Nanoparticles Synthesis of Ternary Titanium Niobium Nitrides by Induction Thermal Plasmas

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Abstract: Titanium niobium nitrides nanoparticles with high purity were successfully prepared by RF induction thermal plasma. The compositions of the synthesized powders were investigated through XRD analysis. Main peaks were assigned to be a cubic TiN structure with a space group of *Fm*-3*m*. The addition of Nb plays a significant role in the structural properties of TiN. Ammonia injection into plasma tail as counter flow is a suitable method for transition metal nitridation.

Keywords: RF thermal plasma, ternary titanium niobium nitrides, nanoparticles

1. Introduction

Transition metal nitrides (TMNs) are a new family of non-noble metal catalysts that have received extensive attention from researchers owing to their unique electronic structure, high conductivity, great hardness, large density, and corrosion resistance [1]. Recently, titanium nitride (TiN) has attracted extensive interests as active materials for electrodes in the fuel cell because of their super high melting points (3000 °C), hardness, wear resistance, high electrical conductivity, and chemical stability [2].

The study by Bharat et al. [3] demonstrated that TiN nanoparticles act as a catalyst support material for proton-exchange membrane fuel cells showing higher catalytic performance than conventional platinized carbon electrocatalysts. Moreover, bimetallic transition metal nitrides (BTMNs) as support for Pt NPs can obviously enhance activity and stability toward methanol oxidation reaction (MOR) activities due to co-catalytic effects introduced by other metal doping. Yang et al. [4] demonstrated that ternary titanium niobium nitrides ($Ti_{1-x}Nb_xN$) as support for Pt NPs can enhance activity and stability toward methanol oxidation reaction. This is due to the co-catalytic effects of Nb addition.

Radio Frequency (RF) thermal plasma has unique advantages such as ultra-high temperature (even up to 10^4 K), high cooling rate (10^4 – 10^6 K/s), no contamination since less of electrode, as well as long residence time. Due to its wide range of operating parameters, RF thermal plasma can be considered as an innovative and powerful tool for synthesis of functional nanoparticles with high purity.

RF thermal plasma was used widely on the TMNs. As early as 1979, Yoshida et al. [5] successfully synthesized the ultrafine TiN particles with a statistical median size of about 10 nm by passing pure titanium powder (<25 μm) through a radio frequency argon-nitrogen plasma. Szépvölgyi et al. [6] synthesized an amorphous Si_3N_4 powder by the vapor-phase reaction of $SiCl_4$ and NH_3 in an RF thermal plasma reactor. Kim et al. [7] synthesized high-purity AlN nanopowders by RF induction thermal plasma.

However, there are few reports about BTMNs prepared by RF induction thermal plasma. Therefore, the purpose of the present work is to synthesize $Ti_{1-x}Nb_xN$ nanoparticles by induction thermal plasma, and to investigate the formation mechanism.

2. Experiment methods

Nanoparticles of $Ti_{1-x}Nb_xN$ (x=0, 0.25, 0.50, 0.75) were prepared by RF induction thermal plasma. The schematic of the experiment setup was illustrated in **Fig. 1**. The setup mainly consists of powder feeder to inject raw materials, plasma torch, reaction chamber, and particle collection filter. The plasma torch works with a water-cooled quartz tube and a water-cooled induction coil (3 turns), coupling its electromagnetic energy to the plasma at a frequency of 4 MHz. In the experiment, the total system was operated at the atmosphere pressure.

The operating conditions are summarized in **Table 1**. The plasma was generated at atmospheric pressure with fixed power of 20 kW. The sheath and inner gases were Ar, the flow rate were 60 L/min and 5 L/min respectively.

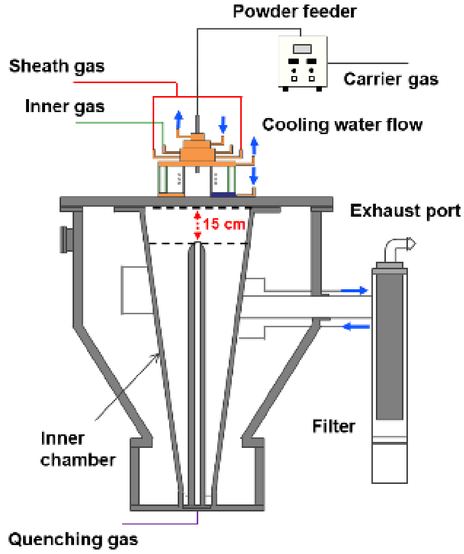

Fig. 1. Schematic of the experimental setup.

Ammonia was selected as the nitrogen source. The quenching gases were Ar (5 L/min) and NH_3 (8 L/min).

Metallic Ti powder (40 μm, purity 99.9%, High Purity Chemicals) and Nb powder (20 μm, purity 99%, High Purity Chemicals) were fed into the torch through the powder feeder by Ar carrier gas (3 L/min). The powder feed rate was fixed at 300 mg/min.

Table 1. Experimental operating conditions for the preparation of $Ti_{1-x}Nb_xN$ nanoparticles.

Input power [kW]	20
RF frequency [MHz]	4
Pressure [kPa]	101.3
Sheath gas rate [L/min]	60 (Ar)
Inner gas rate [L/min]	5 (Ar)
Carrier gas rate [L/min]	3 (Ar)
Feed rate [mg/min]	300
Quenching gas rate [L/min]	5 (Ar)
	8 (NH_3)
Injection position	15 cm

The crystal structure and phase identification of the synthesized nanoparticles were determined through powders X-ray diffraction (XRD, Rigaku Multiflex), operating with a Cu Kα source (λ = 0.1541 nm).

3. Thermodynamic Calculation

Thermodynamic calculations were conducted with software *FactSage 8.1*. The calculations were performed for temperatures up to 5,000 K and pressure of 101.3 MPa for the compositions of the technological mixtures. The Gibbs free energy diagram for the decomposition of N_2 and NH_3 are shown in **Fig. 2**. N_2 molecules dissociate into N radicals above approximately 7,000 K. NH_3 dissociates into NH radicals and NH_2 radicals above approximately 3,000 K. As shown in **Figs. 3** and **4**, the negative Gibbs free energy of Ti/Nb and NH_2/NH radicals below 5,000 K indicates high reactivity. Ammonia can provide a large amount of NH_2 and NH radicals at 3000 ~ 5000 K. These radicals can make Ti/Nb sufficiently nitrided. Therefore, NH_3 was selected as nitrogen source.

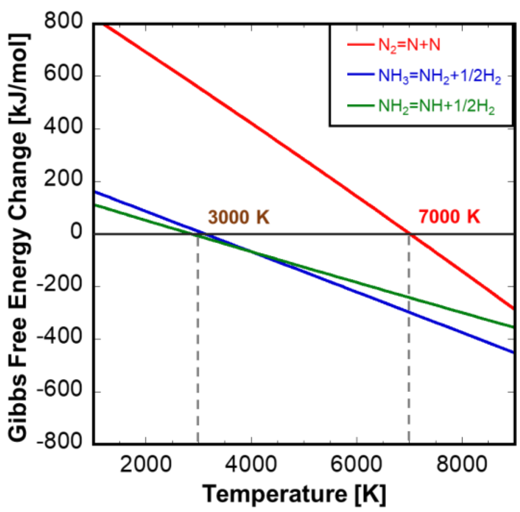

Fig. 2 Gibbs free energy diagram for the decomposition of N_2 and NH_3.

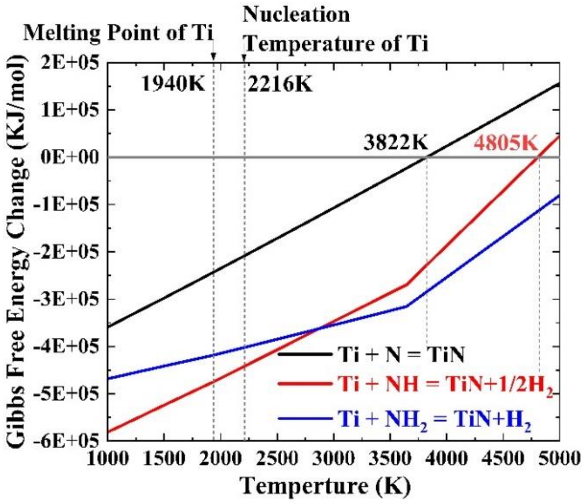

Fig. 3 Relationship between Gibbs free energy change and nucleation point in Ti-N system.

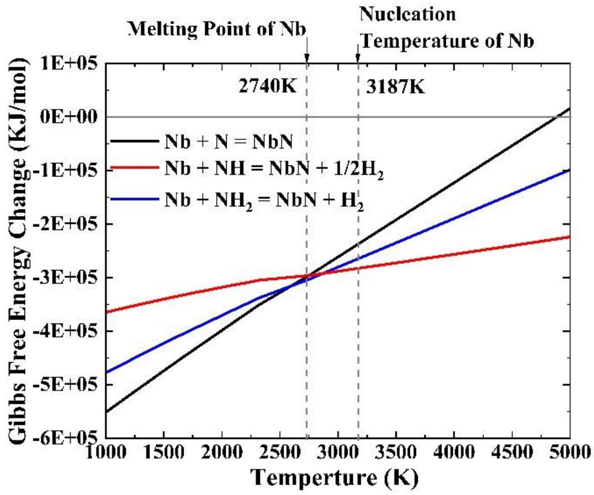

Fig. 4 Relationship between Gibbs free energy change and nucleation point in Nb-N system.

4. Results and discussion

The XRD patterns of $Ti_{1-x}Nb_xN$ nanoparticles with different molar ratios of Ti/Nb are shown in **Fig. 5**. Titanium nitride was successfully synthesized without Nb injection. Main peaks were assigned to be a cubic TiN structure with a space group of *Fm*-3*m*. The diffraction peaks shift to the left with Nb injection and it is more obvious at *x*=0.75. The shift of diffraction peaks suggests the injection of Nb into TiN because the ionic radius of Nb (0.72 Å) is larger than the ionic radius of Ti (0.67 Å). The diffraction peaks are lowered after adding Nb to TiN. This implies that Nb addition plays a significant role in the structural properties of TiN. The results also indicated a small diffraction peak of NbN_x with Nb injection. The content of NbN_x increased with the increase of Nb content.

The obtained results clearly revealed that $Ti_{1-x}Nb_xN$ nanoparticles with high purity are successfully prepared by RF induction thermal plasma.

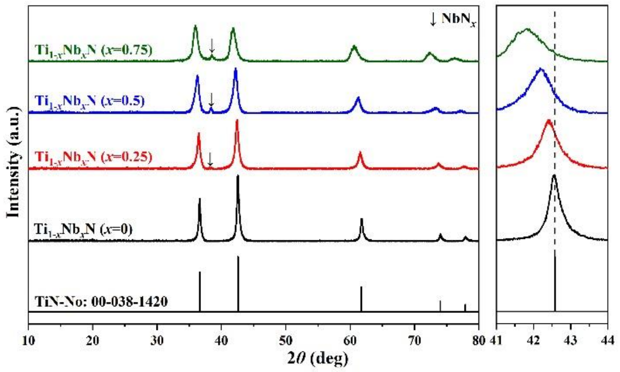

Fig. 5 XRD patterns of $Ti_{1-x}Nb_xN$ nanoparticles with different molar ratios of Ti/Nb

5. Conclusion

Titanium niobium nitrides nanoparticles with high purity were successfully prepared by RF induction thermal plasma. Metallic Ti and Nb powders were used as raw materials. Main peaks were assigned to be a cubic TiN structure with a space group of *Fm*-3*m*. Ammonia injection into plasma tail as counter flow is a suitable method for transition metal nitridation. Induction thermal plasma can provide a highly efficient way to synthesize ternary transition metal nitrides to apply for large-scale industrial production.

6. Acknowledgements

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7. References

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