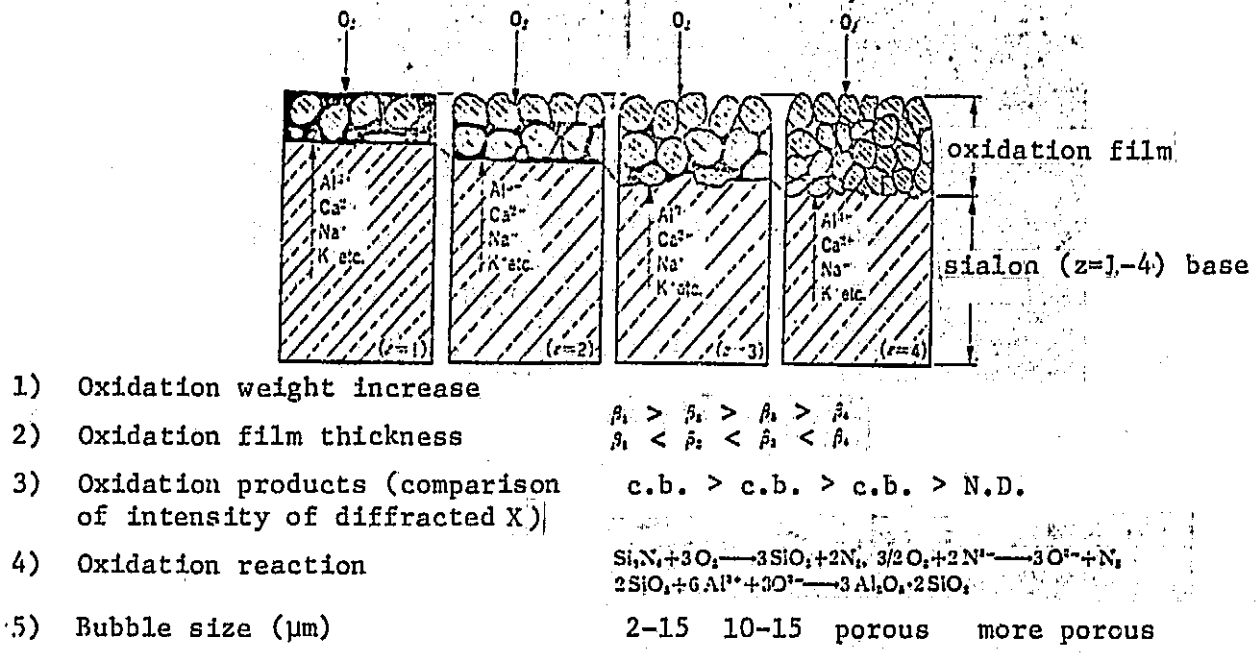


Figure 3. β -sialon pressurized sinter oxidation reaction ($z=1-4$) and chart ($1300^\circ C$, 30d) [2]

Figure 3 shows oxidation of sialon which sinters relatively easily without an agent (can be considered as a single phase). An oxidation experiment with sialon sinter offered an interesting result: from $Z=1$ to $Z=4$, the oxidation weight increase becomes smaller as the number goes up, whereas the thickness of the film increases as the number goes up [2]. The one with the smallest oxidation weight increase, in this case sialon $Z=4$, is believed to possess the best oxidation resistance. But in the case of sialon, $Z=4$ type composition does not necessarily have better oxidation resistance. From the point of oxidation film thickness, the $Z=1$ type composition is considered to have better oxidation resistance. This experimental finding demands a basic re-analysis of conventional oxidation resistance, namely the assessment based on oxidation weight increase. Based upon a study of the oxidation mechanism of SiC, SiC sinter forms crystalline barite on the surface while a part of sinter agents (normally B, C and Al) accumulate on the surface as well, in the same way as Si_3N_4 sinter which is indicated in Figure 1. B oxidizes easily and evaporates as B_2O_3 at or above $1300^\circ C$. As an example, the oxidation weight increase process with B: 0.5 wt % and Al: 1 wt % added is shown in Figure 4. Considering

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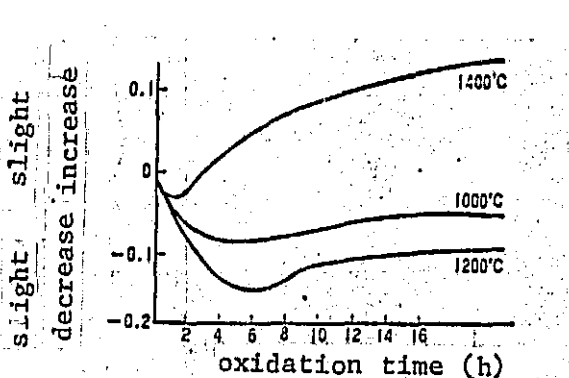


Figure 4. Pressurized sinter SiC (B oxidation mechanism [5]). (B: 0.5 wt %, AL: 1.0 wt %)

the above discussion, silicon ceramic oxidation may seem simple, but in actuality, it is quite a complicated process.

3. ASSESSMENT STANDARD OF OXIDATION PROCESS

In the previous chapter, it was pointed out that the conventional oxidation resistance assessment by means of the

oxidation weight increase entails problems. As assessment criteria of oxidation resistance, aside from weight increase, one may consider the thicknesses of the oxidation film, oxidation product and the nature of oxidation film surface and bubbles. When the primary component of oxidation products is crystalline barite alone, oxidation film exfoliates when it cools down to room temperature, because the crystalline barite $a \rightarrow b$ transition takes place around 27°C. When the coefficient of thermal expansion of an oxidation product differs substantially from that of the base, shear strain occurs on the surface of contact between the oxidation film and the base, which causes exfoliation. The nature of the oxidation film surface is closely related to the oxidation products. When the impurities of the base accumulate on the surface, glass formation with a low melting point among the impurities, causes very uneven oxidation of the film surface due to N_2 , CO gas generated by the oxidation reaction. We have experienced a case where R_{max} reached 100 μm . As discussed, it involves great risk to assess the overall oxidation characteristic from one particular characteristic and it is inevitable to use a comprehensive assessment method. To do so, we made Figure 5 by applying the characteristic factor often used for quality control for oxidation assessment. The factors in this figure are insufficient; therefore, this serves as a reference of the basic assessment method. Generally, the same oxidation experiments do not result in accurately overlapping findings, which makes it extremely difficult to obtain data usable as a data bank. This is because too many factors are involved. For the assessment of oxidation characteristics, we have to specify the characterization of sinter, and to do so we need to characterize the original material.

4. OXIDATION EXAMPLE OF SILICON CERAMICS

As an example, I would like to discuss Davidge and other experiments on reactive sinter Si_3N_4 's oxidation. Organic

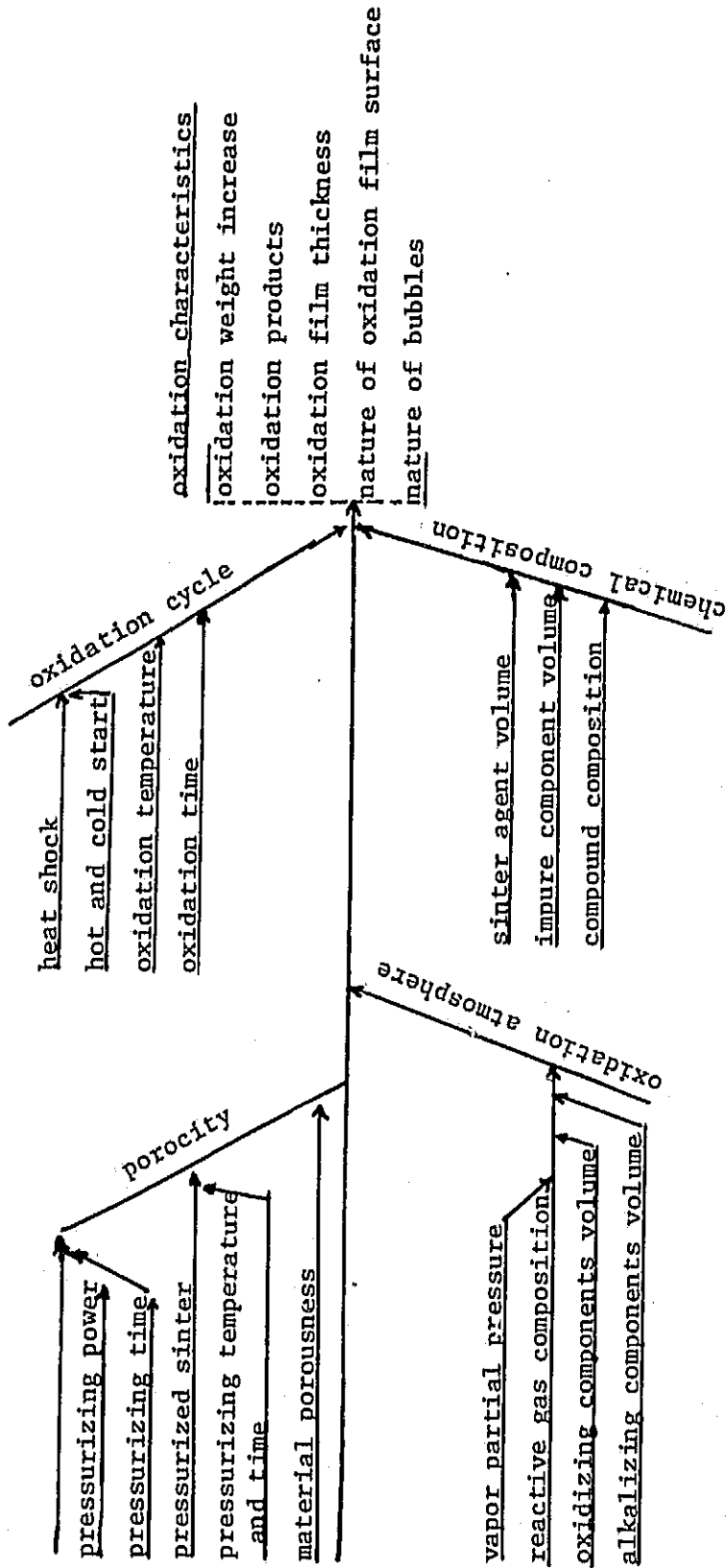


Figure 5. Characteristic factors of oxidation assessment

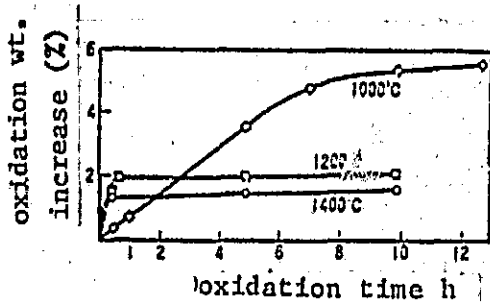


Figure 6. Reactive sinter Si_3N_4 oxidation weight increases in relation to oxidation time (h) [6]

an open furnace at three different temperatures (1000, 1200 and 1400°C) for 150 hours. Figure 6 shows the oxidation weight increase observed in the experiment.

Providing the oxidation mechanism proceeds by a simple diffusion mechanism, two clear steps of oxidation can be observed. At 1000°C, the early stage of oxidation (stage I) takes 3 to 4 days. At 1200°C or 1400°C, however, stage I is completed in about 15 minutes. Moreover, at higher temperatures, the oxidation weight increase (%) during stage I is greater, but the oxidation rate is lower. In this experiment by Davidge and others, low stages (early stage and mid-stage) of the oxidation mechanism were observed. In a series of our experiments on silicon ceramics oxidation, several stages were found as shown in Figure 7.

These stages change depending on oxidation conditions (especially oxidation atmosphere). Note that unit of oxidation time in Figure 7 is days. It has been reported that oxidation is completed primarily in stages I and II and the mechanisms can be explained as simple diffusion mechanism. However, in oxidation over a long period of time (unit = month), stages that cannot be explained by simple diffusion start to appear (stages III-IV in the figure). When there is partial steam pressure, the material reaches stages III-IV within relatively a few days.

binder was added to silicon powder which is available commercially. Then it was pressurized at 500 MNm^{-2} . Then nitriding was done at 1350°C for 20 hours first, followed by 20 more hours of nitriding at 1450°C, which created a test material with a density of 2.53 g/cm^3 . The material was then cut into specific sizes, which was oxidized in

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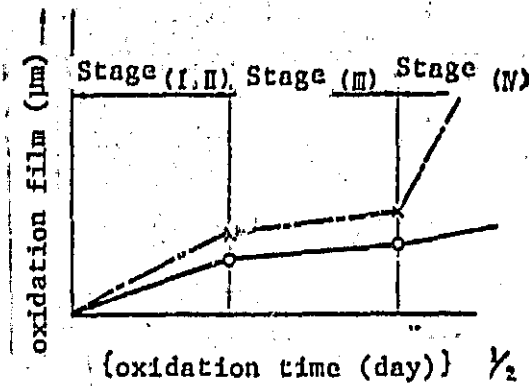


Figure 7. Thickness (μm) of oxidation film when oxidized at a set temperature {oxidation time (day)} $\frac{1}{2}$
 x---x repetitive cooling and heating while maintaining the specific temperature
 o---o keeping a general temperature steady

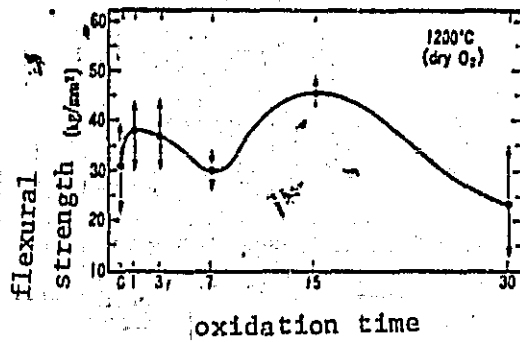


Figure 8. β -sialon ($x=2$) sinter

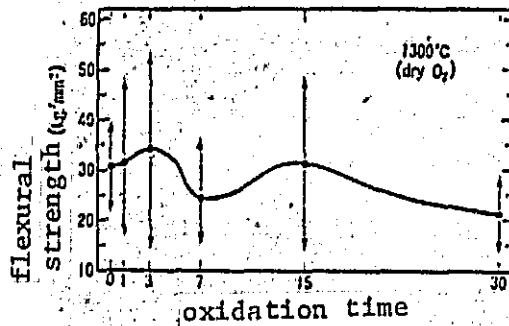


Figure 9. β -sialon ($z=2$) sinter

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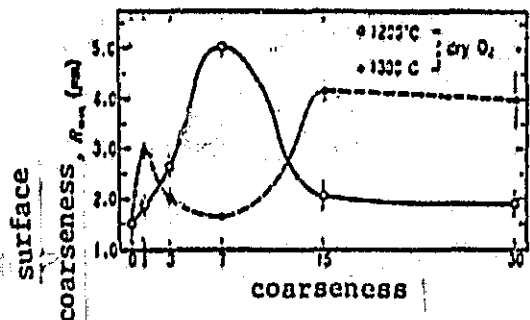


Figure 10. β -sialon ($x=2$)
pressurized sinter surface
coarseness - oxidation
time

We now discuss how strength changes
by oxidation. As an example,
Figures 8 and 9 show data on β -sialon
($z=2$) pressurized sinter.

As shown in the figures, strength
decreases as the oxidation time
increases. At higher temperatures,
the data becomes more inconsistent.

It is nearly impossible to explain these phenomena in the limited
number of words here, but for reference purposes, we touched upon
the relation between strength and coarseness of the surface in
Figure 10.

5. POSTSCRIPT

Oxidation resistance of anti-oxidizing materials depends
mainly on the basic body crystals phase type, grain shape, grain
distribution, grainy phase type and its distribution, porosity
characteristics and distribution. Moreover, the resistance is
determined mostly by physical and chemical properties of the
oxidation film on the surface. Thus, accurate research on oxida-
tion should be initiated with a study on the basic sintering pro-
cess and the compound phase distribution and properties. Based
upon the oxidation characteristics of the oxidation mechanism,
better resistance is observed in the following conditions.

1) Oxidation weight increase: Small weight increases.
Weight increases in the parabolic manner in relation to oxidation
time without drastic change of pace.

2) Oxidation film thickness: Like the weight increase,
the oxidation film is thin, while the thickness increases in a
parabolic manner in relation to oxidation time without drastic
change of pace.

3) Oxidation product: They are non-transferable oxides. They possess a coefficient of thermal expansion similar to that of the basic body. They are not complex oxides consisting of many different components. They form fine layers.

4) Surface of oxidation film: even and smooth surface with no complicated protrusions or deflections.

A sinter with oxidation film which follows the above conditions most clearly is desirable from the viewpoint of oxidation resistance. However, an oxidation film which meets all the above conditions is not available yet. In the end, we would like to express our appreciation to Dr. Hiroshige Suzuki, honorary professor at Tokyo Kogyo University, for providing us supervision.

REFERENCES

- [1] M. E. Washburn, Bull. Am. Ceram. Soc., Vol. 46, p. 667, (1967).
- [2] Y. T. Hasegawa, H. Tanaka, M. Tsutsumi and H. Suzuki, Yogyo-Kyokai-Shi, Vol. 88, p. 292, (1980).
- [3] Y. T. Hasegawa, T. Yamane, K. Hirota, M. Tsutsumi and H. Suzuki, Yogyo-Kyokai-Shi, Vol. 88, p. 46 (1981).
- [4] Yasutoshi Hasegawa, Kazushi Hirota, Noriko Yamane, G. Mitomo, Hiroshige Suzuki, Yogyo-Kyokai-Shi, Vol. 89, p. 148 (1981).
- [5] J. Schlichting and J. Kriegesmann. Ber. Dt. Keram. Ges., Vol. 56, pp. 72-75 (1979).
- [6] R. W. Davidge, A. G. Evans, D. Gilling and P. R. Wilyman. Proceedings of the Fifth Symposium on Special Ceramics, p. 329 (1970).
- [7] Yasutoshi Hasegawa, and others, Yogyo-Kyokai-Shi, ready to be published.
- [8] Yasutoshi Hasegawa, G. Mitomo, Kazushi Hirota, Hidehiko Tanaka, Yoji Fujii, Hiroshige Suzuki, Yogyo-Kyokai-Shi, Vol. 89, p. 533, (1981).

AUTHORS' BACKGROUND

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Graduated from Tokyo Kogyo University, Chemical Engineering Department, in 1955 and joined Onoda Cement Co. Ltd in the same year. Since 1966, he has been working at the National Institute of Research in Inorganic Materials. He is a chief research officer and engineer of departments of chemistry, ceramics and production control, quality control. He is also a professor of engineering at Tokyo Kogyo University.

Kazushi Hirota

He graduated from Tokyo Kogyo University, Science Department, Chemistry Div. in 1957. Completed MA courses at the same university in 1959. In 1960, he became an assistant instructor at the university. In 1971, he joined the National Institute for Research in Inorganic Materials of Science and Technology Agency. Currently, he is a chief research officer of a research group, no. 15.