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Short communication

Effect of sintering atmosphere on the densification behavior of hot pressed TiN ceramics

Jia-Xiang Xue, Hai-Tao Liu, Yun Tang, Chang-Ming Xu, Guo-Jun Zhang*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, China

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Abstract

Using nano-sized starting powders, TiN ceramics were hot pressed under different sintering atmospheres, which were nitrogen, argon and vacuum (5 Pa). The effects of sintering atmosphere on the densification process and microstructures of TiN ceramics were investigated. At 1500 °C, ceramics densified under vacuum demonstrated higher density compared with nitrogen and argon, owing to the high nitrogen vacancy concentration which came from the dissociation of TiN under vacuum circumstance. At 1600 °C, however, the densification process under vacuum will be hindered because of the decomposition of TiN. Combining a lower sintering temperature, smaller grain size and higher grain boundary concentration, the argon atmosphere is more suitable for fabrication of TiN ceramics as nuclear materials.

Keywords: A. Hot pressing; Densification; Nonstoichiometry; Sintering atmosphere; Titanium nitride (TiN)

1. Introduction

To reduce the toxicity of the nuclear waste and enhance the safety of nuclear power, the Gen IV systems have been developed during the last few years [1,2]. Both the gas-cooled fast nuclear reactor (GFR) and accelerator driven sub-critical system (ADS) are planned to transmute transuranium elements using inert matrix fuels (IMF) to optimize the burn up of nuclear fuel. The IMF need to work either at very high temperature or require fast neutron spectra [1–4]. Recent reports show that titanium nitride (TiN), one transition metal nitride, is proposed as an attractive candidate material as IMF due to a combination of excellent physical and chemical properties, including high melting temperature, low neutron absorption cross-section, high thermal conductivity at high temperature, extreme hardness, good corrosion resistance and its superior solubility of minor actinide (MA: Np, Am, Cm) elements [5–10].

For the densification of TiN ceramics, owing to the high melting point, strong covalent bonding and low self-diffusion coefficient, high sintering temperature and pressure are usually essential to obtain densified products. But considering the application in nuclear system, a lower sintering temperature is needed for the densification because some of the actinide nitride, such as AmN, has a tendency to decompose and evaporate at higher temperature [11]. So densification of TiN ceramics at a relatively lower sintering temperature is a new challenge for TiN ceramics used as IMF.

TiN belongs to the cubic system, which is similar to the cubic face-centered lattice of NaCl, and it shows a remarkably broad range of nonstoichiometry by a fairly wide homogeneity range (TiN_x, where $0.37 < x < 1.2$) [12]. For transition metal nitride, for example, the ZrN ceramics, it has been reported that the changes of the sintering atmosphere can produce nitrogen vacancies, which accelerates densification process of the substoichiometric ZrN_x ceramics [13,14]. So in the present work, besides using the nano-sized TiN powders as starting materials to enhance the densification, we tried to densify TiN ceramics by carrying out different sintering atmospheres and studied the effects of the atmosphere on hot pressed TiN ceramics, which included the nonstoichiometry tailoring, densification enhancement and microstructure evolution.

2. Experimental procedure

Commercial nano-sized TiN (titanium nitride, D_{50}=20 nm, specific surface area by BET about 35.7 m^2/g, purity 99%,

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*Corresponding author. Tel.: +86 21 52411080; fax: +86 21 52413122.
E-mail address: gjzhang@mail.sic.ac.cn (G.-J. Zhang).

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nitrogen content 21.8 wt%, Hefei Kaier Nanopowder Co., Ltd.) powders were used as the starting materials in this study. Non-oxide fine powders, especially nitride fine powders, exposed to air are easily contaminated by adsorbed oxygen and water vapor [15]. So, the TiN powders were stored in sealed aluminum foil before being packaged, and then the powders used in this experiment were stored in vacuum desiccators. The starting powders were sieved through a 200-mesh screen to reduce segregation and agglomeration. To study the effect of the sintering atmosphere on the densification and properties of the hot pressed ceramics, three kinds of atmospheres were carried out in the sintering process, which are argon, nitrogen and vacuum (5 Pa). The as-treated powders were placed in a graphite die (30 mm × 37 mm) and the furnace was first pumped to vacuum condition. To minimize oxygen content due to adsorbed oxygen and water vapor during the sieving process, the furnace was heated in vacuum at temperatures below 1000 °C. Then the furnace was back-filled with different gases (nitrogen or agron) or kept under vacuum and a pressure of 30 MPa was applied at temperatures over 1000 °C. The rate of heating was 10 °C $\min^{-1}$. After that, the samples were heated to the final temperature (1500–1600 °C) and held at the final temperature for 60 min for densification. Then the samples were cooled down naturally.

The bulk densities of hot pressing samples were measured by the Archimedes method. The phase compositions and lattice parameters of as-sintered ceramics were identified by X-ray diffraction (XRD, D/Max 2550V, Japan) applying CuKα1 ($\lambda = 1.5405981$ Å) radiation and using Si as reference after removing the surface layers by grinding. Lattice parameters were calculated according to the interplanar spacing equations about cubic (TiN) phases and Bragg equation based on the XRD data. The oxygen content of as-treated powders and part of sintered pellets was measured with Nitrogen/Oxygen Exterminator (TC600, Leco Corporation, St. Joseph, MI). The morphologies of fracture surface of samples were investigated by a scanning electron microscope (SEM, Hitachi TM-3000, Tokyo, Japan). The mean grain size was estimated according to the SEM photographs.

3. Results and discussion

The relative densities and grain sizes of the as-sintered samples, together with the sintering temperature and atmosphere, are shown in Table 1 and the SEM images of the fracture surface of the samples in Fig. 1. It can be seen that at the same temperature of 1500 °C, for different sintering atmospheres, the vacuum circumstance is the most beneficial for the densification, which is better than the argon atmosphere; while the nitrogen atmosphere leads to the lowest density. On the other hand, through the measurement from the SEM images of the fracture surfaces, it demonstrates that TiN sintered under nitrogen atmosphere has smaller grain size (641 nm), while the high densified TiN under vacuum has larger one (961 nm).

As is known, the TiN is a kind of solid solution with a broad range composition and based on the phase diagram, the stable composition of TiN is in the range from $TiN_{0.37}$ to $TiN_{1.2}$. Besides, both thermodynamic calculations and thermogravimetric analysis have demonstrated that at high temperature, no matter what the sintering atmosphere is, some atomic nitrogen will strip away from the crystal lattice, leaving some nitrogen vacancies. The existence of nitrogen vacancies at high temperature will effectively promote the mass transportation and diffusion, and enhance the densification process. In view of this, different sintering atmospheres will play roles of different degrees on the nitrogen vacancy concentration and then affect the densification and microstructure of the TiN ceramics.

As discussed above, the densification process has been dominated by the nitrogen vacancies, and the occurrence of vacancies is controlled by the different sintering atmospheres. When the ceramics are under nitrogen atmosphere, the nitrogen desorption from the TiN material can be hindered effectively owing to the rich nitrogen atmosphere in the furnace. For argon atmosphere, the behaviors of nitrogen desorption becomes better, but it is still not obvious. Under vacuum atmosphere, however, the nitrogen desorption process will become easier and faster, which can remarkably produce more nitrogen vacancies. In terms of the partial pressure, the argon atmosphere and vacuum should have the same nitrogen partial pressure. Different kinetic environment leaded to different results between argon atmosphere and vacuum. In vacuum condition, decomposed nitrogen will be drawn out immediately, while under argon atmosphere, decomposed nitrogen will remain around the TiN sample and then diffuse in furnace slowly.

These vacancies will directly lead to the changes of the lattice parameters. According to the XRD analysis, the lattice parameter and the relative density under different sintering atmospheres, compared with the starting powders, are shown in Fig. 2. It can be obviously seen that different sintering atmospheres will result in the changes of lattice parameters with different degrees. The starting powders has a lattice

Table 1
Relative densities and grain sizes of the TiN ceramics densified under different sintering atmospheres and temperatures.

Sample no.	HP temperature and atmosphere	Relative density (%)	The mean grain size (nm)
TiN-15N	1500 °C/N_2	93.5	641
TiN-15A	1500 °C/Ar	94.1	743
TiN-15V	1500 °C/vacuum	95.2	961
TiN-16V	1600 °C/vacuum	88.9	1587

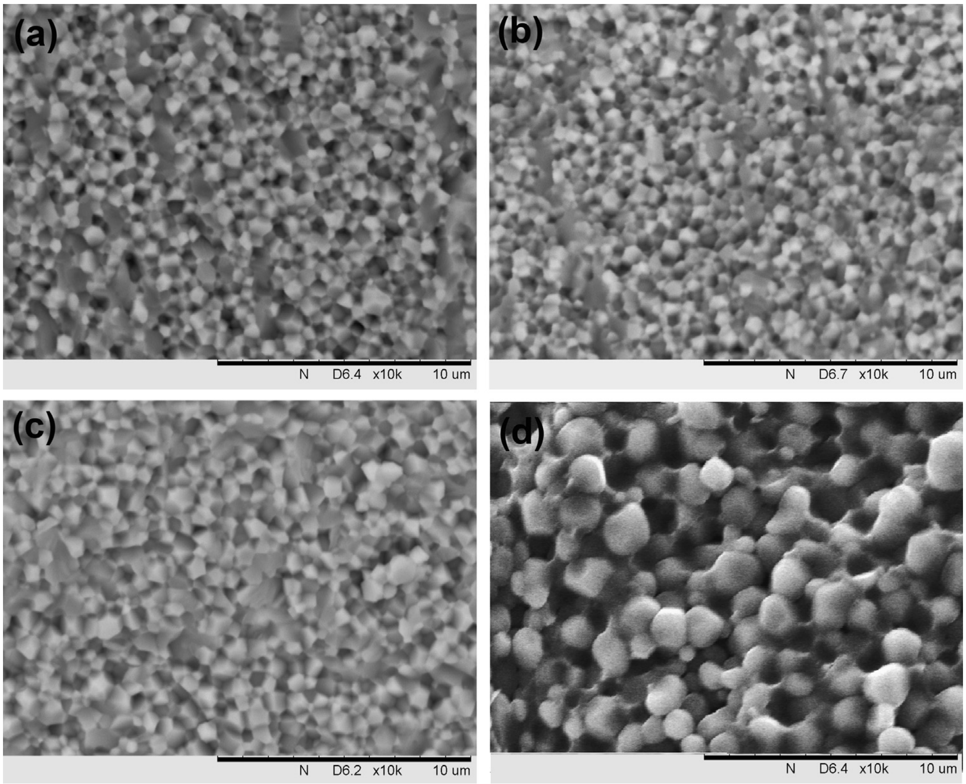

Fig. 1. SEM images of the fracture surface of the TiN ceramics: (a) sample TiN-15N; (b) TiN-15A; (c) TiN-15V and (d) TiN-16V.

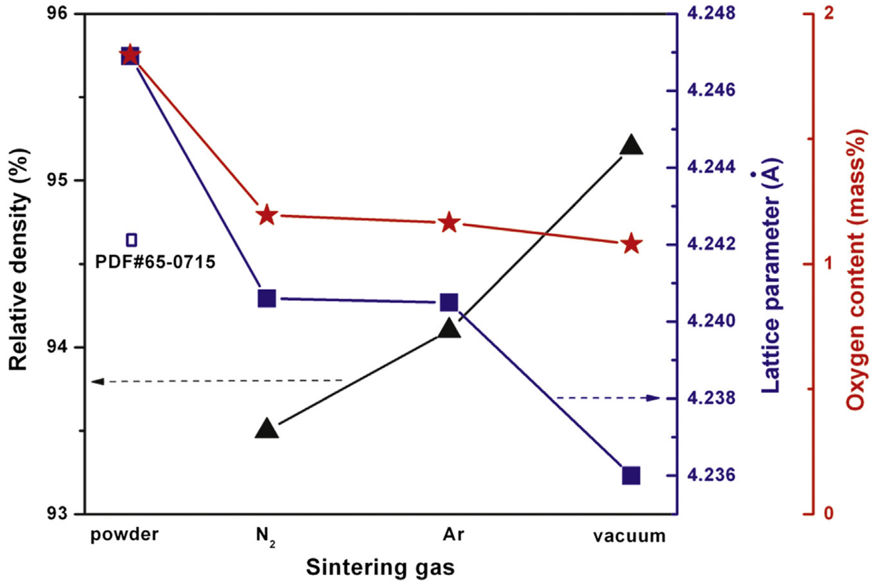

Fig. 2. Relative densities, lattice parameters and oxygen contents of the TiN ceramics densified under different sintering atmospheres at 1500 °C.

parameter of 4.2469 Å, while under the nitrogen or argon atmosphere during the sintering, the lattice parameter reduced to 4.2406 Å and 4.2405 Å, respectively. Furthermore, when sintered under vacuum, the ceramics demonstrates a lattice parameter as low as 4.2360 Å, proving that there occurred severe nitrogen desorption under vacuum which is according to the discussion above. More nitrogen vacancies introduced under vacuum circumstance will effectively promote the densification process, resulting in high densified final products. At the same time, however, the accelerated densification process will be accompanied by the grain growth during the sintering process, which is in accordance with the large grain size of sample TiN-15V (961 nm) in the SEM images, compared with sample TiN-15N (641 nm) and TiN-15A (744 nm), as shown in Table 1. So it can be concluded that during the sintering process at 1500 °C for TiN ceramics, the sintering atmosphere can remarkably affect the densification and the vacuum atmosphere is the best owing to the high nitrogen vacancy concentration produced by severe nitrogen desorption.

In this work, we tried to minimize oxygen contamination, and there was no other impurity phase diffraction peak in XRD patterns. However, generally speaking, oxygen contamination is impossible to avoid completely for nitrides fine powders. To study the effect of sintering atmosphere on the removal of oxygen contamination, the oxygen content of starting powders and sintered samples under different sintering atmospheres was also evaluated and shown in Fig. 2. It can be obviously seen that the oxygen content of starting powders is much higher than that of sintered samples. The starting powders had a oxygen content of 1.83 wt%, while under the nitrogen, argon atmosphere or vacuum during the sintering, the oxygen content reduced to 1.19 wt%, 1.16 wt% and 1.08 wt%, respectively. This result reveals that the oxygen contamination was removed partly during heating. Sakka et al. found that a large amount of gases (H_2O, H_2, CO_2, CO and NH_3) were evolved before 800 °C by heating ultrafine TiN powders which had been exposed to air for long time, and these gases were considered to be formed by the surface reaction of adsorbed gases [15]. This explains why sintered samples had lower oxygen content than starting powders. Besides, comparing three samples under different sintering atmospheres, the oxygen content of TiN-15V was lower very slightly than that of TiN-15N and TiN-15A. This is because the residual oxygen impurities present as titanium oxides at high temperature, are not sensitive to the sintering atmosphere.

In view of the above results at 1500 °C, a higher sintering temperature 1600 °C was then carried out in order to study the effect of temperature on the densification process for TiN ceramics under vacuum. The density, grain size and microstructure were also shown in Table 1 and Fig. 1. It is a pity that under vacuum, higher temperature leads to lower density (88.9%) and larger grain size (1.587 μm). Using a commercial software package (HSC Chemistry, Outokumpu Reaeasrch Oy, Pori, Finland), an equilibrium composition mode based on the thermodynamic calculations as a function of temperature ranging from 1000 to 2000 °C under vacuum is shown in Fig. 3. Thermodynamic calculation shows that at standard conditions, the TiN can be stable when temperature is lower than 2700 °C, however, when under vacuum, Fig. 3 shows that the TiN phase will begin to decompose with the productions of TiN_{1-x} and N_2 (g), even the sintering temperature is as low as 1600 °C. This leads to lower densification, which is only 88.9%. SEM images demonstrate that the grains are of the globular morphology, and the pores are almost open ones. The disappearance of facet grains and the globular morphology reveals that there exist some gaseous products occurring during the high temperature decomposition, which is in accordance with the thermodynamic analysis and calculations. XRD analysis also revealed that the final ceramics are TiN_{1-x} with the lattice parameter of 4.2297 Å, which is much lower than ceramics sintered at 1500 °C under the same vacuum atmosphere.

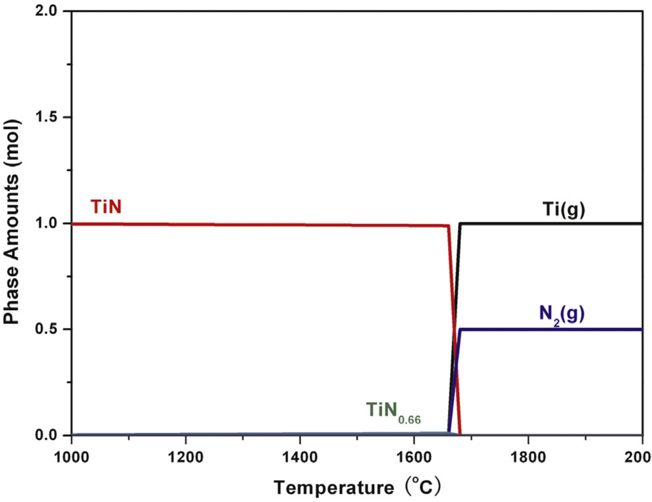

Fig. 3. Equilibrium compositions as a function of sintering temperature ranging from 1000 to 2000 °C under vacuum circumstance by thermodynamic calculations.

Considering TiN ceramics as a potential material for nuclear reactor applications, besides low-temperature-sintering, a good radiation resistance is very important for TiN ceramics. Bai et al. used three atomistic simulation methods to investigate defect-grain boundary interaction mechanisms in copper and proposed that grain boundaries have a surprising "loading–unloading" effect, which results in self-healing of the radiation-induced damage [16]. Ackland pointed out that nanomaterials have excellent radiation resistance because of a high proportion of boundary to bulk [17]. Compared with nitrogen atmosphere, the argon atmosphere is beneficial for the densification process of TiN ceramics at 1500 °C; and compared with vacuum condition, the argon atmosphere is favorable to forming finer microstructure for TiN ceramics. Combining a lower sintering temperature, smaller grain size and higher grain boundary concentration, the argon atmosphere is more suitable for fabrication of TiN ceramics as nuclear materials.

4. Summary

In the present study, the effect of the sintering atmosphere on the densification behavior of hot pressed TiN ceramics was investigated. Compared with nitrogen and argon atmosphere, the vacuum condition is beneficial for the densification process of TiN ceramics at 1500 °C. The densification enhancement is attributed to the mass transportation and diffusion by the help of high nitrogen vacancies concentration, which results from the enhanced nitrogen desorption under vacuum atmosphere. While when increasing the sintering temperature to 1600 °C, owing to the decomposition of TiN under vacuum, the densification process is hindered by the gaseous decomposition products, simultaneously leading to larger grain size and lower density.

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