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# The Characteristic of Titanium Composites Including of Nano-sized $TiN_x$ for Stack Separator

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**Abstract** The fabrication of interconnect from titanium powders and $TiN_x$ powders is investigated. Corrosion-resistant titanium and $TiN_x$ are used as reinforcement in order to reveal high heat and corrosion resistance at the elevated temperature. We fabricated the plates for interconnect reinforced with $TiN_x$ by mixing titanium powders with 10 wt.% of nano-sized $TiN_x$. Spark Plasma Sintering (SPS) was chosen for the sintering of these composites. The plate made of titanium powders and $TiN_x$ powders demonstrates higher corrosion resistance than that of the plate of titanium powders alone. The physical properties of specimens were analyzed by performing hardness test and biaxial strength test. The electrochemical properties, such as corrosion resistance and hydrogen permeability at high temperature, were also investigated. The microstructures of the specimens were investigated by FESEM and profiles of chemical compositions were analyzed by EDX.

**Keywords :** Titanium, Nano-sized $TiN_x$, Spark plasma sintering (SPS), Separator, Fuel cell

## 1. Introduction

The new type of power generating system, solid oxide fuel cell (SOFC) is becoming very attractive due to their feature of converting chemical energy to electrical energy [1-5]. One of the elements used in multilayered fuel cells is an interconnect which serves as a stack separator, which has few tasks. It should work as an electrical contact between two adjacent cells which allows the stack of fuel cells to function as a single power generation unit. The most important task of interconnect is to provide a physical barrier to keep oxidant and fuel gases from mixing. It is very important to take into account that in some SOFC design the interconnect also provides good mechanical support to the SOFC structure.

Since the stack separator is exposed to both the oxidizing and reducing side of the cell at high temperatures, it must be extremely stable at high temperatures. During a long period of time interconnects of traditional SOFCs made from ceramic materials have been more successful than metals due to their high electric conductivity, high temperature resistance and good corrosion resistance properties, and one of the mostly used ceramic materials is lanthanum chromite ($LaCrO_3$) [6]. However, there are some problems to use the lanthanum based interconnects. One of them is lanthanum which is a rare-earth element which results in high cost of fuel cells. This weak point of traditional interconnect material challenged many scientists to find a replacement made of inexpensive materials. Intermediate range of operation temperatures (600-800°C) of resent SOFC allows oxidant resistant alloys to become promising candidates as the stack separator [7]. Metal alloys can increase the efficiency of the SOFC since they

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have very high electrical conductivity, and also they show better thermal conductivity than ceramics. The simplicity of fabrication of metals in a variety of shapes allows designing more complex SOFC designs. The metallic behavior of the metallic contacts as well as the adhesion to the substrate is the parameters which are very essential to achieve good performance and long life of the cell [8].

It is well known that metal and metalloid nitrides, such as $TiN_x$, are of considerable interest due to their desirable properties such as high hardness, high temperature stability, high thermal conductivity, and high corrosion resistance [9]. There are many methods to obtain TiN powders, such as formation of TiN during reactive ball milling of Ti in ammonia [9], combustion synthesis of TiN from titanium powder compact and liquid nitrogen in a closed vessel [10].

In this study, we investigate the fabrication nano-size $TiN_x$ using planetary ball milling of pure titanium powder in $Si_3N_4$ bowl, and the effect of heat treatment on the composites of pure titanium and nano $TiN_x$ fabricated by spark plasma sintering. In order to study the mechanical properties of developed $TiN_x$ powders, the mixture of $TiN_x$ and titanium powder with 45 μm average particle size were sinteredand heat-treated at 850°C during 30 minutes under Ar gas atmosphere by Spark Plasma Sintering equipment.

The characteristics of the developed separator materials were analyzed by performing bending test, corrosion test and hydrogen permeability test. We studied the influence of heat treatment on the strength change and corrosion resistance change of titanium composites separator including of nano-sized $TiN_x$.

## 2. Experimental Procedure

Nano $TiN_x$ was fabricated by planetary ball milling of titanium powders (High Purity Chemicals, Japan) with 99.9% purity and with 44 μm average particle size in $Si_3N_4$ bowl using tungsten carbide balls. Milling was done for 2, 10 and 20 hours at 400 rpm milling speed, respectively and Ti powder to ball ratio was 1:10.

Fig. 1. illustrates the schematic view of milling process of titanium powders. In the beginning of milling process, the powders and ball are mixed, and then they impact the inside surface of $Si_3N_4$ bowl. It is supposed that during this impact $TiN_x$ will be formed around the Ti particles [11, 12].

In order to get specimens for heat treatment, the developed $TiN_x$ powders were consolidated together with pure titanium powders by Spark plasma sintering (Dr. Sinter 1030, Sumitomo Coal Mining Co. Ltd., Japan). The schematic diagram of SPS apparatus is shown in Fig. 2. The weight ratio of $TiN_x$ powders and pure Ti powders were chosen to be 90:10 weight ratios. During the consolidation of powders at SPS, heating rate was 200°C/min and the pressure was 10 KN. Sintering was done at 1100°C during 10

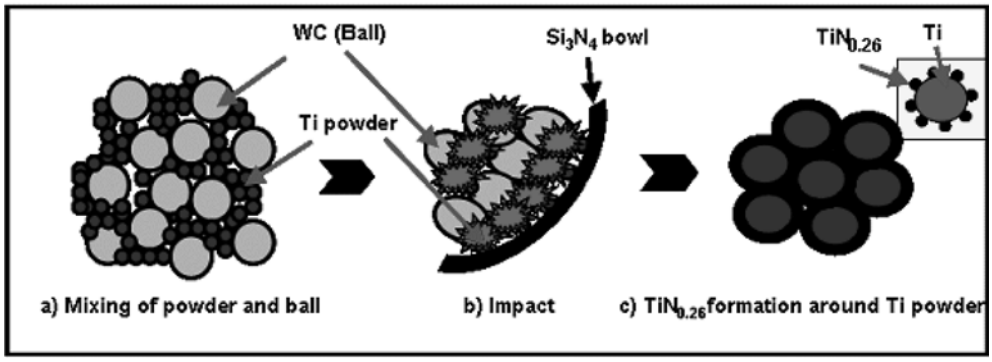


**Fig. 1. Schematic view of milling process.**

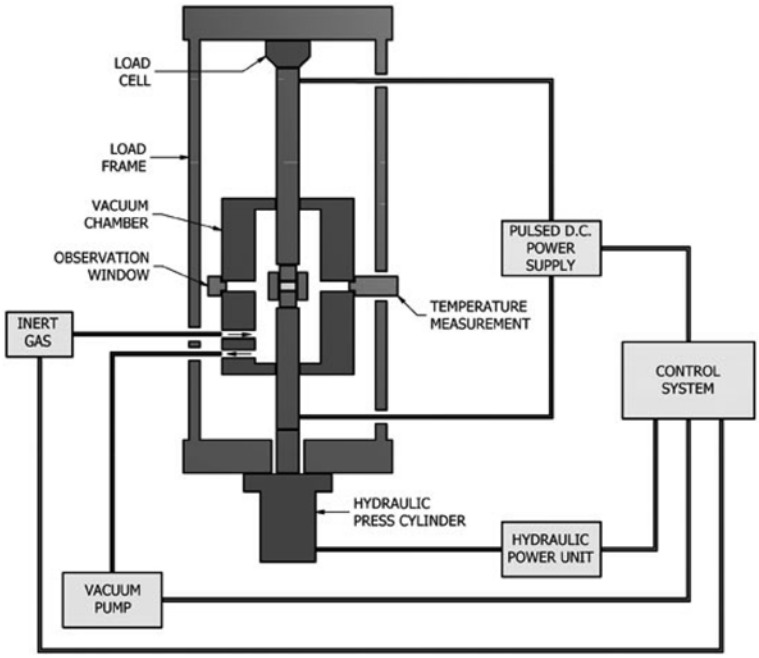


**Fig. 2. Schematic diagram of spark plasma sintering apparatus.**

minutes under Ar-4%$H_2$ gas atmosphere. During the cooling time, the pressure was increased up to 20 KN in order to keep the as-sintered density of the specimens. The heat treatment of the sintered specimens was also conducted in SPS apparatus, and heating rate was 200°C/min, and the specimens were annealed at 850°C for 30 minutes at Ar-4%$H_2$ gas medium.

The crystal structure and the chemical composition of nano-sized $TiN_x$ powders were analyzed by X-ray diffraction (Model D5005, Bruker, Karlsruhe, Germany) equipped with a primary graphite monochromator selecting CoK$\alpha$ radiation. The voltage was 40 KV, and the current was 30 mA. The diffraction angle 2$\theta$ was chosen to be 20-120. The microstructure of the specimens was investigated by FESEM (JSM-6500F, Japan) and the chemical content of nitrogen and titanium of the specimens was evaluated by EDX. The effect of heat treatment on the mechanical properties of composites of pure titanium and developed $TiN_x$ was studied by measuring the bending strength and the hardness of the specimens before and after heat treatment. The three point bending test provides values for the modulus of elasticity in bending, bending stress, bending strain and the bending stress-strain response of the material. The main advantage of a three point flexural test is the ease of the specimen preparation and testing. However, this method has also some disadvantages: the results of the testing method are sensitive to specimen and loading geometry and strain rate. The bending test was done in Universal Testing machine made my Instron® using the ball-on-ball fixture with one loading ball of 5 mm in diameter at the center of the specimens and three supporting balls of 2 mm in diameter, equally separated by 120° on the circle of 12 mm in diameter of the alumina disc specimen. The crosshead speed was 5 mm/min for all specimens. The hardness values of polished specimens were measured 10 times by Vickers's hardness test method, and the average value was obtained for each sample.

The hydrogen permeability property of the specimens was analyzed by Sievert's type automatic pres-

sure-composition isotherm apparatus at 300, 373 and 473 K.

The corrosion resistance of the sintered specimens was evaluated by analyzing of the polarization curves. The testing envelopment was a 1N $H_2SO_4$+2 ppm HF at 80°C. The measurements were conducted using a measuring system Gamry-DC 105. The reference electrode was a saturated calomel electrode with carbon electrode as a support electrode. The measuring of potentiodynamic polarization current with a scan rate 1 mV/s was performed.

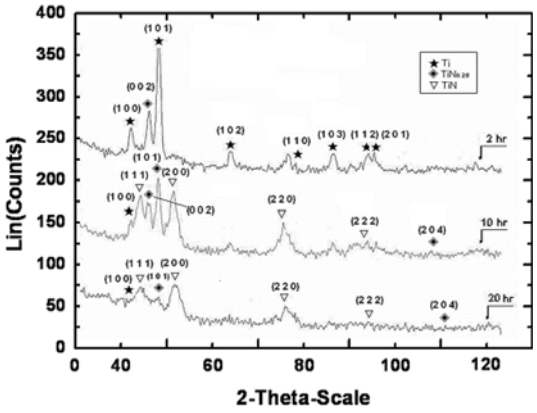


**Fig. 3. XRD patterns of pure Ti and $TiN_x$ powder milled for different times.**

## 3. Results and Discussions

Fig. 3 illustrates the XRD results of pure titanium after 2, 10 and 20 hours of milling, respectively. Clear Ti peaks can be observed on the diagram of XRD data of pure titanium milled for 2 hours. In the case of powders after ball milling for 10 hours, from the results of XRD on the top of the figure it can be seen that clear $TiN_x$ peaks are already developed. This means that by increasing milling time, the width of the titanium peaks starts to increase and the height of the peaks becomes lower and lower. Long time high energy ball milling resulted in developing amorphous powders with broaden peaks. This can be

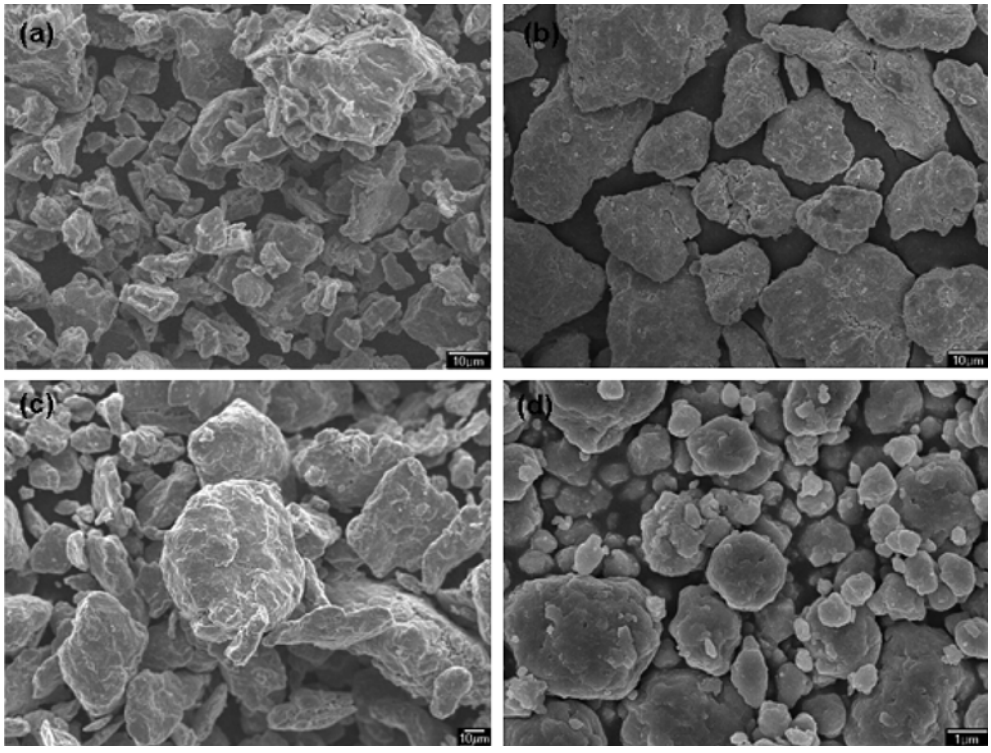


**Fig. 4. $TiN_x$ morphology of on the surface of powder milled for (a) pure Ti, (b) 2hr, (c) 10hr, (d) 20hr.**

observed from XRD results of the powders milled for 20 hours.

The morphology of the fabricated powders was analyzed by FESEM. From Fig. 4 it can be seen that milling time plays an important role in the average particle size of the milled powders. By increasing milling time the average particle size decreases. Fig. 4(b) is the FESEM image of the powder milled for 2 hours. The powder mainly consists of coarse particles, and the development of fine-size particles are starting. The particles with ultra fine size have already been developed in the powders milled for 10 hours (Fig. 4(c)). The average particle size of the powders will continue to decrease with increasing milling time up to 20 hours.

Fig. 5(a-c) shows the EDX analysis results of the surface of the composites. Fig. 5(a) illustrates the surface of the powder milled for 2 hours. Comparatively wider and lower Ti intensities can be observed from the results. However, Ti peaks become smaller with increasing milling time. Nevertheless, the peaks of some impurities are also detected in this experiment. The impurity of Si particles can be explained by the reaction of used $Si_3N_4$ bowl with Ti, and C peaks resulted from WC balls for milling.

The stack separator should have good hardness and bending strength in order to provide good mechanical support to fuel cell system. Fig. 6, 7 summarizes the bending strength and microhardness data of the sintered and heat-treated specimens. As it was expected the finer microstructure of the titanium nitride powders helps to increase the mechanical properties of the composites. The pure Ti sintered

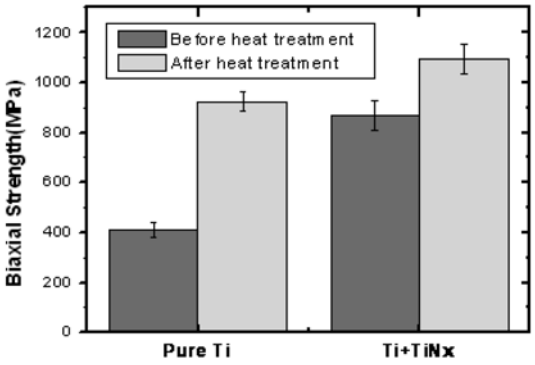


**Fig. 6. Biaxial strength of the specimens.**

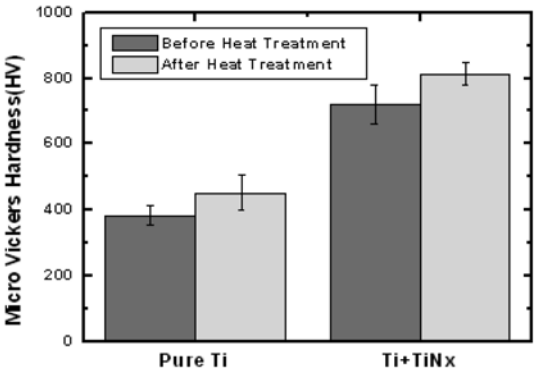


**Fig. 7. Vickers's micro hardness of the specimens.**

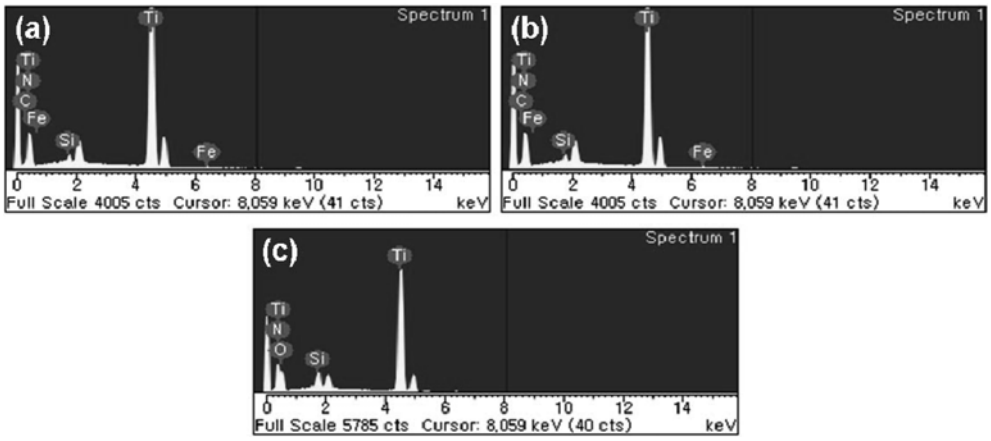


**Fig. 5. EDX image of the specimen powder milled for (a) 2 hours, (b) 10 hours, (c) 20 hours.**

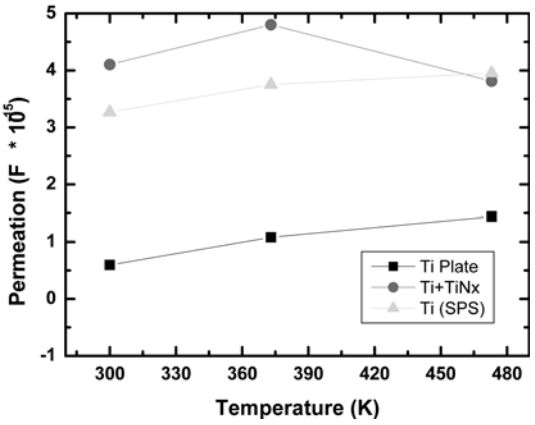


**Fig. 8. Variation of hydrogen permeability of the specimens.**

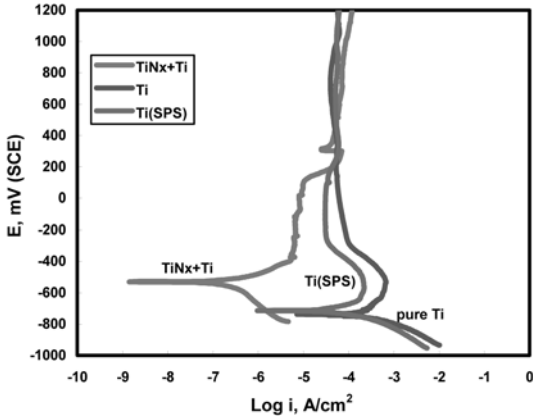


**Fig. 9. Potentiodynamic diagrams of Ti and Ti+$TiN_x$ composites.**

specimen demonstrates the lowest biaxial strength as well as microhardness. The heat treatment process of the pure titanium sintered and the Ti+$TiN_x$ sintered results in increase of both biaxial strength and hardness of the specimens.

The hydrogenation behavior is one of the most important parameters for hydrogen storage. There have been many attempts to produce fuel cell components with low hydrogen permeability. Fig. 8 shows the hydrogen permeability of pure titanium plate before and after spark plasma sintering and Ti+$TiN_x$ composites. From the results it can be observed, that the Ti plate before and after sintering demonstrates increasing hydrogen permeability at higher temperatures. The specimen prepared from Ti+$TiN_x$ composites shows relatively higher hydrogen permeability values at room temperature, however, the hydrogen permeability values of this specimens starts to decrease with increasing the temperatures above 373 K, and a sharp decrease can be observed between 373 and 473 K. Low hydrogen permeability value is more desirable for the stack separator, since the fuel cell usually operates at relatively higher temperatures.

During the fuel cell operation, the stack separator interacts with oxidizer in one side. This interaction makes another requirement for stack separator. The stack separator should have higher corrosion resistance in order to provide long-time operation of fuel cell. Fig. 9 illustrates the corrosion resistance test results of the specimens. The corrosion potentials of pure titanium plate and spark-plasma sintered Ti plate demonstrate higher value, and the specimen obtained from mixture of pure titanium and $TiN_x$ shows lower current density in active region, which means that $TiN_x$ is more stable. The addition of $TiN_x$ affects the polarization effect of the composites. Generally, Ti plate and sintered Ti plate demonstrate almost no change in corrosion current density, which means that these materials have passivity behavior in active region. However, the increase of corrosion current density of the sample prepared by mixing pure titanium and $TiN_x$ is the smallest. From these results it can be concluded that Ti+$TiN_x$ is more noble material with high corrosion resistance property, and this property doubtless allows the use of this material for making stack separator.

## 4. Conclusion

The preparation of the separator using nano-sized $TiN_x$ based composites was investigated in this paper. The stack separator used in fuel cells is one of the most important components of fuel cells. As separator is exposed to both the oxidizing and reducing side of the cell at high temperatures, it must be

extremely stable at high temperatures. Nano $TiN_x$ was obtained by planetary milling using commercial titanium powder. Long time milling resulted in finer microstructure of the milled powders. Heat treatment of the composites of pure titanium and nano-sized $TiN_x$ played an important role in the mechanical properties, such as bending strength of the composites. Heat-treated specimens demonstrated higher values in both biaxial strength and microhardness. Ti plates before and after sintering gave higher hydrogen permeability results at high temperatures, however $Ti+TiN_x$ composites showed decreasing hydrogen permeability value at increasing temperatures.

From the potentiodynamic diagrams it can be observed that the composite of $Ti+TiN_x$ has more noble properties than Ti sintered one such as high corrosion resistance.

## Acknowledgment

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