

**Alumina Based Ceramic Composites**

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**ABSTRACT**

As the representative alumina based ceramic composites, SiC whisker-reinforced composites, including in-situ prepared one by whiskerizing reaction of mullite with carbon black, and two new sorts of reaction-bonded type, namely zirconia-toughened one and alumina/(Si) in-situ composite, as well as a thermal-shock resistive alumina composed of secondary particulates, are introduced and briefly discussed.

**I. INTRODUCTION**

Within only one year after the beginning of industrial production of silicon carbide whiskers, SiC(w), in 1982<sup>1)</sup>, in which the author participated, SiC(w) reinforced Si<sub>3</sub>N<sub>4</sub> composite was developed also in Japan<sup>2)</sup>. In parallel with this research work, an approach to the SiC(w) reinforced Al<sub>2</sub>O<sub>3</sub> was carried out in United States<sup>3)</sup>. Since then, a variety of research on this type of Al<sub>2</sub>O<sub>3</sub> composite has been made, which is most recently reviewed by Yasuda<sup>4)</sup> at E-MRS Meeting/Strassbourg in 1991. With respect to various other ceramic composites reinforced by the same whiskers, the author summarized them as a review on the domestic situation<sup>5)</sup>, as well as another review on the foreign trend<sup>6)</sup>.

On the other hand, a series of research on in-situ preparation of SiC(w) in  $\text{Si}_3\text{N}_4$ <sup>7)</sup>,  $\text{SiO}_2$ <sup>8)</sup>,  $\text{ZrO}_2$ <sup>9)</sup> matrices, as well as in  $\text{Al}_2\text{O}_3$ <sup>9)</sup> has been carried out by our research group in order to reduce the hazard in handling the whiskers themselves, and also to expect more homogeneous dispersion of them in the matrices because of difficulty in mixing the whiskers and matrices due to a remarkable difference in shape of the both. After a brief introduction of Yasuda's review, a result of the in-situ preparation of the whiskers in  $\text{Al}_2\text{O}_3$  is summarized here.

The other types of  $\text{Al}_2\text{O}_3$  based composite, such as the reaction-bonded one and  $\text{Al}_2\text{O}_3/(\text{Si})$  type in-situ composite, as well as the secondary-grain-reinforced body having better thermal shock resistivity due to the composed structure in spite of its improved mechanical strength, are also reviewed.

## II. SiC(w)-REINFORCED ALUMINA

During these several years, the effect of reinforcement brought about by SiC(w) has been investigated from a variety of view-points. The main items are the influence of their shape, size orientation and also of interface with  $\text{Al}_2\text{O}_3$ .

Figure 1<sup>10)</sup> shows a relationship between effective fracture energy of SiC(w) reinforced  $\text{Al}_2\text{O}_3$  and whisker dimension.

Concerning the fracture toughness, it is illustrated in Figure 2<sup>11)</sup> for example of the influence of interface, as a function of oxygen content of the whiskers employed.

It can be understood by these figures, what important roles these factors of whiskers play in this type of composite.

## III. IN-SITU PREPARATION OF SiC(w) IN ALUMINA<sup>9)</sup>

The principle of this procedure is to convert  $\text{SiO}_2$  in mullite to SiC(w) due to the reduction by co-existing C, added as a member of raw materials, resulting in SiC(w) reinforced  $\text{Al}_2\text{O}_3$  as a final form, keeping the residual  $\text{Al}_2\text{O}_3$  remained.

Weight ratios between 3 - 5 / 10 of a sort of carbon black / mullite, were mixed with water, followed by heat-treatment in a

graphite crucible at 1600°C for 2 - 3 h in Ar atmosphere. Excess carbon was removed by air oxidation of in-situ whiskerized product thus obtained, at 600°C for 3 h.

Figure 3-A shows the product of in-situ whiskerizing reaction where  $\text{Al}_2\text{O}_3$  and  $\text{SiC}(w)$  are coexisting; while Figure 3-B shows the waste-thread like part in the whiskers observed at a larger magnification.

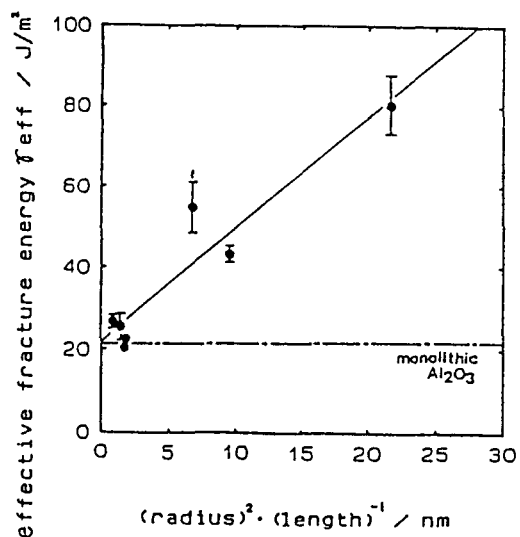


FIG.1. Effective fracture energy of  $\text{SiC}(w)/\text{Al}_2\text{O}_3$  vs. whisker dimension

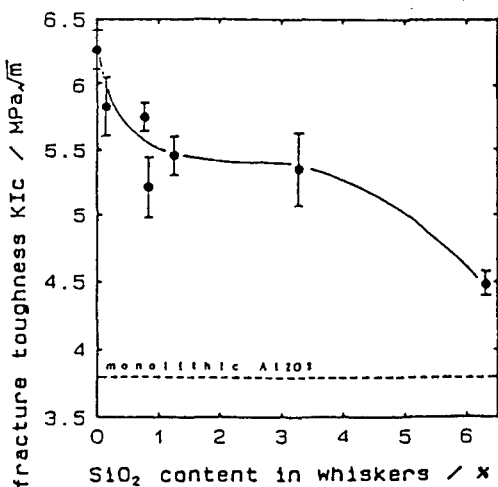
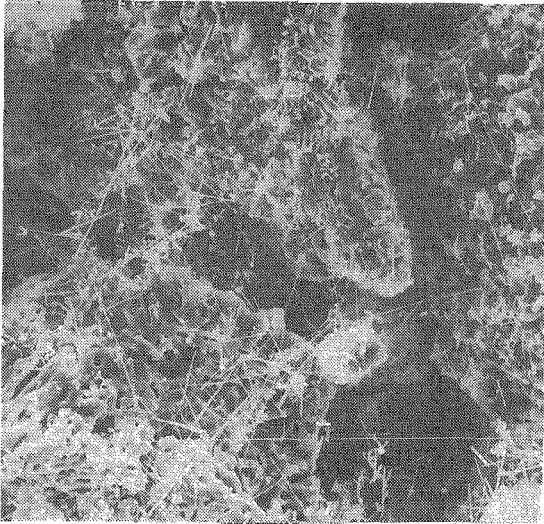


FIG.2. Fracture toughness vs.  $\text{SiO}_2$  content of  $\text{SiC}(w)$

Such whiskers having waste-thread like part, not straight but crooked, must play a negative role in their reinforcing effect. It was then found out that the addition of NaCl to the raw material mixture showed a remarkable behavior, scarcely to form such part in the reaction product. The reason why such an effect can be seen, may lie in the fact that the added NaCl boils at the beginning stage of the whiskerizing reaction, providing room enough to facilitate the whisker-growth. No trace amount of remaining NaCl could be detected in any resulting product. In-situ preparation of  $\text{SiC}(w)$  "among"  $\text{Si}_3\text{N}_4$  under pressure to obtain thicker whiskers, was observed only in the case of employing NaCl together with starting materials. This fact may suggest that NaCl

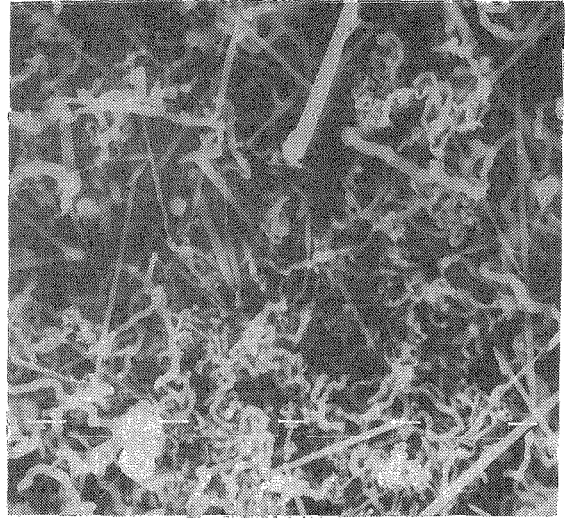
plays a role of space-making for this purpose.

As observed in Figure 4, no part having waste-thread like shape can be seen, and the in-situ prepared whiskers look remarkably straight being favorable in their reinforcement.



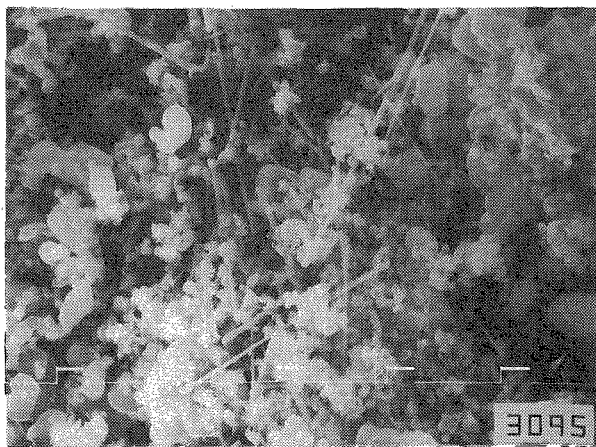
100 $\mu$

FIG.3-A. In-situ formed SiC(w) in  $Al_2O_3$  from mullite & C



10 $\mu$

FIG.3-B. Waste-thread-like part in FIG.3-A.



10 $\mu$

FIG.4. Straight SiC(w) in-situ formed in  $Al_2O_3$

The reaction product was treated by a tumbling mixer, followed by hot-pressing. After hot-pressing several specimens, however, it was found that the mechanical properties could not be improved in comparison with those in the case of regular physical mixing of SiC(w) with Al<sub>2</sub>O<sub>3</sub>, although the density was closed to the theoretical value in every former case.

As result of S E M investigation, the grain growth of Al<sub>2</sub>O<sub>3</sub> during the whiskerizing reaction was evidently observed, which was considered to be the main cause of these unsatisfactory mechanical properties. The efforts to solve the problem are now being made.

It may be of interest that similar procedures in the cases of SiO<sub>2</sub> plus C, zircon plus C, talc plus C and cordierite plus C, provided in-situ formed SiC(w) in silica, in zirconia, in magnesia and in spinel, respectively<sup>9)</sup>.

#### IV. REACTION-BONDED ALUMINA

##### A. Zirconia-Toughened Reaction-Bonded Al<sub>2</sub>O<sub>3</sub> (ZT-RBAO)<sup>12)</sup>

Claussen et al have recently made clear that the reaction bonding of Al<sub>2</sub>O<sub>3</sub> is strongly affected by addition of either ZrO<sub>2</sub> or Zr metal.

As is well known, the reaction forming procedure of ceramics has various advantages, such as low processing temperature, low raw material costs, near-net-shape tailorability and glass-phase-free grain boundaries.

The principle of this RBAO technology is illustrated as a schematic diagram in Figure 5. In the green state, "old" Al<sub>2</sub>O<sub>3</sub> particles are bridged by contacting Al particles containing oxide dispersions from mechanical alloying, followed by the reaction stage with an expansion, where the molten Al transforms to nano-sized Al<sub>2</sub>O<sub>3</sub> particles which sinter at temperatures above 1200°C.

The mechanism for the oxidation of molten Al is as suggested in Figure 6. Here, oxygen is transported either through the gas phase or by lattice diffusion through ZrO<sub>2</sub> particles to the Al particles. The high grain boundary density of the newly

formed  $\text{Al}_2\text{O}_3$  crystals represents the further fast pathway to the Al melt. Due to the increasing pressure in the confined Al particle, resulting from the 28% volume expansion on oxidation, the  $\text{Al}_2\text{O}_3$  scale ruptures and liquid Al spills into the void space.  $\text{ZrO}_2$  particles assist in transporting oxygen to the Al particles by lattice diffusion. During oxidation in air, this selective  $\text{O}^{2-}$  diffusion reduces the probability of  $\text{N}_2$  clogging the oxygen access. Especially in the later oxidation stage, i.e., when pores close due to rapid sintering of nanometer-sized  $\text{Al}_2\text{O}_3$  crystals, thorough and rapid oxidation of the RBAO body is guaranteed.

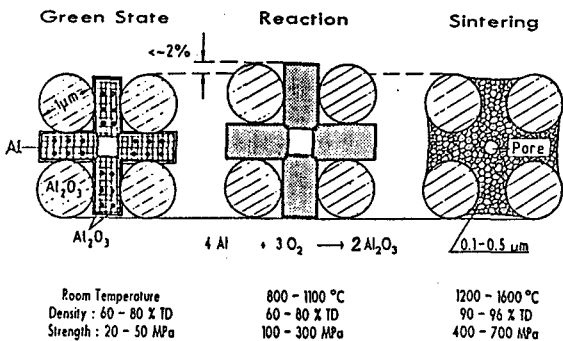


FIG.5.Principle of RBAO technology

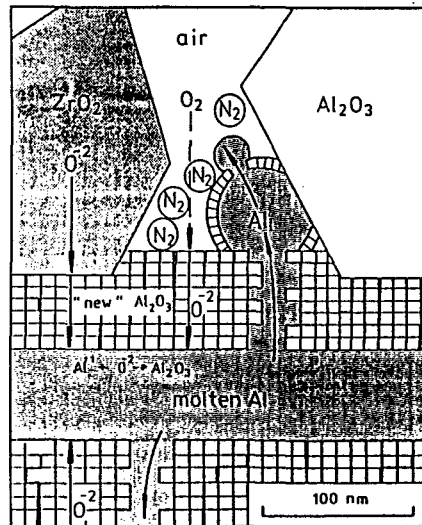
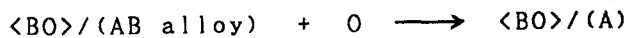


FIG.6.Suggested mechanism for reaction of Al

B.  $\text{Al}_2\text{O}_3$ /(Si) In-situ Composite<sup>13)</sup>

The principle to prepare this type of composite can be expressed as it follows;



where first fabricated  $\langle \text{BO} \rangle / (\text{AB alloy})$  composite is re-oxidized to form a metal B-free composite of  $\langle \text{BO} \rangle / (\text{A})$ .

For examples, Al-Mg-Si alloy as shown in Table 1 was directly oxidized at 1400 - 1700<sup>o</sup>K for 5 - 30 h, resulting in  $\text{Al}_2\text{O}_3 / (\text{Si})$  composite having no remaining unoxidized Al. A typical weight gain curve for the 4 different Al alloys in Table 1 is as shown in Figure 7.

TABLE 1. Chemical composition of Al-Mg-Si alloy (wt%)

Alloy	Mg	Si	Al
(A):Al-10Mg-5Si	9.5	5.6	bal.
(B):Al-5Mg-5Si	5.3	5.5	bal.
(C):Al-5Mg-10Si	5.2	10.3	bal.
(D):Al-10Mg-10Si	9.8	10.6	bal.

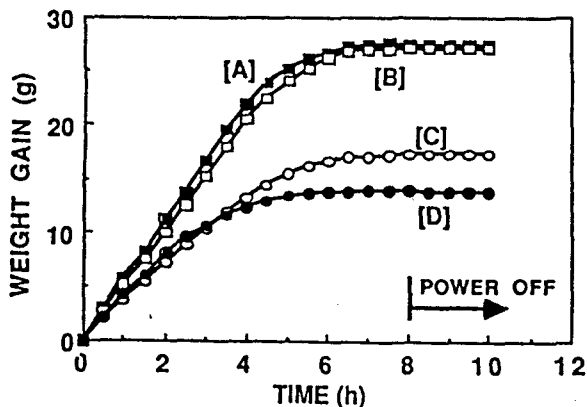


FIG.7. Plots of weight gain versus time during oxidation of liquid Al-Mg-Si alloys (A,B,C,D are the same as in TABLE 1.)

The content of Si influences the growth rate, but the content of Mg does not appear to influence it.

$\text{Al}_2\text{O}_3 / (\text{Al alloy})$  composite was first formed by the direct oxidation of viscous flow of Al alloy melt, because the standard free energy of  $\text{SiO}_2$  formation is higher than that of  $\text{Al}_2\text{O}_3$ . After the formation of  $\text{Al}_2\text{O}_3 / (\text{Al alloy})$  composite, oxygen diffuses

via three-dimensionally inter-connected  $\text{Al}_2\text{O}_3$  and the remaining unoxidized aluminum, which is located among formed  $\text{Al}_2\text{O}_3$ , is oxidized. In brief, the selective oxidation of Al in  $\text{Al}_2\text{O}_3$ /(Al alloy) composite leads to form  $\text{Al}_2\text{O}_3$ /(Si) composite. The formation speed of  $\text{Al}_2\text{O}_3$ /(Al alloy) composite can be controlled by the ratio of external pressure to the internal of the naturally formed vessels.

It should be noted that the long-length SiC fibers (Nicalon)/ $\text{Al}_2\text{O}_3$ /(Si)-composite was obtained from Al-5Mg-5Si alloy through this procedure. The microscopic picture is as shown in Figure 8.

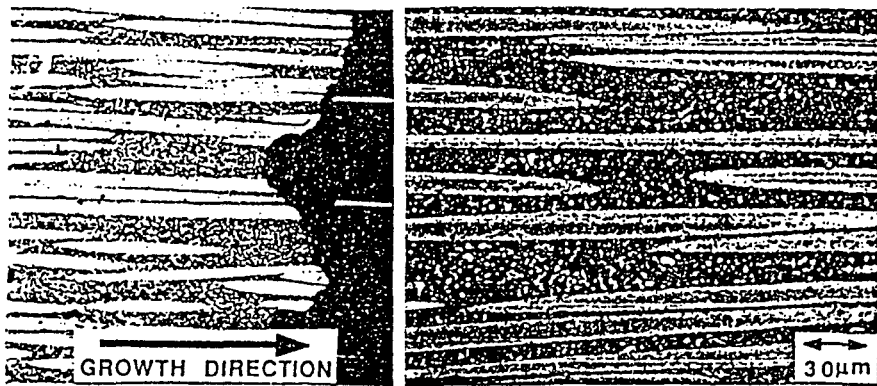


FIG.8. A microscopic picture of SiC(Nicalon)/ $\text{Al}_2\text{O}_3$ /(Si) composite

#### V. IMPROVEMENT OF THERMAL SHOCK RESISTIVITY BY "SECONDARY PARTICULATE PROCESS" ON $\text{Al}_2\text{O}_3$ -BASED BRICK<sup>14)15)</sup>

It is well known that the densification of refractory materials needed for severer operating condition in high temperature industries makes lower resistivity against thermal shock, i.e. so-called spalling, inevitably. This can be regarded as a fatal contradiction for the proper purpose in this field.

Under such circumstances, Ueno proposed a unique procedure, called "secondary particulates process" to solve this basic problem in 1977. This process was then developed in industries and applied to a variety of high temperature factories, where



this product was recognized in reality as an excellent one in the industrial sense in 1983<sup>16)</sup>. By this opportunity, the author would like to introduce this result as a sort of  $\text{Al}_2\text{O}_3$ -based ceramic composite, since this successful fact has not very widely informed yet for its industrial merit.

The way of thinking about this type of composite was originated by two following ideas; first, the density of secondary particulates must be high enough not to increase itself by any out-side pressure, and secondly, the particules must deform without fracture under the pressure just like clay, so that the total volume of void among the grains can decrease, resulting in a homogeneous green body having the same density at every part. If the particulates reduce to the primary fine or ultra-fine particules, the lamination is apt to occur during the forming process, which is one of the main causes to make both of thermal shock resistivity and strength poorer.

The most desirable results are obtained with respect to spalling resistance in a dense structure refractory when the proportions of the fine powder, fine grain and more coarse particles are kept within specified ranges. The proportion of fine grain particles of the secondary particulate of the 0.1-0.5 mm size range should be from 0 to 30% and the balance, 60-100% should be composed of particles of the secondary particulate which are as coarse or coarser than the intermediate grain size and are larger than 0.5 mm. The specimens having the content range of secondary particulates of 0.1 - 0.5 mm in size, were found to be well-balanced from the both stand-points of spalling resistivity and high density, where high density means high chemical resistivity.

In the case of alumina refractories, for example, Figures 9A and 9B are schematic diagrams which show the structure of the refractories that are obtained by molding followed by firing a mixture of the particle size composition that consists of 5% of a secondary particulate which is less than 0.1 mm in size, 15% of a secondary particulate which is within the range of 0.1-0.5 mm in size, 30% of a secondary particulate within 0.5-1 mm, and 50% within 1-3 mm, according to the above mentioned technical

concept. Figure 9A schematically illustrates a boundary region that is formed between the fine powder and fine grain secondary particulate and the intermediate coarse grain secondary particulate in alumina refractories. Figure 9B is an enlarged illustration of the boundary region.

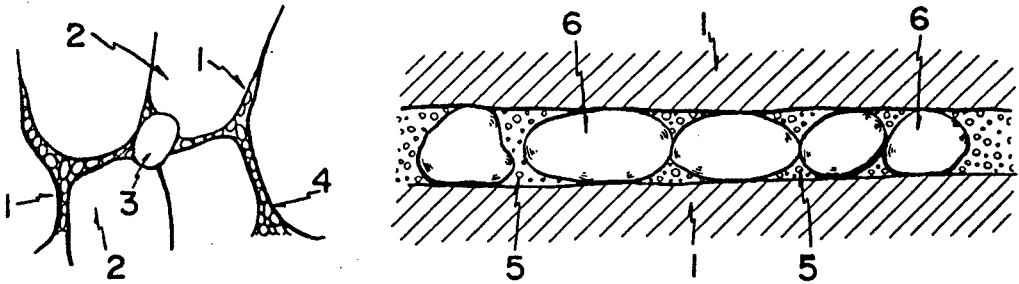


FIG.9A. A schematical boundary region      FIG.9B. An enlarged boundary region

In Figure 9A, 1 refers to the coarse grain secondary particulate, 2 indicates the coarse grain secondary particulate having been deformed by pressing, 3 shows the intermediate grain secondary particulate and 4 represents the boundary region deformed from the fine grain secondary particulate. 1 in FIG.9B is the coarse secondary particulate, 5 is the finely powdered secondary particulate and 6 is the fine grain secondary particulate. The coarse and intermediate grain secondary particulates become a high density area and the boundary region forms a low density area. This heterogeneity of the structure increases the spalling resistivity, whereas the homogeneous texture provides a poor spalling resistivity. Interstices formed by the control of forming pressure to avoid the deformation of secondary particulates, play a big role to improve the spalling resistivity, although they have a negative effect to the chemical resistivity. Cracks caused by thermal stress to the low - density area, develop in zigzag manner along this area, and release the stress.

Several typical examples of improvement of thermal shock resistivity on  $\text{Al}_2\text{O}_3$ -based refractories are summarized in Table 2, which are only a few results selected from a large number of experiments.

TABLE 2. A typical example of improvement of thermal shock resistivity on  $\text{Al}_2\text{O}_3$ -based brick

	secondary particulate process				ordinary particulate	
	No.1	No.2	No.3	No.4	No.5	No.6
particle size						
3-5 mm	0	0	30	30	30	0
1-3 mm	0	60	40	40	40	60
0.5-1 mm	40	30	15	30	30	30
0.1-0.5 mm	40	0	15	0	0	0
smaller than						
0.1 mm	20	10	0	0	0	10
apparent spe- cific gravity	3.78	3.76	3.86	3.88	3.96	3.87
bulk specific gravity	3.46	3.61	3.64	3.53	3.13	3.20
apparent poro- sity(vol%)	8.3	4.1	4.2	8.6	21.0	17.3
panel spalling test, the number of times*	1	6	11	12	13	16
$p/p_o$ ****	0.96	0.98	1.00	0.98	**	***

\* The condition for the test:

Specimens were a standard shaped brick of 230 x 114 x 65 mm, the test consisting of heating one side of the specimen in a laboratory furnace at  $1200^{\circ}\text{C}$  for 15 min. and subsequently cooling in cold air and repeating this heating and cooling. The results are expressed as the number of times the specimen will stand this treatment without spalling.

\*\* inferior appearance, very brittle.

\*\*\* slightly inferior appearance, brittle.

\*\*\*\*The value of specific gravity of the molded green product,  $p$ , can be adjusted in the range 0.95 to 1.00 of the value of the average bulk specific gravity of the secondary particulate,  $p_0$ . If  $p$  is lower to some degree than  $p_0$ , many cracks will develop in the structure of the fired brick obtained from the green one. The reason is that since the secondary particulate consists of ultra-fine particles, shrinkage produced in the particles of the secondary particulate by the sintering results in pulling apart of the particles from each other.

In addition to such a basic improvement, it has been recognized that this procedure has several other advantages in industry, such as the possibility to make a mass-production, and also that to apply to a tunnel-kiln process, as well as a high dimensional accuracy of the formed bodies and an easiness to prepare the composite system in texture.

## VI. SEVERAL OTHER MISCELLANEOUS MATTERS

Research works on a variety of nano-composite containing  $Al_2O_3$  matrix have recently been quite remarkable. Table 3 summarizes an example of them in comparison with the other matrices<sup>17)</sup>.

As one of the other topics, it should be noted that a SiC(W)-reinforced  $Al_2O_3/ZrO_2$  composite showed a remarkable improvement of the flexural strength.

The application of  $Al_2O_3$  powder, reinforced by SiC(w) or by  $Si_3N_4$ , to a plasma spraying process as a coating material for fusion reactor, is also of interest. The thermal shock resistivity of the coat was improved by the whisker addition to a remarkable extent<sup>18)</sup>.

TABLE 3. Improvement of mechanical properties by the preparation of nano-composite structure

Nano-composite	Fracture toughness (MPa.m <sup>1/2</sup> )	Strength (MPa)	Heat-proof temperature (°C)*
Al <sub>2</sub> O <sub>3</sub> / SiC particle	3.5 → 4.8	350 → 1520	800 → 1200
Al <sub>2</sub> O <sub>3</sub> / Si <sub>3</sub> N <sub>4</sub> particle	3.5 → 4.7	350 → 850	800 → 1300
MgO/ SiC particle	1.2 → 4.5	340 → 700	600 → 1300
Si <sub>3</sub> N <sub>4</sub> / SiC particle	4.5 → 7.5	850 → 1550	1200 → 1500

\* Maximum available temperature under high load

## VII. Conclusion

Several sorts of recent alumina based ceramic composite are summarized. It consists of SiC(w) reinforced types including an in-situ prepared whiskers, newly developed types of the reaction bonded ones, secondary-grain-processed one having an excellent thermal shock resistivity, as well as nano-sized one and the other types. The common purpose is to improve the strength, fracture toughness or thermal shock resistivity. The problems seem to have been solved to a certain extent, but further research is still required.

## ACKNOWLEDGEMENT

The author is greatly indebted to Prof.S.Somiya, and Prof.E.Yasuda for their kind and thoughtful suggestions, and

also to Mr.H.Ueno of Kurosaki Refractories Co.Ltd., and Mr.J.Oka of Kansai Ceramics Co.Ltd. for their profitable advices and eager helps.

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