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SINTERING OF URANIUM MONONITRIDE

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Sintering of Uranium Mononitride

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Uranium mononitride was produced by decomposing the sesquinitride in vacuum at vorious temperatures. Sintering of the mononitride at 1800 ℃ for 4 hours in argon was studied for the powders prepared under different conditions. The sintered density considerably depended on the milling time of the powders; the highest density attained was 95 % of the theoretical for the nitride milled for 66~72 hours. The decomposition temperature of U_2N_3 into UN did not so much influence the sintered density as the milling time did. In the sintered material open pores dominate below density 90 % of the theoretical, and closed pores do above this value. Some of characterizations of the sintered specimens were also carried out.

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窒化ウランの焼結

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（1975年2月6日受理）

三窒化二ウランを種々の温度で真空中で熱分解して，一窒化ウランの生成を行った。種々の条件で調製された粉末を用いて，アルゴン中，1800℃において，4時間，一窒化ウランの焼結性を調べた。焼結密度は粉砕時間に著しく依存して，66～72時間粉砕された窒化ウランについては，その最高密度が理論密度の95％にも達した。U_2N_3 からUNへの分解温度は焼結密度にあまり影響を与えなかった。理論密度の90％以下の密度範囲では開気孔が豊富で，90％以上の範囲では閉気孔が優勢であった。焼結された試料のキャラクタリゼーションがいくつか行なわれた。

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目　次　な　し

1. Introduction

The fabrication of uranium mononitride and uranium-plutonium mononitride have been studied by many workers. Since a fabricaton of these materials by cold-pressing and sintering has been often reported to be difficult to achieve a high density, other fabrication works such as hot-pressing and arc-melting have been conducted. To obtain a higher density pellet of nitride by the method of cold-pressing and sintering, several conditions affecting the sinterability of it have been studied; the effects of oxide[1-3] and uranium sesquinitride[4], and the effect of milling time of powders to be sintered[2,5], in addition to the sintering temperature and the sintering time. The effect of nitrogen pressure has been also studied[8].

In the present study, an effort was particularly endevored to the effect of milling time of UN powders and that of the decomposition temperature of the sesquinitride U_2N_{3+x} on the densification of sintered UN. Through the studies on the parmeters of these effects, the characterization of the prepared specimens was carried out. The sintered UN specimens with a wide range of densities were obtained, which enabled to study the density dependence of some properties such as thermal conductivity of uranium mononitride.

2. Experimental

2.1. Preparation of uranium mononitride.

Formation of uranium sesquinitride by a reaction between uranium hydride and nitrogen and the decomposition of the sesquinitride into the mononitride were studied with use of a thermo-balance. The decomposition U_2N_{3+x} to UN was also studied in a vacuum and in a nitrogen atmosphere.

Uranium nitride used in this experiment was provided in 220~250 g batches. Uranium metal block, cleaned by leaching with nitric acid, was placed in a beryllia cruicible and heated at 200 ℃ in a graphite furnace in a flowing atmosphere of purified hydrogen. The reaction product was determined to be UH_3 from the weight increase of the reactant. At 350 ℃ UH_3 was decomposed into uranium metal powder and hydrogen in hydrogen atmosphere of 1 atm.

Uranium hydride thus obtained was converted at a higher temperature in nitrogen atmosphere into the higher nitride ($UN_{1.7}$). The reaction between UH_3 powder and nitrogen started at 300 ℃. The nitride formed by this reaction was determined to have Mn_2O_3 type b.c.c. structure from an X-ray diffraction pattern and the value of nitrogen to uranum ratio was estimated to be about 1.7 from the weight increase of the specimen.

The product U_2N_{3+x} obtained by the reaction around 700 ℃ was decomposed into the mononitride at temperatures 1100, 1200, 1300, 1400 and 1500 ℃ in vacuum of 3×10^{-5} Torr. The results of the decomposition of U_2N_{3+x} in thermogravimetry are shown in fig.1. The decomposition began in a vacuum around 900 ℃ and finished at 1100 ℃. In nitrogen atmosphere it began at 1300 ℃ and finished at 1600 ℃. The curve of weight decrease showed the plateau at the N/U ratio of 1.5. Decomposition of UN began around 1800℃ in a vacuum, whereas it did not take place up to 2200 ℃ in nitrogen.

Then, the powders of UN thus obtained were ball-milled for various times; 0, 24, 48, 72 and 100 hours using an alumina pot mill filled with argon gas. The resulting powders were examined with an electron microscope of two stage replica method.

Figure 2 shows electron micrographs of the UN powders formed at various decomposition temperatures and those after ball milling. The particle size of UN powder was found to be about 10 μm or more before milling and 0.5~1 μm after milling.

The compacts, which were pressed at 3 t/cm^2 with no binder in dies lined with tungsten carbide, were sintered at 1800 ℃ for 4 hours in flowing argon, as a standard case.

2.2. Characterization method of the specimens.

Various properties of sintered uranium mononitride prepared by the way above described were examined. Apparent density was measured by a displacement method using xylene, which was easily penetrated to open pores by vacuum impregnation. The density of xylene was measured with a specific gravity float. Bulk density was determined from a measurement of the dimension of the specimen. Open and closed porosities were calculated from the both desities above cited.

Nitrogen content of the specimen was chemically analyzed by the Dumas method; the typical value was found to be about 5.42 wt%. The lattice parameter was measured by X-ray diffraction method. A small amount of uranium dioxide phase was observed in a X-ray diffraction pattern for each specimen. The content of UO_2 phase was determined from a calibration curve of the UO_2 concentration versus the intensity of 1 1 1 reflection.

Microstructure of the specimen was observed with an optical microscope and a free surface of the sintered specimen with an electron microscope.

3. Results and discussion.

3.1. Effect of milling time on density

Sintered bulk density and green density are shown in fig.3 versus milling time before sintering. Bulk density of sintered UN specimen was found to be strongly dependent on the milling time. Sintered bulk densities of the specimens obtained without milling were 68～78 % of the theoretical density (%TD). The green densities were in the range from 55 to 61 %TD, increasing with the decomposition temperature. In the case that the powders had been milled for the first 24 hours, the sintered and green densities were increased. The increase of sintered density was remarkable, arriving at 83～90 %TD. These results are relevalent to that a particle size of the powder thermally decomposed alone without milling was large; the sintered and green densities were small, comparing to those which had been milled after decomposition. In addition, UN powder formed by themal decomposion, which is agglomerated, seems to be easily milled during the milling process. For the nitride milled for 48 hours, sintered densities were 90～94 %TD. For the nitride milled for 66～72 hours of the powders decomposed at 1100, 1200, and 1400 ℃, the highest of the sintered density achieved was 95 %TD.

The results that the sintered densities were strongly increased with the milling time and that the highest density about 95 %TD was achieved for the compacts after milling for ～70 hours show the similar tendency to the results obtained by Goodyear et al.[5] and McLaren et al.[2] On the other hand, with regard to the dependence of milling time on the green density the results are contradict to the results by Goodyear et al.[5], who observed that it was gradually decreased with milling time.

3.2. Effect of the decomposition temperature on density.

Figure 4 shows the green and sintered bulk densities versus decomposition temperature for various milling times. While green density was monotonously increased with decomposition temperature, sintered density was slightly decreased with it. This fact suggests that during the decomposition process sintering partly have occured at a range of decomposition temperature to inhibit a densification at the higher sintering temperature of 1800 ℃. The sintered bulk density arrived at 95 %TD and 92 %TD for the specimens decomposed at 1100 and 1500 ℃ respectively. Some workers have observed an enhancement of densification of UN due to the existence of U_2N_3 phase in the material.[4] The slight decrease of the density with the decomposition temperature might be related to this fact other than the reason discussed above.

3.3. Effect of sinterd temperature on the density for the case of wet milling.

In a preliminary experiment preceding that was described in the above sections, the effect of the sintering temperature on the sintered density was examined for UN powder wet-milled using the same ball-mill as used in the above experiments. The powders that was not satisfactorily sintered were produced. The density achieved was not more than 88 %TD, when the powders milled for 48 hours were sintered, as shown in fig.5. In this figure, the effect of sintering temperature on the densification is found not to be clear, as far as for the exmined temperature, 1800, 1900, and 2000 ℃, whereas the milling time is effective to the density, being similar to the case of the dry milling. The results that the sintering temperature above

1800 ℃ affects little the density are consitent with the experimental results conducted by Goodyear et al.[5], which include the same temperature range. In addition, the density lower than that of dry-milling has been also observed by McLaren et al.[2]

In a ceramographic examination, the specimen sintered at 2000 ℃ was found to have continuous grain boundary networks of free uranium.

3.4. Effect of sintering time on the density.

The effect of the sintering time on the density was also studied for the wet- milled compacts, for the various conditions of wet-milling time and sintering temperatures. As shown in fig.6, the sintered density was found to be little dependent on the sintering time.

3.5. Sintering behavior of the compact obtained with use of a laboratory planetary ball-mill.

An alternative powder treatment was attempted using a laboratory planetary ball-mill. As shown in fig.7, a few hours of milling (dry) introduced a great increase of the sintered density after firing at 1600 ℃ in vacuum. For the sintering at 1700 and 1800 ℃ in argon flow the highest density 93 %TD was obtaind for the compact sintered at 1800 ℃ following the powder milling for 4 hours. Whereas a correlation between the density and the preparation conditions is not clear and the values of the sintered densities are slightly less by a few per cents, comparing to the case of roll type milling described in the above sections.

3.6. Shrinkage and weight change of the sintered pellet.

Shrinkage of diameter and length of the sintered pellet produced with the dry pot-milled powders was measured. As shown in fig.8, the shrinkage of the sintered specimen was large, as the milling time was increased and as the decomposition temperature was decreased. These behaviors are corresponding to the density change after the sintering. The rate of the shrinkage of diameter was found to be larger than that of length.

Weight change of UN compact during sintering was studied, which is shown in fig.9. The lowest value of weight loss was 0.2 wt% for the nitride decomposed at 1300 ℃ without milling. The highest value was 0.65 wt% for pellets of a decomposition temperature 1100 ℃ and a milling time 66 hours. Weight loss was monotonously increased with the milling time, except for the specimen decomposed at 1100 ℃.

3.7. Abundance of open and closed pores.

In fig.10, volume fraction of open pores which was determined from the measurement of apparent density is plotted by a full curve. A dashed line simply means a relation between total porosity and density. The difference between the dashed line and the full curve provides a volume fraction of closed pores. These curves indicate that there became closed pores abundant above the density about 90 %TD, comparing with the open pores. The distribution of the closed and open pores in this result is consistent with the data of uranium dioxide[6]. The characteristics of this abundance of open and closed pores is essentially relevalent to the behavior such as the porosity

dependence of thermal conductivity of the UN specimins, as described briefly in the later section.

3.8. Microstructure of the sintered specimen.

Microstructure of the sintered uranium mononitride was observed; the typical ones of it are shown in fig.11. The micrograph of fig.11(a) was obtained using a specimen etched with 30 lactic-10 nitric-2 hydrofluoric acids and that of fig.11(b) etched with H_2PO_4(conc.) at 125 ℃. From these observations the measured values of the grain size of sintered material are shown in fig.12 versus milling time of powders. The specimen sintered for 4 hours at 1800 ℃ in argon flow had an average grain size of 6 to 15 μm, increasing with the increase of milling time. Dependence of grain size on decomposition temperature was not remarkable. Obseravation of grain size was difficult for the sintered UN obtained without milling, because of its less sinterability.

Free surface of the sintered UN was observed with the replica electron microscope. Figures 13 (a), (b) show electron micrographs of the specimen sintered after the milling for 100 hours. Apit with fine steps of cubic symmetry was observed, which suggests a relatively regular crystallite growth took place during sintering.

3.9. Lattice parameter of UN and UO_2 phases within the specimen.

The X-ray diffraction pattern of a surface of a specimen sintered in argon flow indicated the existence of UO_2 and U_2N_{3+x} phases. These phases were often reported to be observed in sintered UN and to be sometimes related to the improvement of the sintering of UN.[1-4] The present results mean a possibility

that there were these phases on the surface of UN body. Lattice parameter and UO_2 content in some of the sintered specimens are shown in fig.14; the lattice parameters are in the range from 4.8891±0.003 Å to 4.8903±0.0003 Å, and UO_2 contents were within a range 0.5 to 1.5 wt%, increasing with the density.

3.10. Hardness of the sintered UN.

Micro Vicars hardness of the sintered UN before and after polishing was measured, which is summarized in table 1. Hardness of a polished specimen of 91.5 %TD was 500~506 kg/mm^2 at the center position of a pellet and 516 kg/mm^2 at the side. The surfaces of the specimens of 95.2 and 95.4 %TD had somewhat higher hardness values of 525~552 kg/mm^2 than those of the polished specimen. These different values of hardness is presumed to be owing to the density of the UN specimen and or the existence of UO_2 phase on the surface.

3.11. Thermal diffusivity of UN of various densities.

Using the specimens of various densities, thermal diffusivity was measured in a temperature range from 300 to 1500 ℃ by a laser flash method. In the results of thermal diffusivity as well as themal conductivity derived from the diffusivity, porosity dependence of thermal diffusivity and conductivity was found to have a break point around a porosity value of 0.1. This behavior is shown in fig.15 and fig.16. More details of the results and the discussons have been published elsewhere.[7)]

4. Conclusions

1. Uranium mononitride powders were produced by decomposition of the sesquinitride in vacuum at different temperatures and by ball-milling for various times 0～100 hours.

2. Sintering of uranium mononitride was studied at 1800 ℃ for 4 hours in flowing argon, using the UN powders prepared through various conditions.

3. The sintered density was much dependent on the milling time of powders; the milling was conducted for 0, 24, 48, 72 and 100 hours. The highest density achieved was 95 %TD.

4. The decomposition temperature of U_2N_3 to UN did little affect the sintered density, comparing with the milling time.

5. The effect of sintering temperature and time on the sintered density was not clear in the temperature range from 1800 to 2000 ℃.

6. The abundance of open pores was dominant below the density 90 %TD, whereas that of closed pores was dominant above this density.

Acknowledgement

The authors are grateful to Mr.K Shiozawa for his helpful work of the electron microscopy of the sprcimens.

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Figure captions

Fig. 1. Weight change of uranium nitride with temperature.

Fig. 2. Replica electron micrographs of surfaces of UN powders.

Fig. 3. The effect of dry milling time on the sintered bulk density and green density of UN. Sintering: 1800 ℃, 4h, Ar.

Fig. 4. The effect of temperature of decomposition on the sintered bulk density and green density of UN.

Fig. 5. The effect of sintering temperature on bulk density for the case of wet milling.

Fig. 6. The effect of sintering time on bulk density.

Fig. 7. The effect of sintering temperature on bulk density. Milling machine: planetary ball mill(dry), sintering time:4h.

Fig. 8. The effect of dry milling on the shrinkage of diameter and length.

Fig. 9. Relation between weight loss and milling time.

Fig. 10. Relation between sintered bulk density and porosities.

Fig. 11. Microstructure of a sintered UN at 1800 ℃ to 94.7 % of theoretical density. 64 h milling. x600. (a) 30 Lactic-10 Nitric-2 Hydrofluoric Etch. (b) H_2PO_4(conc.) 125 ℃ Etch.

Fig. 12. Relation between grain size and milling time. 1800 ℃, 4h, argon flow.

Fig. 13. Electron micrograph of free surface of sintered UN: 100h milling, decomppsed at 1500 ℃, density, 91 %TD.

Fig. 14. Relation between lattice parameter and UO_2 content in sintered UN pellets.

Fig. 15. Temperature dependence of thermal diffusivity of uranium mononitrides of various densities.

Fig. 16. Porosity dependence of themal diffusivity of uranium mononitride for various temperatures. The slope of diffusivity versus porosity curve is larger for the larger porosity than for the smaller porosity range.

Table 1. Micro- Vickers Hardness.

Lapping	Before polishing		After polishing	
position	Center		Center	Side
Milling time (dry), h	66	90	100	
Decomposition temperature, ℃	1100		1500	
Bulk density, % TD	95.2	95.4	91.5	
Average of micro-Vickers hardness, kg/mm^2	532 540	552 525	500 506	516

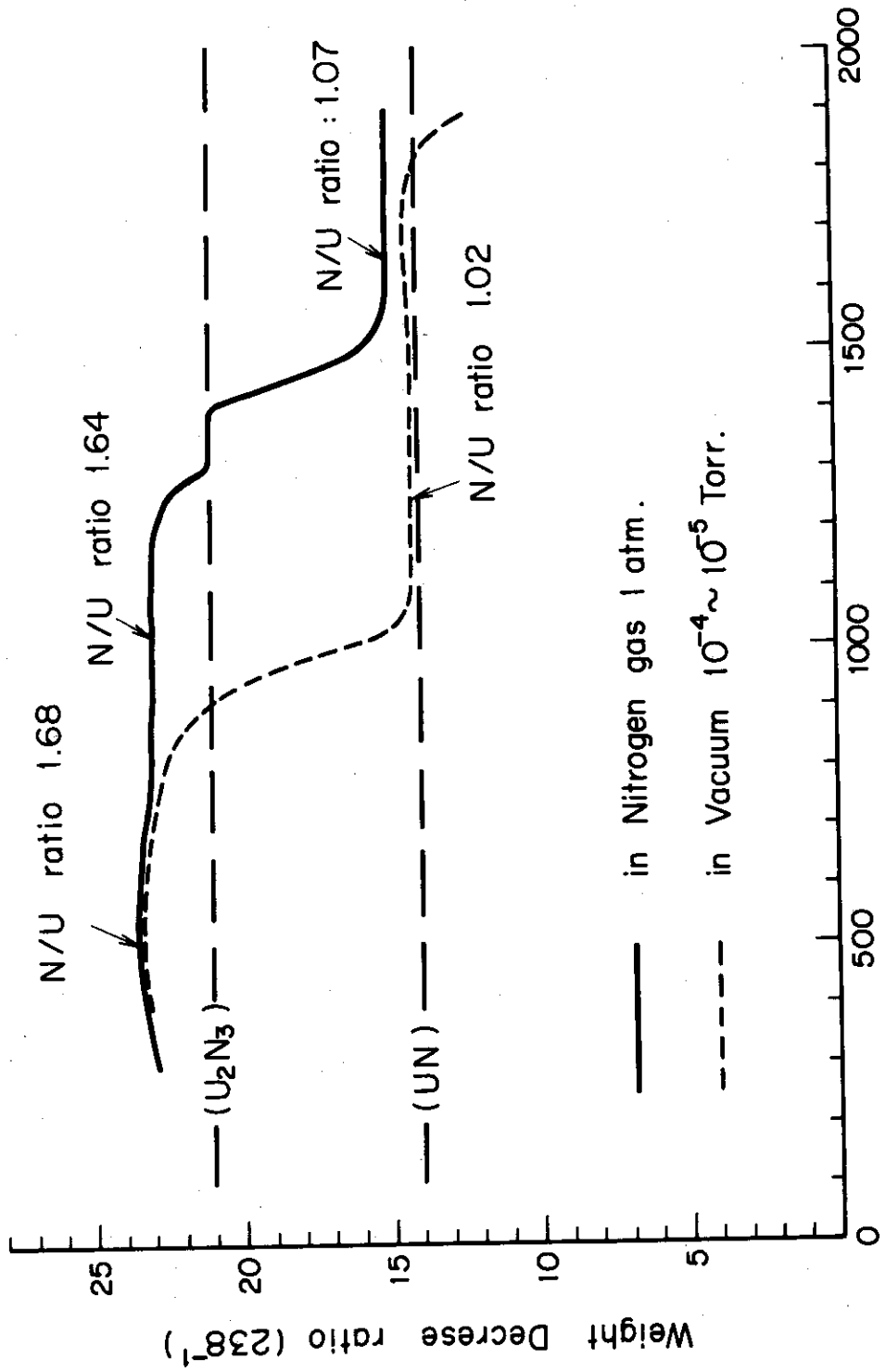


Fig. 1 Weight change of uranium nitride with temperature.

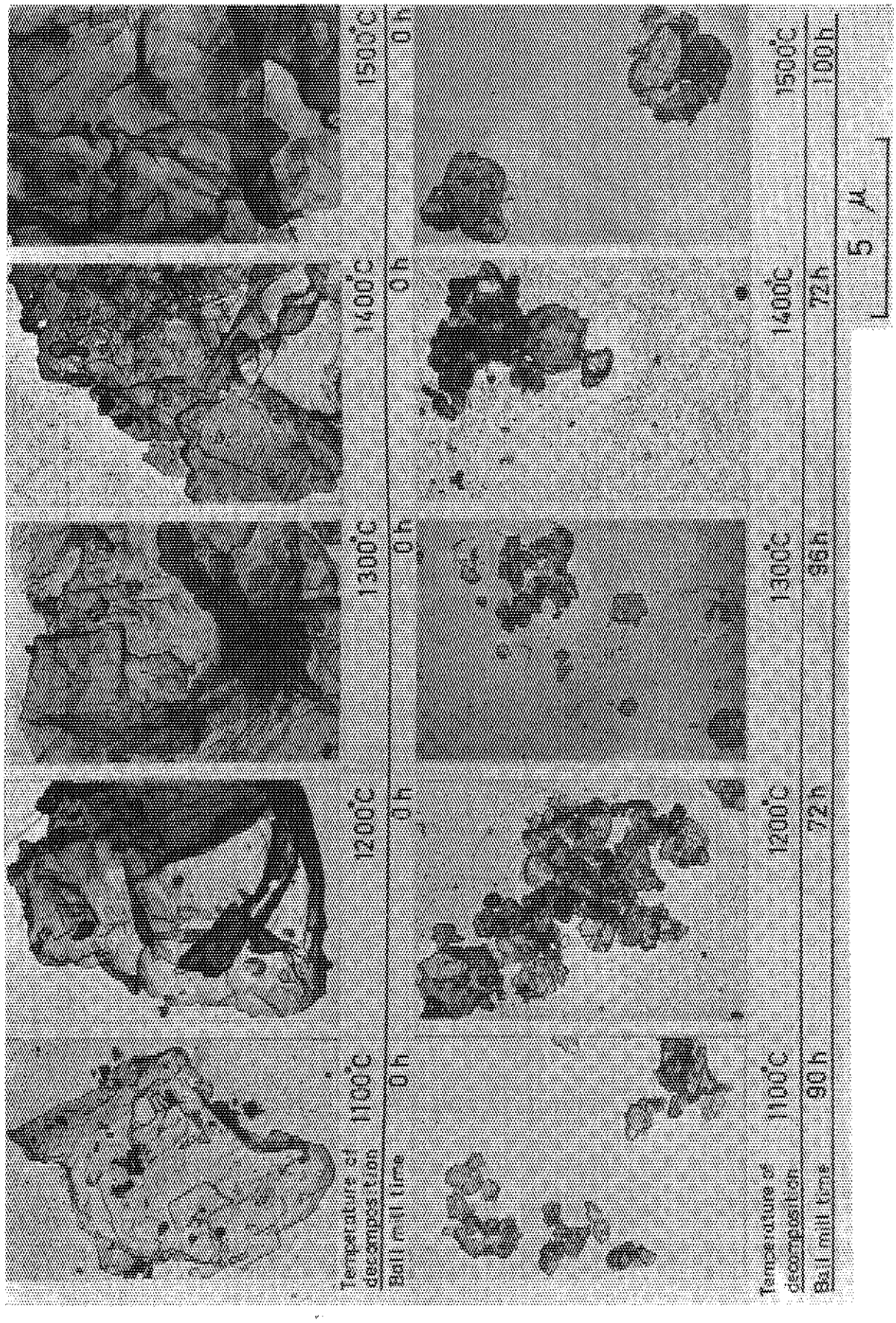


Fig. 2 Replica electron micrographs of surfaces of UN powder

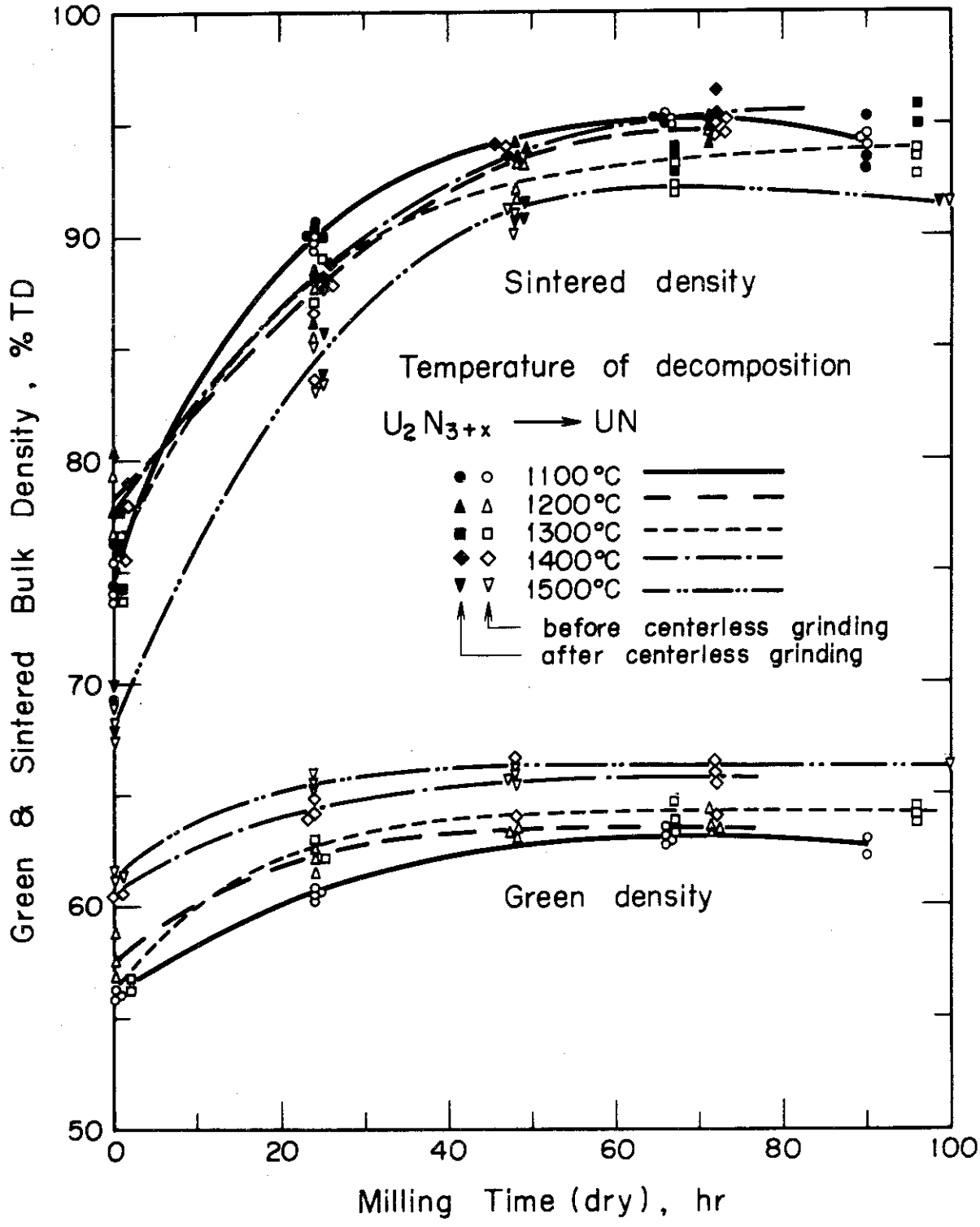


Fig.3 The effect of dry milling time on the sintered bulk density and green density of UN. sintering : 1800 °C 4h in Ar.

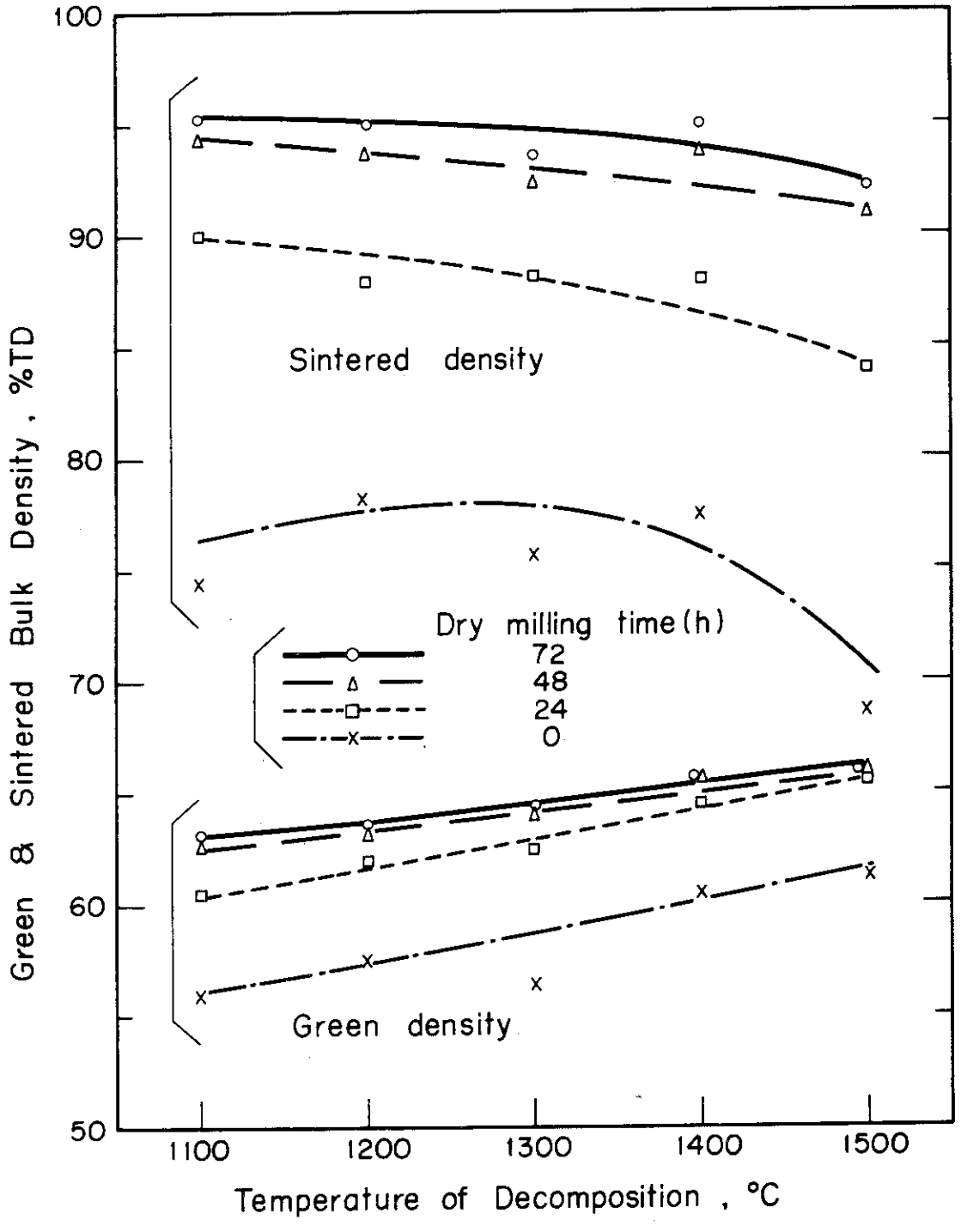


Fig. 4 The effect of temperature of decomposition on the sintered bulk density and green density of UN.

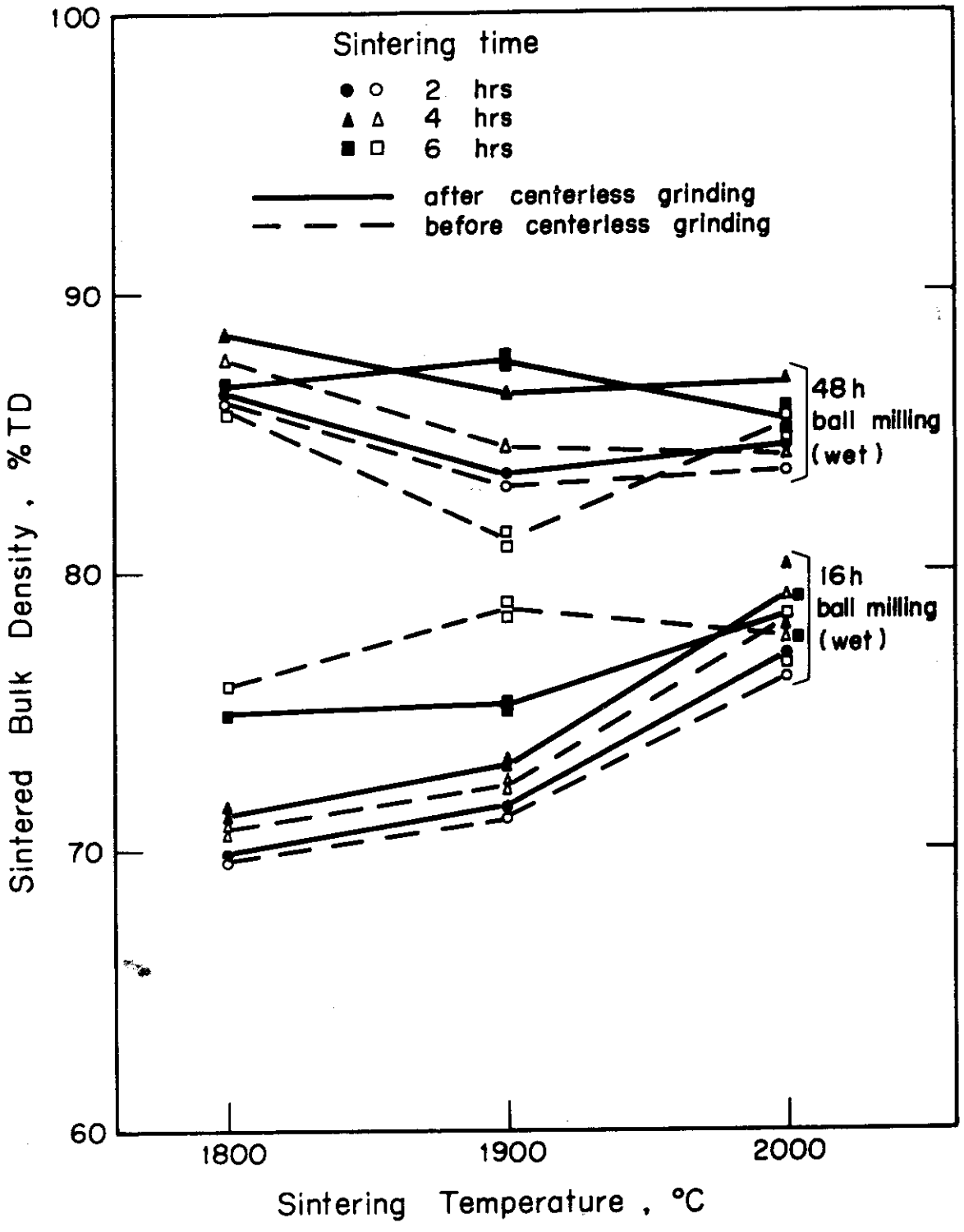


Fig. 5 The effect of sintering temperature on bulk density for the case of wet milling.

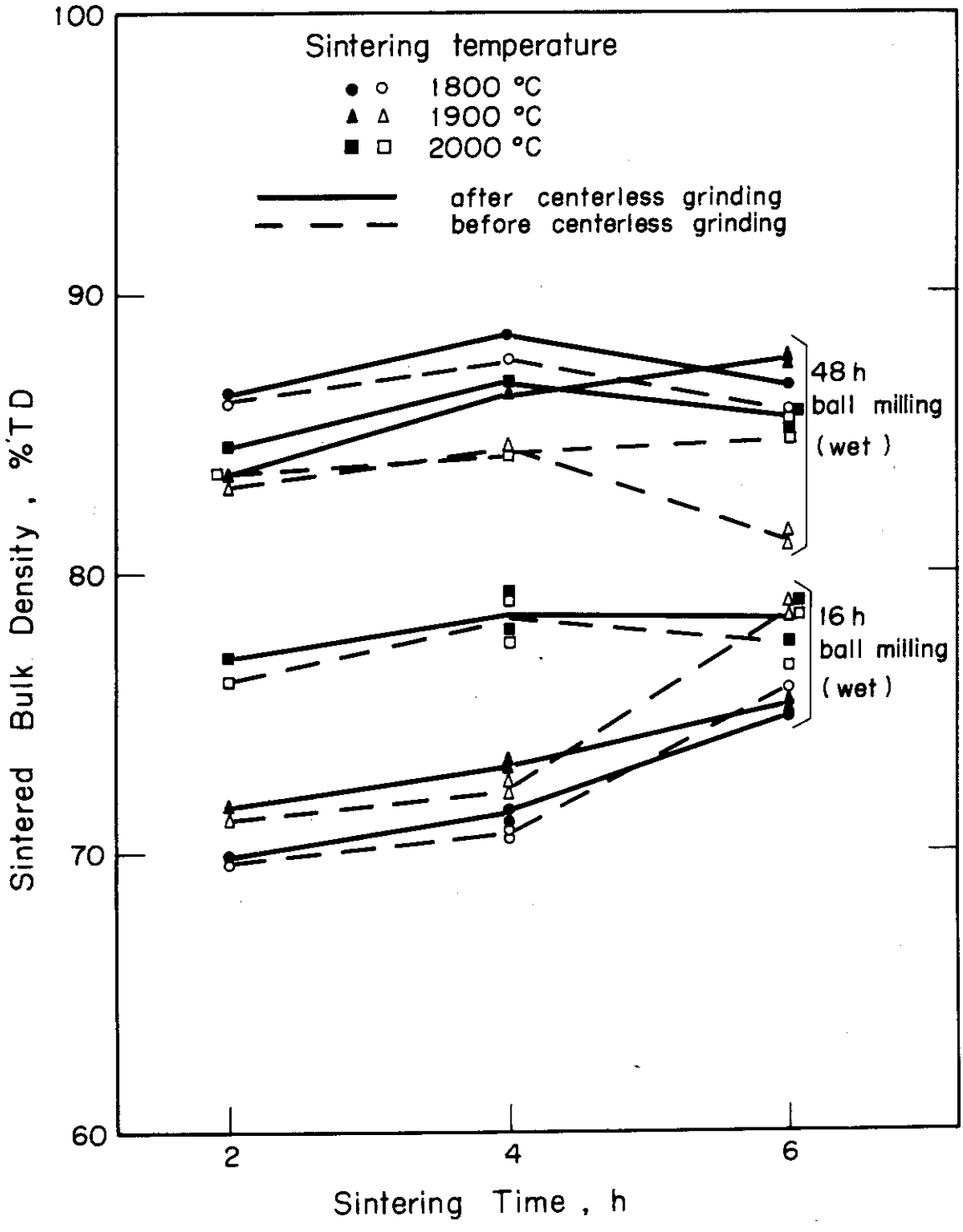


Fig. 6 The effect of sintering time on bulk density.

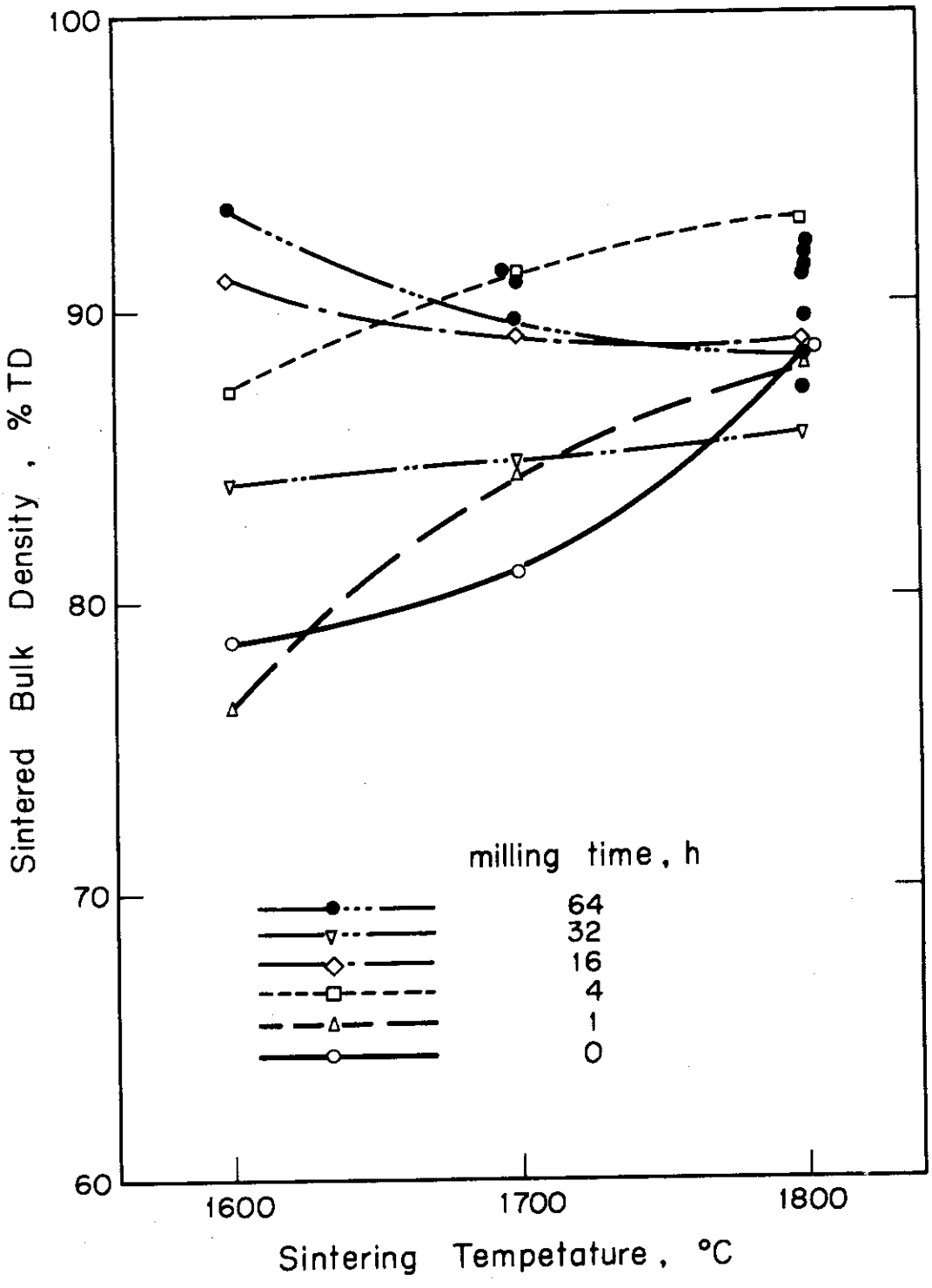


Fig. 7 The effect of sintering temperature on bulk density, Milling machine : planetary ball mill (dry), Sintering time : 4 h

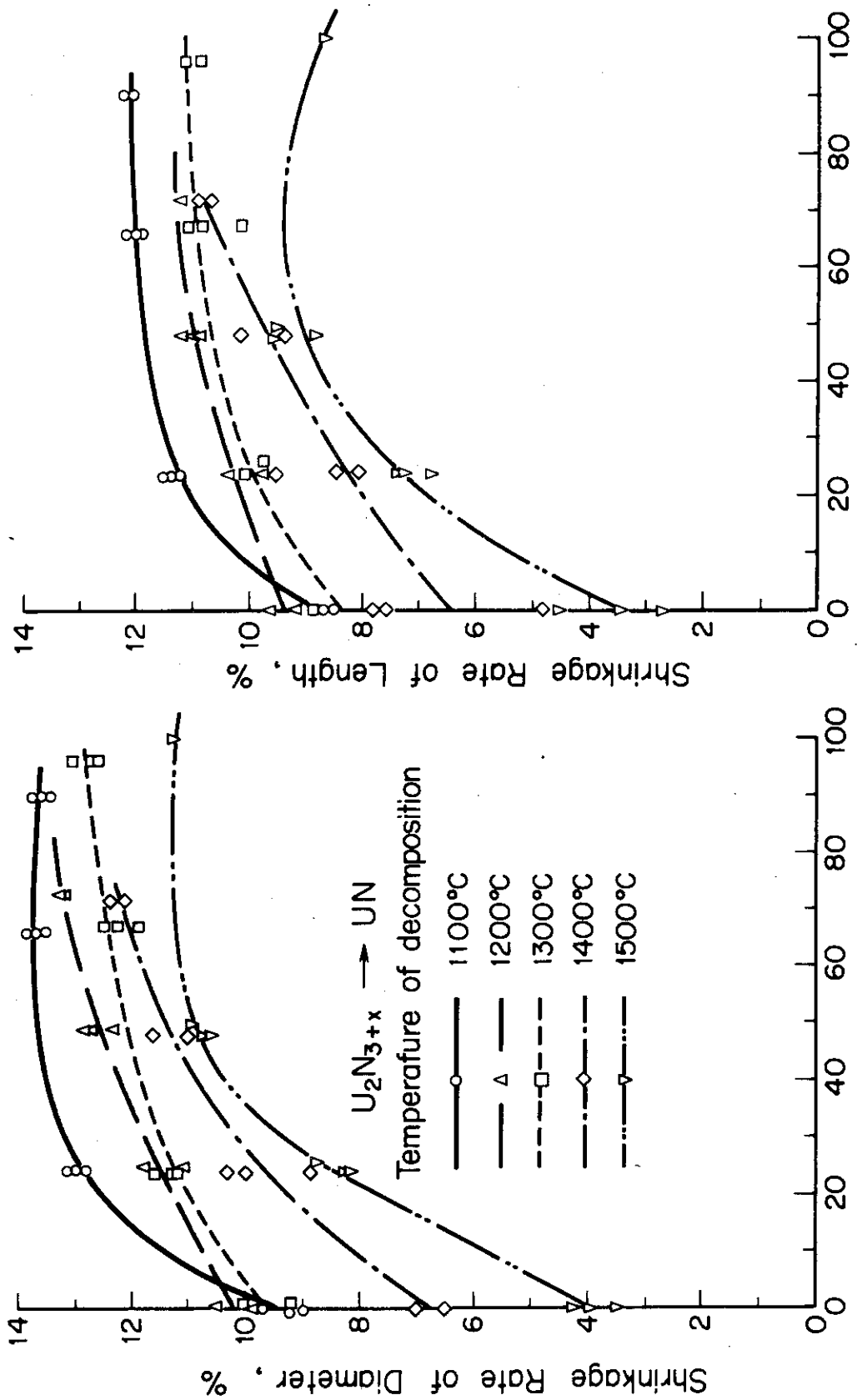


Fig. 8 The effect of dry milling on the shrinkage of diameter and length.

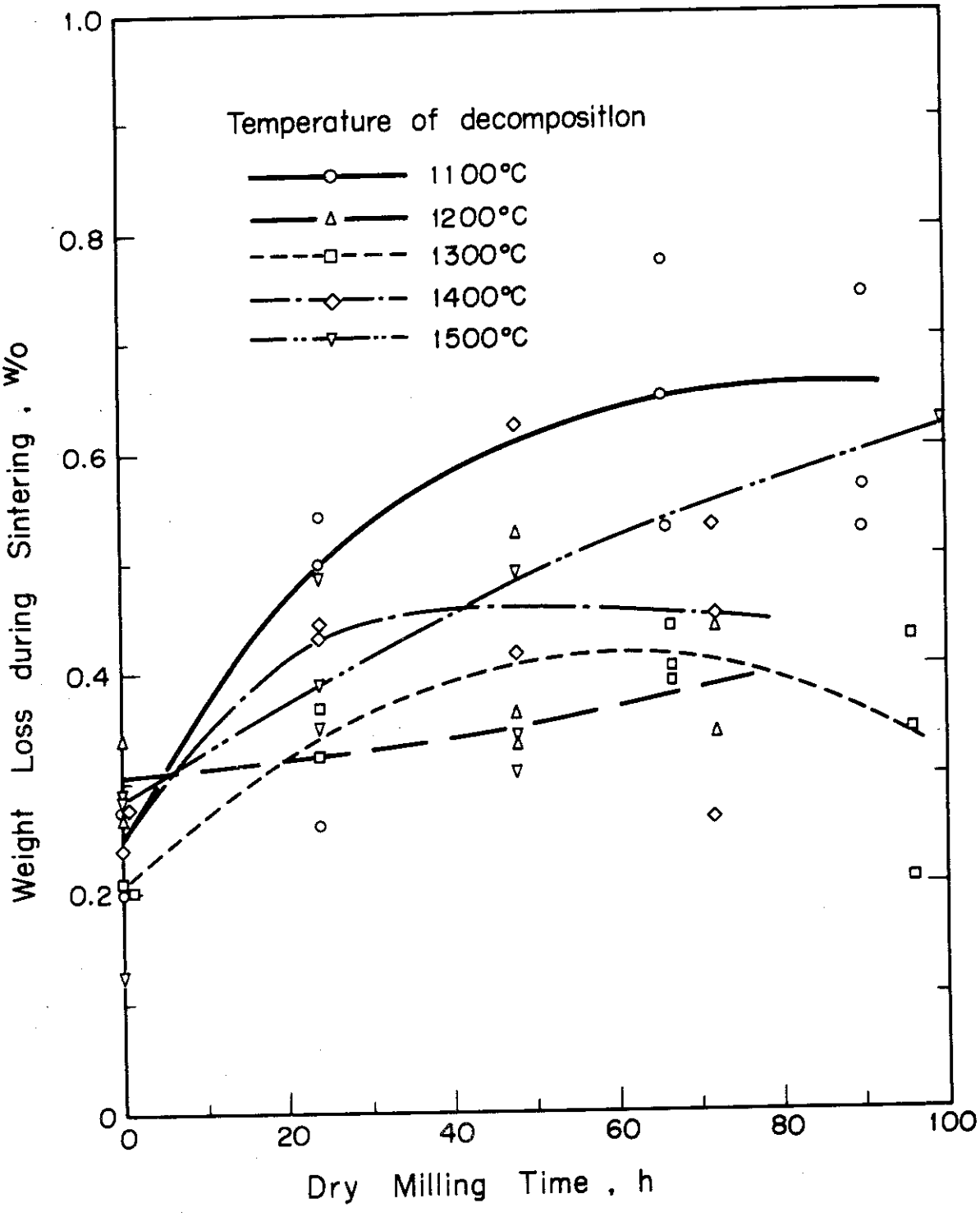


Fig. 9 Relation between weight loss and milling time.

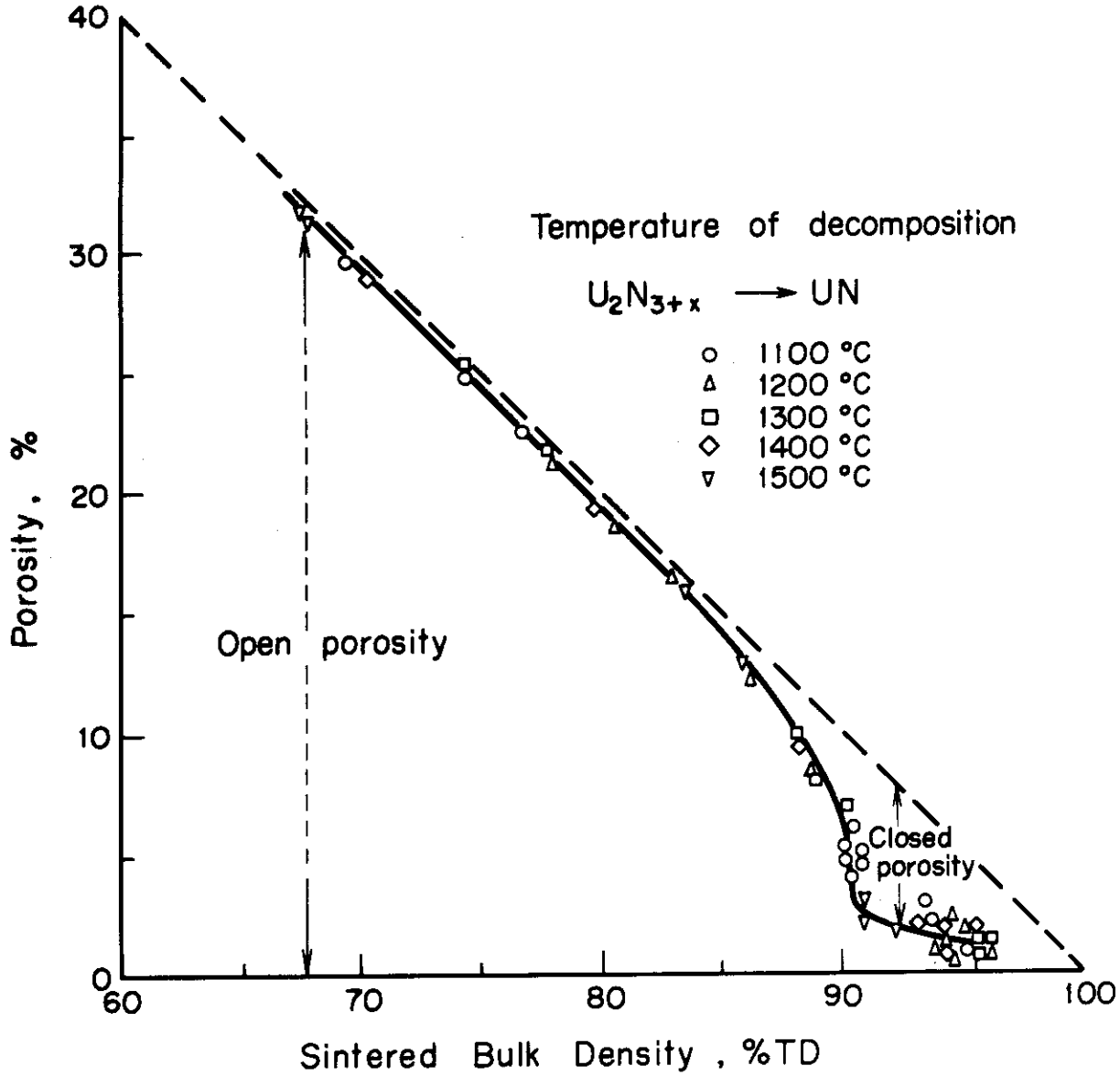
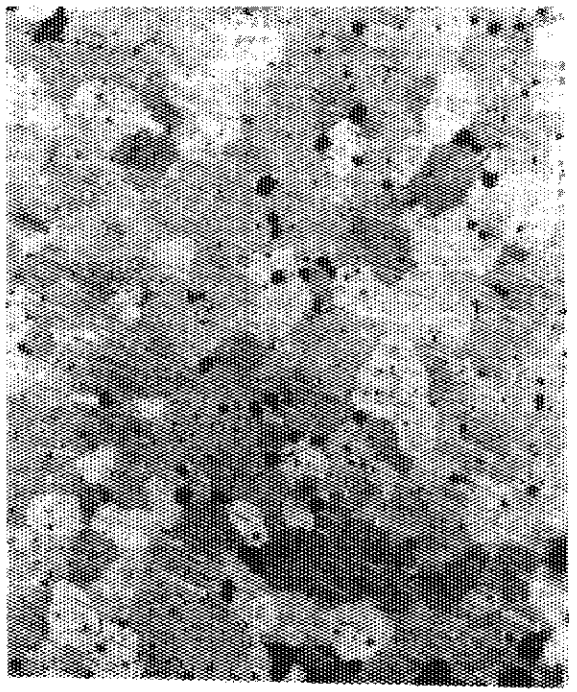
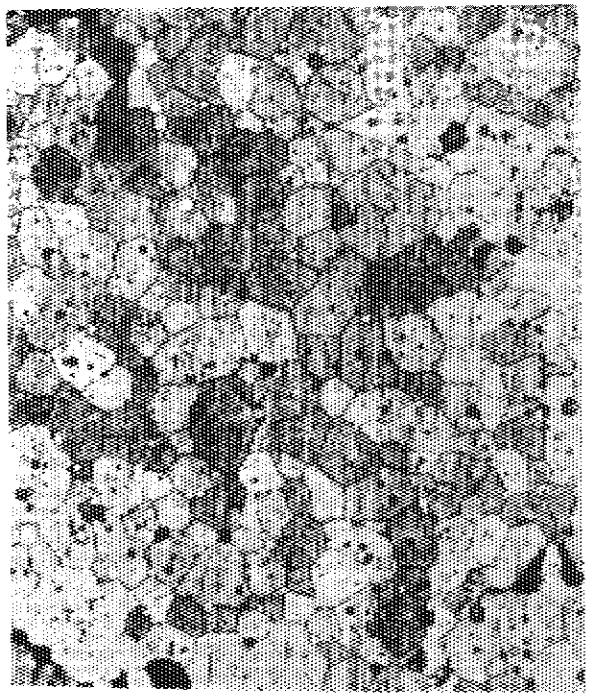


Fig. 10 Relation between sintered bulk density and porosity.



(a)



(b)

Fig.11 Microstructure of a sintered UN at 1800 °C to 94.7 % of theoretical density: 64 h milling. x 600

(a) 30' Lactic-10 Nitric-2 Hydrofluoric Etch.

(b) H_2PO_4 (conc.) 125 °C Etch.

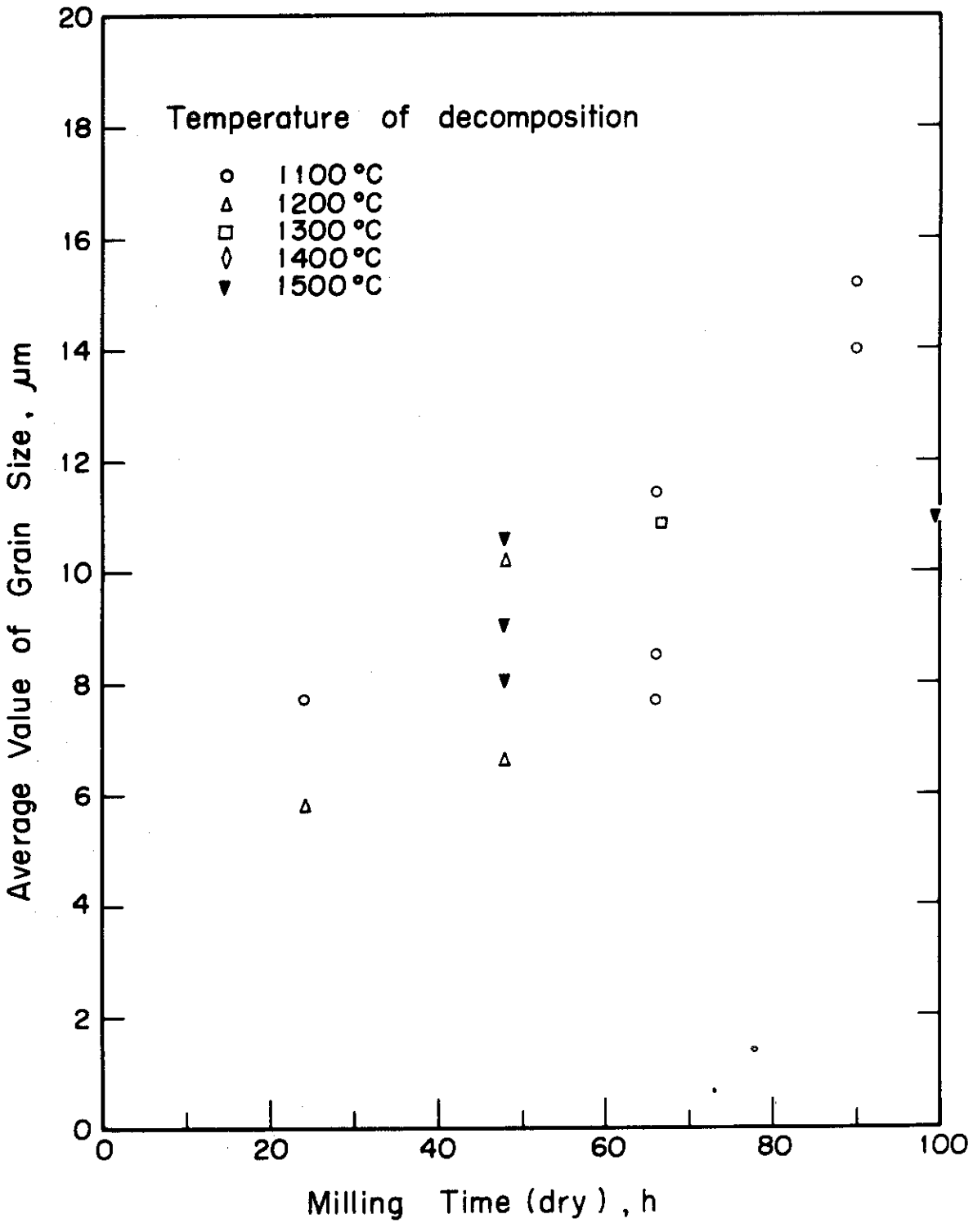


Fig. 12 Relation between grain size and milling time. Sintering : 1800 °C 4h argon flow.

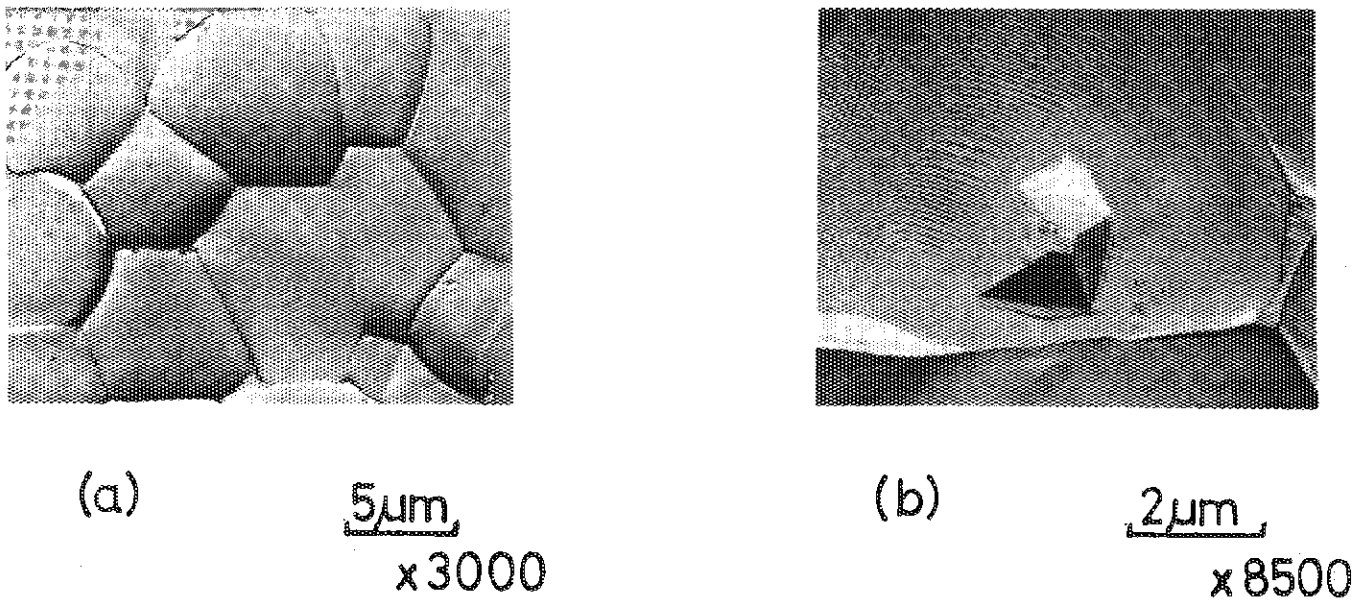


Fig. 13 Electron micrograph of free surface of sintered UN: 100h milling, decomposed at 1500°C: density, 91% TD.

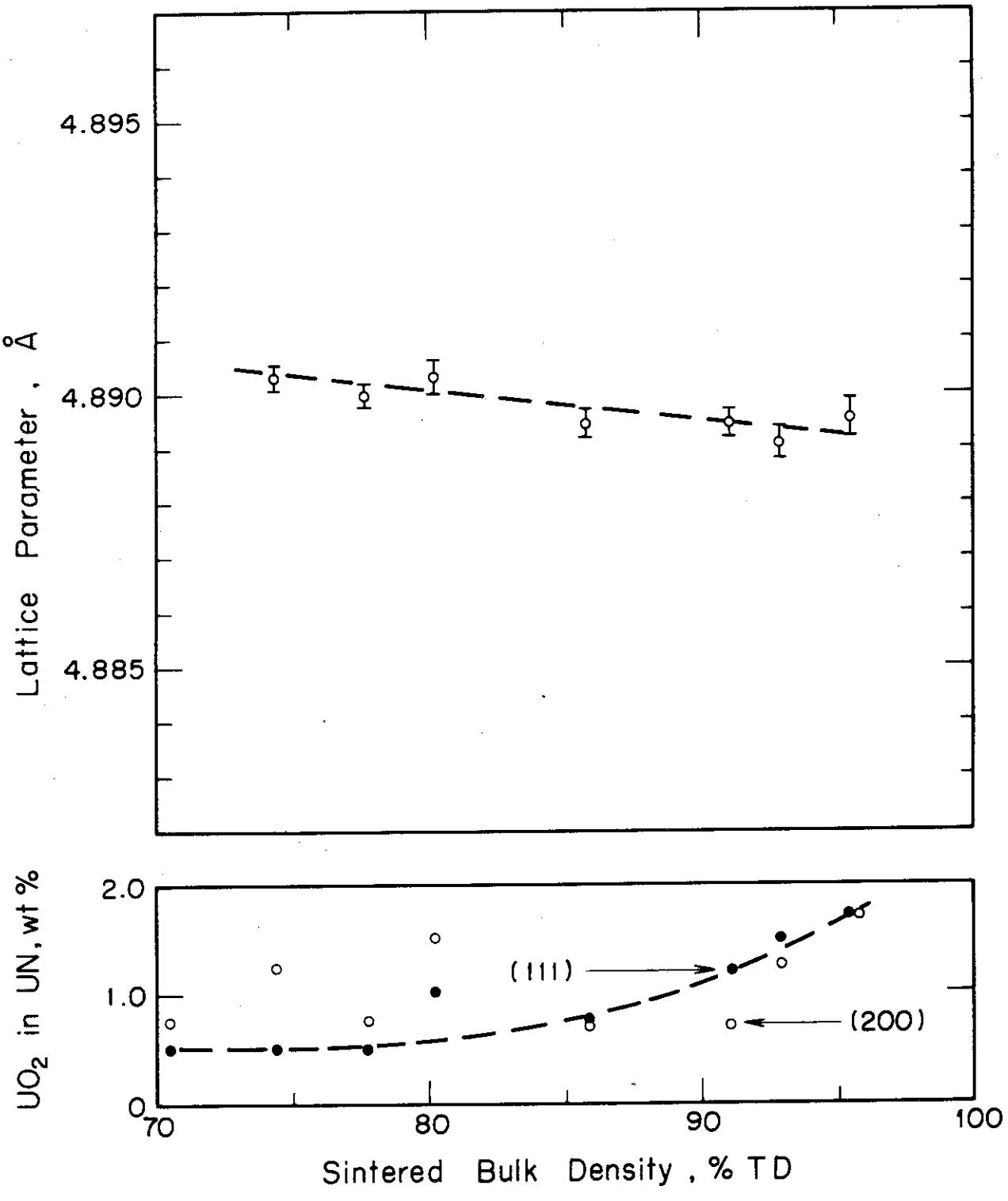


Fig. 14 Relation between lattice parameter and UO_2 content in sintered UN pellets.

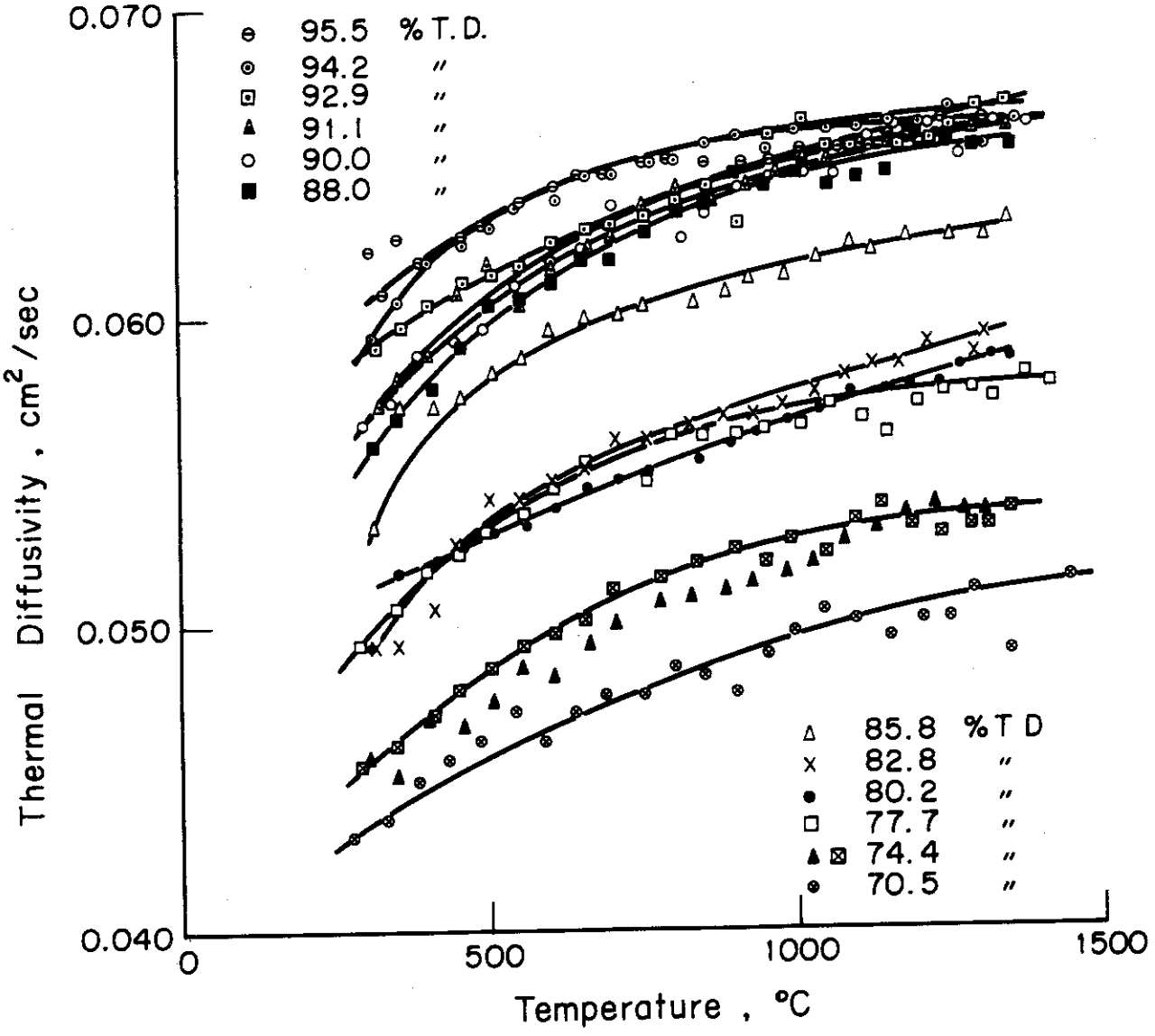


Fig. 15 Temperature dependence of thermal diffusivity of uranium mononitrides of various densities.

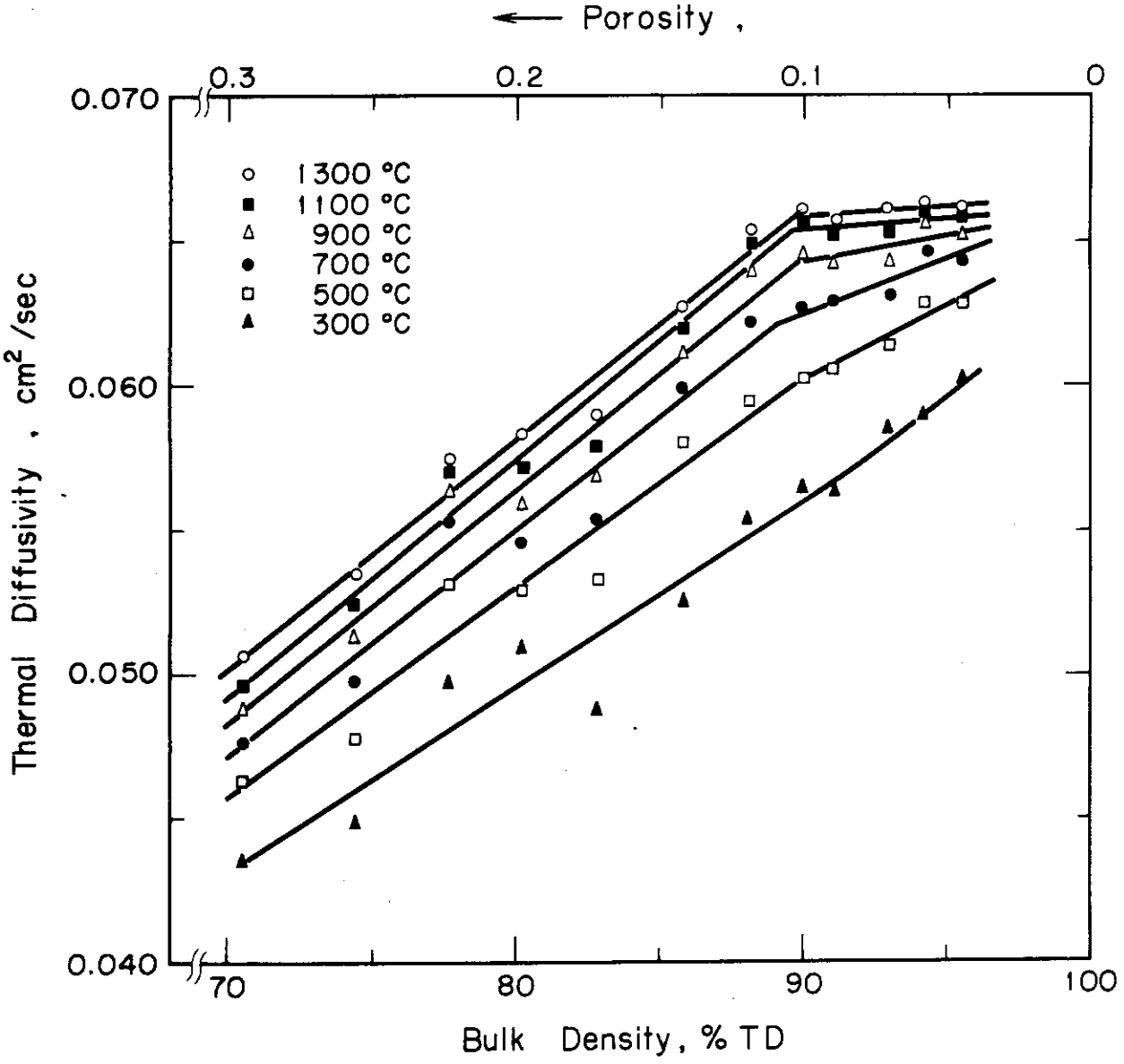


Fig. 16 Porosity dependence of thermal diffusity of uranium mononitride for various temperatures . The slope of diffusivity verious porosity curve is larger for larger porosity than for smoller porosity range.