# Formation Mechanism of Metal-doped ZrN by Induction Thermal Plasma

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**Abstract:** Metal-doped zirconium nitride nanoparticles were firstly synthesized by induction thermal plasma with mole ratio of Zr:dopant = 90:10. Analyses based on XRD, XPS, and STEM-EDS exhibit that each metal is successfully doped into zirconium nitride structure. Formation mechanism was clarified from nucleation temperature and thermal equilibrium calculation. Zirconium nitride firstly nucleates and dopant elements enter zirconium nitride during the co-condensation process to form final product.

Keywords: Induction thermal plasma, metal doping, nanoparticle synthesis.

## 1. Induction

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

Zirconium nitride (ZrN) is widely used as diffusion barriers, hard coatings, and corrosion-resistant layers on optical and mechanical components. Limited oxygen resistance restricts further usage of ZrN, especially when temperature surpasses 700°C. Doping reactive elements is considered as a useful mean to inhibit oxidization because dopant ions diffuse outwardly and segregate in grain boundaries. This phenomenon reduces inward diffusion rate of the oxygen molecule effectively during hightemperature oxidation [1]. Furthermore, doped ZrN nanoparticle has large potential on the field of photocatalyst due to the decrease of band gap energy [2].

Induction thermal plasma has been widely applied on the material doping. Ishigaki et al., reported the synthesis and formation mechanism of cobalt and iron-doped  $TiO_2$  nanopowder by induction thermal plasma [3-4]. This research aims to synthesize metal-doped ZrN nanoparticles with high purity and understand formation mechanism.

## 2. Experiment

## 2.1 Experiment Setup and Conditions

The experiment equipment mainly consists of plasma torch, reaction chamber, power supply of 4MHz at plate power of 20 kW, and quenching tube. The schematic diagram of thermal plasma equipment is demonstrated in **Fig. 1**. The raw materials are supplied as powder along with carrier gas and injected into plasma torch. Raw materials then evaporate instantly and nanoparticles are produced through homogeneous nucleation and heterogeneous condensation in the tail region of plasma flame. Final product is collected from inner chamber wall and filter.

Detailed experiment condition is shown in **Table 1** during nanoparticle synthesis under atmospheric pressure. Argon is taken as sheath gas, carrier gas, and inner gas. The mixture of ammonia and argon is used as quenching gas.







Fig. 2. XRD pattern of nanoparticle with Zr : dopant (Nb, Ta, Al) =90 : 10.

Each experiment was conducted with the quenching tube fixed at 150 mm downstream from the end of the torch. The raw material is composed of ZrN and dopant materials including Ta, Nb, and AlN. ZrN and dopant materials are mixed at given composition and then fed into plasma system at feed rate of 300 mg/min.

Input power [kW]	20
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)
Quenching gas rate [L/min]	10 (NH <sub>3</sub> ) and 5 (Ar)
Discharge time [min]	8
Feed rate [mg/min]	300
Powder mole fraction	Zr: dopant (Ta, Nb, and Al)=90:10

Table 1. Experiment parameters of thermal plasma.

#### 2.2 Analysis

The phase composition of product and lattice constant was detected by X-ray diffractometry (XRD, Rigaku Multiflex), operating with a Cu K $\alpha$  source ( $\lambda = 0.1541$  nm). Lattice constant *a* is calculated by the following equation, based on the Bragg's law.

$$a = \frac{\lambda \times \sqrt{h^2 + k^2 + l^2}}{2 \times \sin(\theta)} \tag{1}$$

where  $\theta$  is diffraction angle, "*h*, *k*, *l*" is Miller index of facet, and  $\lambda$  is X-ray beam of product. Element distribution were measured by scanning TEM-energy dispersive X-ray spectrometry (STEM-EDS, JEOL JEMARM 200F). Element mole ratio and bond information were obtained by X-ray photoelectron spectroscopy (XPS). The mole fraction of element x (*C<sub>x</sub>*) was calculated from the following equation.

$$C_x = \frac{\frac{l_x}{s_x}}{\sum_{i}^{l_i}} \tag{2}$$

where *I* and *S* are peak areas of specific elemental core lines and appropriate atomic sensitivity factors respectively.

#### 3. Result and discussion

The XRD patterns of Ta, Nb, and Al-doped ZrN nanoparticles are shown in **Fig. 2**. The products under all experiment conditions exhibit main peak from ZrN. The peak of  $ZrO_2$  comes from passivation process and  $Zr_2N$  is generated from nitridation deficiency. This result can confirm high purity of final product. Lattice constants of three different doping conditions are obtained from Bragg's law calculation, which is presented in **Fig. 3**. Lattice constant of ZrN decreases when Zr ions are replaced by elements with smaller ionic radius (Nb<sup>5+</sup> and Al<sup>3+</sup>). Lattice constant does not change with doping of Ta, which has the same ionic radius as Zr<sup>4+</sup> ions.



Fig. 3. Relationship between ZrN lattice constant and dopant ionic radius with 10 mole percent doping.



Fig. 4. XPS survey analysis of nanoparticle with Zr: dopant (Nb, Ta, Al) =90 :10.

Table 2. Mole ratio of Zr to dopant elements in final product with the doping of Ta, Nb, and Al.

Dopant	Zr : dopant mole ratio
Nb	92.9:7.1
Та	90.2:9.8
Al	93.1:6.9

The XPS survey analysis of different metals-doped ZrN is shown in **Fig. 4**. Main peaks come from Zr, N, O, and dopant elements. Other peaks belong to Au from reference and carbon from conductivity type. The integrated intensity of Zr and dopant peak from survey scan analysis can provide information about mole ratio of Zr to dopant in final product with the aid of Eq. (2). The mole ratio is

shown in **Table 2**. The mole ratio is similar with that of raw material, indicating most dopant elements enter final product. Narrow scan analysis of dopant elements is shown in **Fig. 5**. Metal-nitride bonds exist in all samples, which come from  $Zr^{4+}$  replacement in ZrN lattice. Metal-oxide bonds are from oxidation on particle surface.

Nanoparticle with mole ratio of Zr : Al=90:10 is selected as representative to exhibit the element distribution of Zrand dopant. Element mapping image by STEM-EDS is shown in **Fig. 6**. Mole ratio obtained from 6 points in mapping image is concluded in **Table 3**. Results suggest that Zr is well overlapped by Al, indicating that elements distribute evenly in the whole particle.

Table 3. Mole ratio of Zr to Al in element mapping image

Point	Zr : Al mole ratio
1	94.9:5.1
2	94.2:5.8
3	90.7:9.3
4	94.5:5.5
5	93.3:6.7
6	94.9:5.1

Homogeneous nucleation temperatures of metals can be calculated based on nucleation theory considering nondimensional surface tension. The homogeneous rate J is obtained from the following equation.

$$J = \frac{\beta_{ij} n_s^2 S}{12} \sqrt{\frac{\theta}{2\pi}} exp \left[ \Theta - \frac{4\theta^3}{27(\ln S)^2} \right]$$
(3)

where *S* is saturation ratio and  $n_s$  is the equilibrium saturation monomer concentration at temperature *T*.  $\beta$  is collision frequency function. The dimensionless surface tension is calculated from the following equation.

$$\Theta = \frac{\sigma s_1}{kT} \tag{4}$$

where  $\sigma$  is the surface tension and  $s_1$  is the monomer surface area. When nucleation rate is above unity, nucleation can become stable. The saturation ratio at this time has dominant influence on determining nucleation temperature. Compound melting point is normally considered as nucleation temperature because compounds usually nucleate near their melting point.

The nucleation temperature of each element is summarized in **Fig. 7**. The nucleation temperature of ZrN is the highest with the doping of Nb and Al, indicating that ZrN nucleates firstly during synthesis of Nb and Al-doped ZrN. However, nucleation temperature of Ta and TaN is higher than that of ZrN. Thermal equilibrium of 10mol% of Ta doping is demonstrated in **Fig. 8**. The equilibrium diagram shows that Ta amount is sufficiently small to decrease nucleation temperature of TaN, which is lower than ZrN nucleation temperature. The existence of Ta vapor is observed after ZrN nucleation, indicating Ta is likely to be doped into ZrN.



Fig. 5. XPS narrow analysis of Nb 3d, Ta 4f, and Al 2p.



Fig. 6. Element mapping of Zr and Al of Zr: Al=90:10 and 6 points selected to detect mole ratio.

Formation mechanism is clarified based on abovementioned discussion. Raw material is evaporated in thermal plasma region. ZrN nucleates firstly at 3253 K and dopant element and Zr-N vapor then condense near ZrN nucleate from upstream to downstream of synthesis process. Passivation is finally operated to form oxidation protect layer on particle surface.

### 4. Conclusion

Metal-doped ZrN nanoparticles were successfully synthesized by induction thermal plasma. The product exhibits even element distribution, enough doping amount, and high purity. Formation mechanism was clarified based on nucleation temperature and thermal equilibrium calculation. ZrN firstly nucleates and dopant elements enter zirconium nitride during the condensation process to form final product.

### Acknowledgements

The authors thank the Ultramicroscopy Research Center (Kyushu University) for STEM-EDS observation. The authors also thank the center of Advanced Instrumental Analysis (Kyushu University) for XRD and XPS analysis.



Fig. 7. Nucleation temperature of each element.



Fig. 8. Thermal equilibrium diagram of Zr: Ta=90:10.



Fig. 9. Formation mechanism of product.

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