N O T I C E

NASA TECHNICAL MEMORANDUM NASA TM 75744

HIGH PRESSURE SINTERING OF NON-OXIDE MATERIALS

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(NASA-TM-75744) HIGH PRESSURE SINTERING OF NON-OXIDE MATERIALS (National Aeronautics and Space Administration) 7 p HC A02/MF A01 CSCL 11F

N80-21491

Unclas G3/26 46854

Translation of "Hikinzoku No Koatsu Kessho", J. of Japan Society of Powder and Powder Metallurgy, vol. 25, no. 8, Dec., 1978, pp. 275-276.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 NOVEMBER 1979

STANDARD TITLE PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-75744		

4. Title and Subtitle	5. Report Date / 6. Performing Organization Code
HIGH PRESSURE SINTERING OF NON-OXIDE MATERIALS	November 1979
7. Author(s)	8. Performing Organization Report No.
Masahiko Shimada, Noriyuki Ogawa, Mitsue Koizumi	10. Work Unit No.
9. Performing Organization Name and Address	11. Contract or Grant No.
SCITRAN Box 5456 Santa Barbara, CA 93108	NASW-3198
	13. Type of Report and Period Covered
	Translation
12. Sponsoring Agency Name and Address	14. Sponsoring Agency Code
National Aeronautics and Space Administration Washington, D.C. 20546	

15. Supplementary Notes

Translation of "Hikinzoku No Koatsu Kessho", J. of Japan Society of Powder and Powder Metallurgy, vol. 25, no. 8, Dec., 1978, pp. 275-276.

16. Abstract

High pressure sintering of pure materials of AIN, α-Si_3N_4 and TiC, without additives, was carried out at 800-1400°C under the pressures of 30 kbar and 50 kbar for 0.5 hours. The maximum density of sintered bodies for the cited materials was nearly 100% for AIN, 98% for TiC and 96% for α-Si_3N_4. 9 refs. In Japanese.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22.
Unclassified	Unclassified	7	

NASA-HQ

High Pressure Sintering of Non-Oxide Materials** /27*

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High pressure sintering of pure materials of AIN, α- Si_3N_4 and TiC without additives was carried out at 800-1400°C under the pressures of 30 kbar and 50 kbar for 0.5 hr. The maximum density of sintered bodies for the above materials was nearly 100% for AIN, 98% for TiC and 96% for α-Si_3N_4.

1. Introduction

One of the characteristics of ceramic materials is their high heat resistance. This feature was discovered particularly in recent years. Many attempts have been made to use non-oxide ceramic materials such as Si_3N_4, SiC and AIN as high temperature, high stress, structural materials which replace metals in the high temperature range beyond the limit of their heat resistivity. However, non-oxide materials which are excellent high temperature, high stress, structural materials generally have strong covalent bonds and the rates of the self-diffusion of the computers are very small. Consequently, they are not easily sintered compared to the case of oxides. Therefore, in order to increase the density of sintered bodies, the hot press method is usually applied to make dense ceramics. In this method, appropriate additives are added to the materials. As additives for sintering Si_3N_4, MgO[1] and Y_2O_3[2,3] are well known. For AIN, Y_2O_3[4] is used. Metals such as iron and aluminum[5] and B_4C and Al_2O_3[6] and a mixture of boron and carbon[7] are used as good additives for sintering the SiC ceramics. However, the additives used for making denser materials are often reduced as the second phase, such as a glass layer at the boundary of sintered bodies. Consequently, mechanical prop-

* Numbers in margins indicate foreign pagination.
**Reported in the spring meeting of the present society in May, 1978.
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erties of the materials are weakened significantly in the high temperature range[3].

Therefore, in order to obtain non-oxide ceramics which possess good mechanical properties at high temperatures, it is necessary to obtain sintered bodies of high purity and high density having a theoretical density without using these additives. For this purpose, we have been experimenting in sintering non-oxide materials such as carbides and nitrides of high purity and high density by using a high pressure sintering method without using additives. These materials are believed to be difficult to sinter. In the present report, we present the summary of our study.

2. Test samples and the experimental procedure.

The raw materials used for the high pressure sintering experiment are AIN made by Nippon Denko Co., α-Si_3N_4 made by the Stark Co. and TiC made by Keunametal Co. Their characteristics are shown in Table 1.

The high pressure cell used in high pressure sintering is a regular hexagonal high pressure cell (DIA-15) which has an aubill of 15mm. As is shown in Figure 1, pyrophylite was used for the pressing materials, and heating was done by electric currents in a graphite heater. The temperature was measured by a thermocouple placed inside the cell. First, the pressure of the sample room in the cell was measured by using the Bi I-II transition at 25.5 k bars and Ba I-II transition at 55 kbars at room temperature. These Bi and Ba are the pressure detectors. The high pressure sintering experiment was carried out for 30 minutes at temperatures of 800°C-1400°C and pressures of 30 kbar and 50 kbars. The densities of sintered bodies were measured by the Archimedes method. The values are shown in Table 1 as the relative densities using the theoretical density values. Also, we found the values T/T_m, where T is the sintering temperature and T_m is the melting point

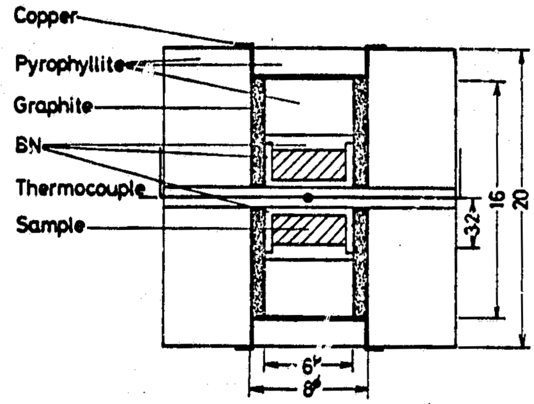

Figure 1. Diagram of high pressure cell assembly used for high pressure sintering.

shown in Table 1, and analyzed their values with respect to the relative density. /28

Table 1 Characteristics of the pure materials

	Crystal structure	Purity (%)	Particle size (μ)	Theoretical density (g/cm³)	Melting or dissociation point* (°C)
AlN	ZnS-type	96	2.5	3.27	2200*
Si_3N_4	α-Si_3N_4-type	99.9	2.0	3.18	1850*
TiC	NaCl-type	99.7	1.3	4.92	3257

3. Experimental results and discussions

Figure 2 shows the case when AIN, α-Si_3N_4 and TiC were high pressure-sintered at 30 kbars and 50 kbars without using additives. The horizontal axis T/T_m in Figure 2 represents the calculated values explained in the section for the experimental procedure. The sintering temperature was normalized by using the melting point which is characteristic of each material. This variable was used to compare the effects of pressure and temperature on increasing densities of various materials.

As shown in Table 1, AIN has 96% purity. Therefore, because

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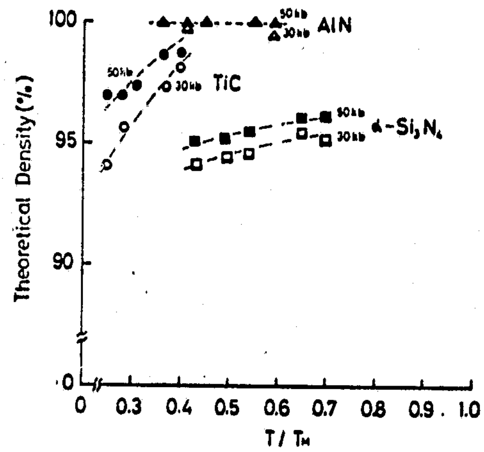

Figure 2. Densification of pure materials under high temperature-pressures.

of effects of the impurities, we obtained the sintered body having a theoretical density. However, when α-Si_3N_4 of higher purity were used, the density of the former could not increase beyond 96% of the theoretical values and the latter 98% of the theoretical value, in spite of the high pressure of 50 kbars and the sintering temperature of 1400°C. The pressure had a small effect on the densities of both materials. However, the temperature had almost no effect in the case of α-Si_3N_4. This is probably due to the small self-diffusion rate of nitrogen in α-Si_3N_4 as reported by Kizima, et al.[8] Also the rate does not increase significantly with temperature, in contrast to the case of oxides. Therefore, in order to obtain sintered bodies of the Si_3N_4 ceramics having the theoretical densities without additives. We must either sinter β-Si_3N_4 which has a large nitrogen self-diffusion rate at a high temperature and a high pressure, or use non-crystalline Si_3N_4 as the starting material and sinter it at a high pressure and a high temperature, with simultaneous crystallization.

On the other hand, the temperature had a large effect on increasing the density. This is in contrast to the cases of TiC and α-Si_3N_4. At 50 kbar pressure we could obtain sintered bodies of theoretical density at the values of T/T_m of $\sim$0.5. For the same carbide SiC, Nadeau[9] carried out high pressure sintering experiments without using additives. He found that the density could reach almost the true specific weight at 800°C, and above 1500°C, sintered bodies of self-bonding were obtained. Concerning non-oxide ceramic materials, there are few experimental reports which used the usual hot press method or the high pressure sintering method without using additives. Therefore, we can not compare and examine effects of pressure and temperature and also effects of particle size of the initial materials on the sinter reaction. We intend to try the high pressure sintering method on many non-oxide materials in the future, and examine effects of temperature, pressure, time, the granular size of initial materials and difference of crystal phase on the density. We also intend to observe the fine structures of sintered bodies and the hardness in the high temperature range in order to clarify the sintering mechanism of non-oxide materials which are normally very difficult to sinter.

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