Effect of Thermal Annealing on Mechanical Properties of the Stainless Steel with TiC_xN_y Composites

Bunyod Allabergenov, Oybek Tursunkulov, Amir Abidov, Sang-Yeop Kim, Heung-Woo Jeon, Soon-Wook Jeong, and Sungjin Kim

***Abstract*—In this work we fabricated STS430L-TiC_xN_y composites by spark plasma sintering. As sintered STS:TiC_xN_y samples were annealed at 800 ~ 1100 ℃ and their morphological and mechanical properties were analyzed. All properties before and after annealing were compared in order to study the thermal annealing effect on mechanical properties. The annealing process at high temperature led to the crystallization of the STS:TiC_xN_y and increased the grain size, which was confirmed by FE-SEM analysis. Micro-hardness value was 750 MHV at 800 ℃ and reached its maximum value of 918 MHV at 1000 ℃, respectively. A heights corrosion resistance property was observed for the samples annealed at 1100 ℃. Overall, composites with micro TiC_xN_y after high temperature annealing show improved properties compared to as sintered composites, making it possible to be utilizes in fuel cell.**

***Index Terms*—Composites, mechanical properties, titanium carbonitride, stainless steel, spark plasma sintering, thermal annealing.**

I. Introduction

It is well known that proton exchange membrane fuel cells have received broad attentions due to their low operation temperature, low emission and quick startup [1], [2]. This type of fuel cells is an electrochemical cell that is fed hydrogen, which is oxidized at the anode, and oxygen that is reduced at the cathode. The protons released during the oxidation of hydrogen are conducted through the proton exchange membrane to the cathode. Since the membrane is not electrically conductive, the electrons released from the hydrogen travel along the electrical detour provided and an electrical current is generated [3]. Their distinguishing features include lower temperature and pressure ranges, a special polymer electrolyte membrane, high power density, low operating temperature, relatively quick startup, and rapid response to varying loads [4]. With the proper selection of fuel such as pure hydrogen, the fuel cell energy is fairly clean, showing great potential of mitigating the environmental pollution problem of modern industrial world.

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Bipolar plates are main part of proton exchange membrane fuel cells which made from different type of industrial steel. Therefore one of candidate materials for metal bipolar plates, stainless steel has (STS) attracted much attention because of a favorable combination of mechanical properties [5], corrosion resistance [6], [7] and cost effectiveness when compared other metallic alloys for fuel cells [8]. On other hand, separators made of metallic alloys can increase the efficiency of the solid oxide fuel cells because they have a high electrical conductivity and they demonstrate better thermal conductivity than polymers. Among alloys, stainless steel with metalloid nitride and carbonitride are optimal material because of its relatively high strength and chemical stability, it is also cost-effective and available in a wide range of alloy types [9], [10]. Recently Lee et al investigated corrosion behavior of dissimilar brazed joints between titanium and STS. According reported data authors show that corrosion tests in a sea water environment, a corrosion of TiAg layer and a repetitive formation and breakdown of Ti–O oxide film were responsible for a galvanic corrosion of the dissimilar metal joint with a layered structure [11]. In this paper, the fabrication of stack separator using low-price STS metal powders and ultrafine titanium carbonitride (TiC_xN_y) powder is investigated. Spark plasma sintering (SPS) technique was applied for sinter the samples. The mechanical properties of the fabricated stack separator were evaluated by performing hardness test, corrosion resistivity, chemical composition and microstructures of the specimens were analyzed using XRD, FESEM and EDX.

II. Experimental Procedure

A. Ball Milling

Stainless steel powder (STS) with average particle size 15 μm (Alfa Aesar STS430L) and titanium carbonitride powders (TiC_xN_y) with average particle size 15~50 μm with 99.99% purity and were used as initial materials. Previously micro-structured sub-stoichiometric initial powder successfully mixed by planetary ball milling technique [12]. The grinding bowls rotates on their axis while simultaneously rotating through an arc around the central axis. The grinding bowl and the supporting disc rotate in opposite directions, so that the centrifugal forces alternatively act in the same and opposite directions. This results in, as a frictional effect, the grinding balls running along the inner wall of the grinding bowl, and impact effect, the balls impacting against the opposite wall of the grinding bowl.

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B. Sintering

The consolidation of all specimens was performed using spark plasma sintering technique (Dr. Sinter 1030, Sumitomo Coal Mining Co. Ltd., and Japan). The weight ratio of TiC_xN_y powders and pure STS powder (Alfa Aesar STS430L) were chosen to be 7:93 wt%. The obtained mixtures were filled inside the mold of 19,8 mm diameter and the carbon paper was used to separate the powders from upper and lower punches. During the consolidation of powders at SPS, heating rate and pressure were 100 ℃ /min and 60 kN, respectively. Sintering was carried out at 900 ℃ during 10 minutes under Ar-4%H_2 gas atmosphere. Heating rate was 20 ℃/min, and the specimens were annealed at 800 ~ 1100 ℃ for 60 minutes at Ar gas medium with flow rate of 0,5 L/min in Mini Box Type Furnace (model-C-A14, with quartz tube size Ø 50x250 mm) for protect from influence carbonization of the specimens.

C. Characterization

The crystal structure and the chemical composition of obtained powders were analyzed by X-ray diffraction (Model D5005, Bruker, Karlsruhe, Germany) equipped with a primary graphite monochromatic selecting the Co Kα radiation. The voltage was 40 kV, and the current was 30 mA. The diffraction angle 2Θ was chosen to be 30-90°. The scanning speed was 0.020 per 0.8 seconds. The microstructure of the specimens was investigated by FESEM (JSM-6500F, Japan) and the chemical content of iron and titanium of the specimens was evaluated by EDX. The effect of heat treatment on the mechanical properties of the composites was studied by measuring the hardness of the specimens before and after annealing. The hardness values of polished specimens were measured 10 times by Vickers's hardness test method, and average value was obtained for each sample [13]. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The corrosion resistance of the sintered STS: TiC_xN_y specimens were evaluated by analyzing of the polarization curves. The testing electrolyte was 0.5M H_2SO_4 aqueous solution at 80 ℃. 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 [13], [14].

III. Result and Discussion

A. Microstructural Analysis

X-ray diffraction was used to characterize the structure and composition of the STS and TiC_xN_y ($STiC_xN_y$) compound samples fabricated by spark plasma sintering. The X-ray diffraction patterns of the STS and TiC_xN_y powders before the sintering process are shown in Fig. 1 (a). From the results we can confirm representative peaks corresponding to (110), (200), (211) planes of STS as well as (111), (200), (220) planes of TiC_xN_y powders. Fig. 1(b) represents x-ray diffraction patterns of the STS:TiC_xN_y composite after annealing at 1000 ℃ and 1100 ℃. It is clearly seen that as-sintered sample is weakly crystallized showing low STS peak intensities. After the heat treatment at 1000 ℃, intensities of STS (110), (200), (211) peaks have dramatically increased. As peak intensity increases, full width and half maximum (FWHM) of the peaks decreased. Accordingly, crystalline size of the composite is increases, which consequently, decreases the structure compressive stress. However, further increasing the annealing temperature to 1100 ℃, the intensity of the STS (110) peak have slightly decreased, which led to decrease the mechanical properties of the composite (see Fig. 3).

B. Morphological Analysis

Detailed microstructure and chemical content of the STS: TiC_xN_y specimens were evaluated by field-emission scanning electron microscopy and EDX, which are shown in the Fig. 2 ((a) ~ (c)), respectively. Fig. 2 (a), (b) and (c) show surface view of the as prepared sample and after annealing at 1000 ℃, 1100 ℃, respectively. From Fig. 2 (a) we can observe smooth porous surface with large grains for micro-sized TiC_xN_y. The TiC_xN_y grains within the STS matrix can be well distinguished from the surface FE-SEM view, which appear with dark contrast.

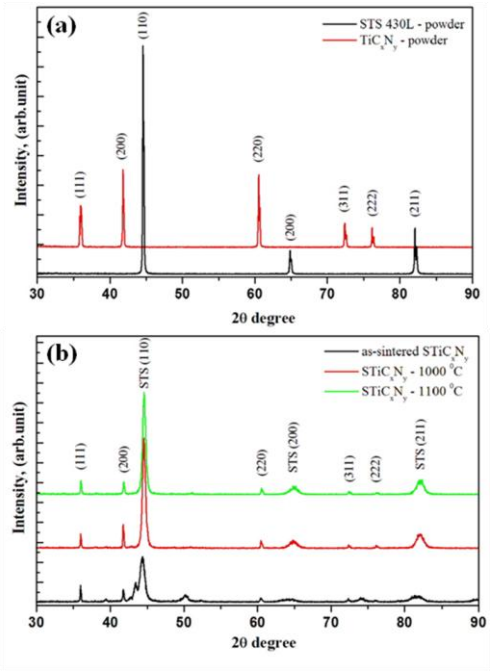

Fig. 1. X-ray diffraction patterns of STS and TiC_xN_y composites: (a) initial STS and TiC_xN_y powders; (b) as-sintered $STiC_xN_y$ composite and annealed at 1000-1100 ℃.

The grains sizes for STS 430L - TiC_xN_y composites were decreased after thermal annealing at 1000 ℃ and 1100 ℃, as shown in Fig. 2 (b) and (c), respectively. Thus after increasing heat treatment up to 1000 ℃ pores in micro-sized STS:TiC_xN_y surface increased and different types of thermal defects were generated in surface (Fig. 2 (b)). Probably these defects can be influence on mechanical characteristics of STS:TiC_xN_y samples. After 1100 ℃ thermal annealing of micro-sized TiC_xN_y samples surface become rough which caused that surface in homogeneity was increased (Fig. 2. (c)). EDX analysis results of the surface of the STS:TiC_xN_y

composites after annealing is shown in Fig. 2(d). After annealing the $STiC_xN_y$ composite at 1100 ℃, the Ti Kα observed in the mapping area of TiC_xN_y impurity distribution on the surface of composite. On the other hand, from the areas other than TiC_xN_y, only Fe Kα peaks were observed.

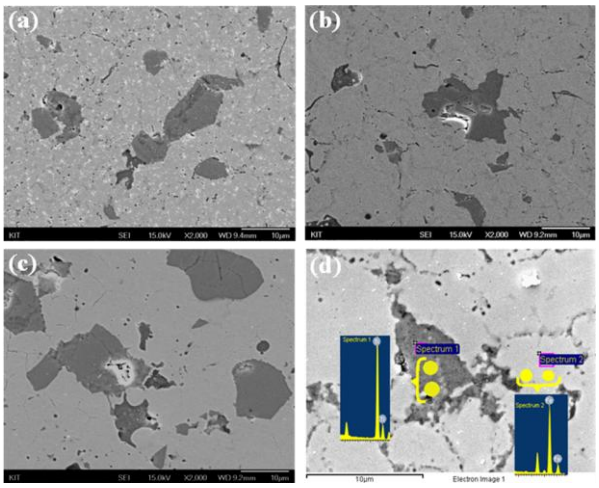

Fig. 2. FE-SEM image of microstructures of the sintered composites on the base of $STiC_xN_y$ with micro-sized TiC_xN_y: (b) as-sintered, (d) annealed at 1000 ℃ and (f) annealed at 1100 ℃. (d) EDX spectrum of $STiC_xN_y$ composite annealed at 1100 ℃.

C. Mechanical Analysis

From the results shown in Fig. 3, it can be clearly seen that the annealing at high temperatures of the composite improves the mechanical properties of the specimens. The hardness of both micro-sized TiC_xN_y based specimens sharply decreased after annealing at 800 ℃, due to the recrystallization, which removes internal stress of the structure. In order to obtain maximum hardness, annealing temperature was further increased up to 1100 ℃. Hardness of the samples was increased until 1000 ℃ and starts to decrease from 1100 ℃. As mentioned above in Fig. 1 (b), change of the crystalline size and compressive stress during annealing at high temperatures has influenced the micro-hardness. In particular, micro-hardness value as high as 918 MHV was obtained for the sample annealed at 1000 ℃. Effect of grain growth and increasing of density of $STiC_xN_y$ composite can be other possible factors that contribute to the improvement of the mechanical properties.

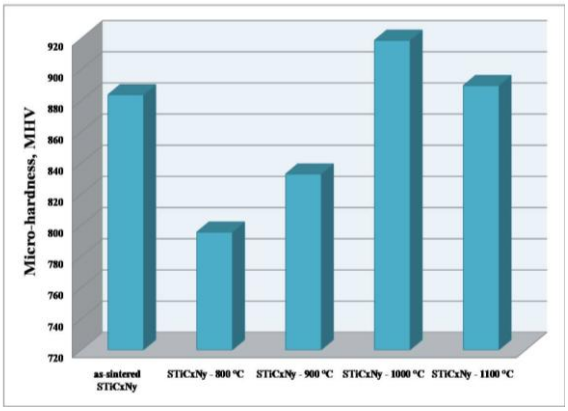

Fig.3. Vickers's micro hardness of the specimens at different temperatures.

D. Electrochemical Analysis

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. 4 illustrates the potentiodynamic diagrams of the specimens. According this figure potentiodynamic polarization curves were obtained for different type of annealing temperatures of $STiC_xN_y$ samples. A higher corrosion resistance rate was observed for $STiC_xN_y$ annealed at 1000 ℃ as compared with as-sintered samples (Fig. 4 (a) and (b)). Corrosion resistance rate reached maximum value with increasing annealing temperature up to 1100 ℃ for samples with addition of micro-sized $STiC_xN_y$, as shown in fig. 4 (c). These corrosion tests indicate that a thermal annealed $STiC_xN_y$ samples have improve the corrosion resistance of composites in the operating environment of a fuel cell. To achieve improvement corrosion properties for the stainless steels in addition of TiC_xN_y it is necessary to choice optimal chemical composition of initial powder size, density, mixing condition and additional thermal annealing.

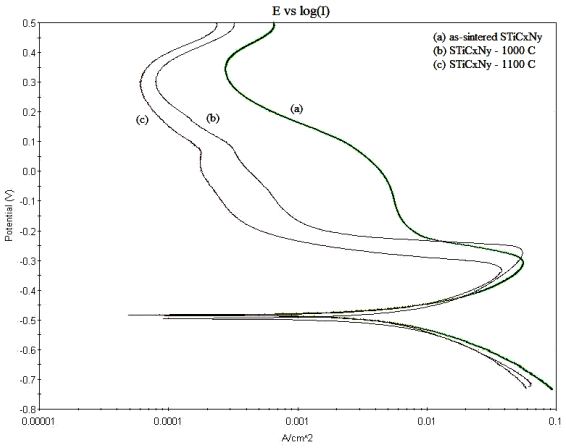

Fig. 4. Potentiodynamic diagrams of $STiC_xN_y$ composites: (a) $STiC_xN_y$ as-sintered; (b) annealed at 1000 ℃; (c) annealed at 1100 ℃.

IV. Conclusions

In this study $STiC_xN_y$ based composites were synthesized by spark plasma sintering, and their mechanical properties were investigated. The XRD results of the micro sized TiC_xN_y samples showed increased intensity peaks after annealing at 1000 ℃ and 1100 ℃. It is believed that increasing intensity was caused by increasing crystalline size of the composite. There micro-structural changes of high temperature annealed samples showed improved mechanical and chemical resistance properties. Corrosion resistivity of the composite with micro sized TiC_xN_y after high temperature annealing showed the highest corrosion resistance. Overall, composites with micro TiC_xN_y after high temperature annealing show improved properties compared to as sintered composites, making it possible to be utilizes in fuel cells.

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