

Characterization of NiO nanoparticle coating on YSZ powder prepared by precipitation

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NiO nanoparticle coating on YSZ particles was prepared by precipitation using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The coated powder was calcined in air at temperatures between 300 °C and 800 °C. XPS and X-ray line profile analysis were employed to ascertain NiO coating. The growth of NiO crystallites on YSZ particles was significantly retarded during heat treatment. The Williamson-Hall analysis suggested that the retardation of NiO growth was associated with the strain developed by underlying YSZ particles. The results of XPS showed that NiO coating was initially continuous but became discontinuous as the calcination temperature increased.

Key words: NiO coating, YSZ, Crystallite growth, Williamson-Hall method, XPS.

Introduction

Coated powders have received much interest because of many advantages over mechanically mixed powders. Sintering of composites prepared with mechanically mixed powders is restricted due to the formation of a rigid network between the reinforcing particles and inhomogeneous packing of the matrix phase [1]. However, the use of coated powders can significantly reduce these sintering impediments [1,2]. It has been reported that the densification of powders coated with rigid inclusions is very similar to that for powders containing no inclusions [3,4]. In addition, the coated powder can be used in processing that requires the uniform distribution of small amounts of additives. It has been claimed that the coating of additives on particles not only improves the green density and sinterability but also enhances phase uniformity and mechanical properties of the sintered body [5,6].

Since the use of coated powders has considerable fabrication benefits, various coating methods have been employed including precipitation [7-12], sol-gel [13,14], and electroless plating [15]. The coated powders have been investigated with TEM, AES, FTIR, XPS, etc., but it is not easy to characterize them as their particle sizes become nano-scale. XRD peak broadening analysis may be considered as an additional technique. Peak broadening arises mainly from two factors: crystallite size and lattice strain [16,17]. The effects of crystallite size and lattice strain can be separated by the

Williamson-Hall method. Nanoparticles of single phase will show only crystallite size effect because they can grow freely during calcination and no strain exists. Whereas, nanoparticle coating will show both effects if its growth is retarded by underlying particles.

In the present work, NiO coating on YSZ particles was prepared by precipitation and characterized with SEM, XRD, and XPS. The growth of NiO nanoparticles during the calcination process was studied by measuring the crystallite size, and XRD peak broadening of the coating was investigated using the Williamson-Hall method.

Experimental Procedure

A slurry was prepared by mixing YSZ powder (Tosoh, TZ-8Y) with 2M Ni nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Junsei) solution. The 1M ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$, Sigma-Aldrich) solution as a precipitant was slowly added to the slurry and mixing was continued until complete precipitation. The resulting slurry was filtered, repeatedly washed with water and ethanol, and then dried for 12 hrs at 80 °C. The dried powder was calcined in air at temperatures between 300 °C and 800 °C for 4 hrs at a heating rate of 5 °C/min. The amount of NiO in the powder was 56 wt% (52.4 vol%). In addition, NiO powder was prepared from Ni precipitates obtained under the same condition as the coated powder.

The calcined powders were examined with XRD (Cu K_α , M03XHF, Bruker) and SEM (FEI XL-30 FEG, FEI). The powder surface was analyzed with XPS (Al K_α source, Sigma Probe, Thermo VG) using carbon as a calibration standard for chemical analysis.

The crystallite size of NiO was calculated using the

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Scherrer formula [16],

$$D = \frac{\kappa\lambda}{\beta \cos \theta} \quad (1)$$

D is crystallite size (nm); κ a constant which is 0.9; λ the wavelength of Cu K_α (0.15418 nm); θ the diffraction angle; β the half-width of the diffraction peak. The half-width β was corrected using the equation, $\beta^2 = \beta_m^2 - \beta_i^2$ where β_m refers to the measured half-width and β_i to the half-width of the instrument. The half-widths were measured from NiO peaks obtained at a scanning speed of 0.5° 2 θ /min in the range of 30°~80°. The half-width of (200) NiO peak was used for the crystallite size measurement. The half-width of the instrument was obtained from NiO powder (Sumitomo, 99.9%) having crystallites fully grown at 1400 °C. All peak positions were corrected with high purity Si as a diffractometer calibration standard.

After subtracting the instrumental broadening, the half-width is expressed as [16]

$$\beta = \beta_{\text{crystallite}} + \beta_{\text{strain}} \quad (2)$$

The widths due to crystallite size ($\beta_{\text{crystallite}}$) and lattice strain (β_{strain}) are given by $\frac{\kappa\lambda}{D \cos \theta}$ and $\eta \tan \theta$, respectively. Rearranging Eq. (2) gives the Williamson-Hall equation

$$\beta \cos \theta = \frac{\kappa\lambda}{D} + \eta \sin \theta \quad (3)$$

Plotting of $\beta \cos \theta$ against $\sin \theta$ gives a straight line with a slope (η) and an intercept ($\frac{\kappa\lambda}{D}$). Ni precipitates and Ni precipitate-coated YSZ powder calcined at 600 °C were used in the Williamson-Hall plot.

Results and Discussion

Fig. 1 represents SEM images of NiO-coated YSZ powder. The as-prepared powder in Fig. 1(a) shows Ni precipitate-coated YSZ particles consisting of agglomerated primary nanoparticles of <~100 nm in size. These particles became severely agglomerated in the calcination process at 800 °C, as shown in Fig. 1(b). It was not able to recognize NiO coating from SEM images.

Fig. 2 shows XRD patterns of NiO-coated YSZ powders calcined at various temperatures. Miller indices corresponding to NiO peaks were given in Fig. 2. Increasing NiO peak intensity with temperature reveals that NiO grew to well-developed crystalline phase. However, YSZ particles did not grow at all calcination temperatures as indicated by no change in peak intensities. Fig. 3 illustrates the broadening of (200) NiO diffraction peaks for NiO and NiO-coated YSZ powders. NiO powder was already crystallized at 300 °C and continued to grow up to 800 °C (Fig. 3(a)). However, NiO in the coated powder was in an amorphous form at

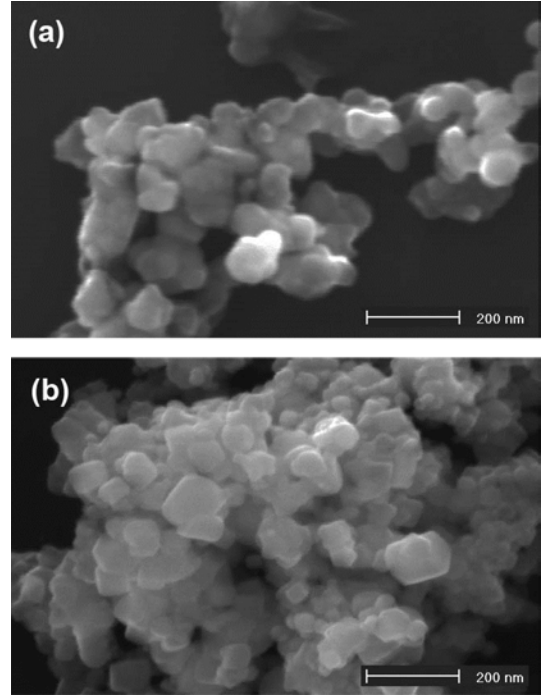


Fig. 1. SEM images of NiO-coated YSZ powders: (a) as-prepared and (b) calcined at 800 °C.

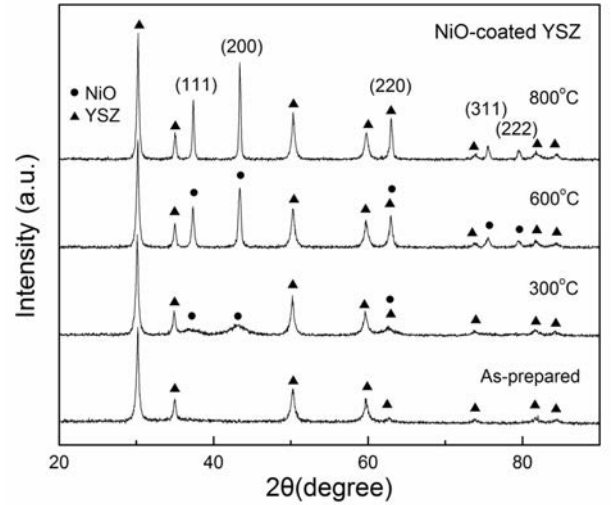


Fig. 2. XRD patterns of NiO-coated YSZ powders calcined at various temperatures.

300 °C and did not grow at higher temperatures as much as the single-phase NiO (Fig. 3(b)).

Fig. 4 is an Arrhenius plot of NiO crystallite size versus reciprocal absolute temperature, showing the temperature dependence of NiO growth. The straight lines with the same slope for NiO and NiO-coated YSZ powders are indicative of the same growth mechanisms, but the growth rates are different from each other. The crystallite size of NiO for the single-phase NiO powder was 10.1 nm at 300 °C and rapidly increased to 105.6 nm at 800 °C. Whereas, the growth of NiO for the coated powder was retarded by underlying YSZ

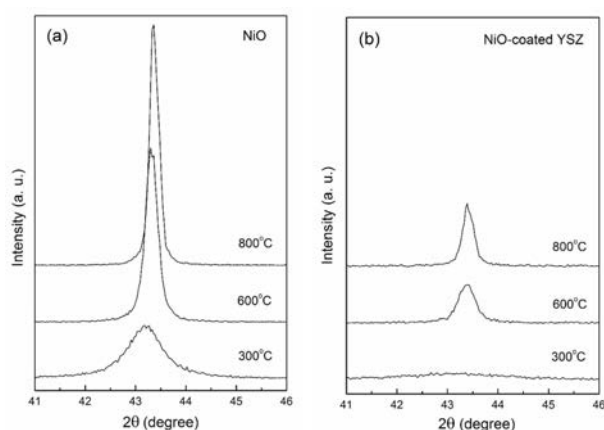


Fig. 3. Broadening of (200) NiO diffraction peak for (a) NiO and (b) NiO-coated YSZ powders at various temperatures.

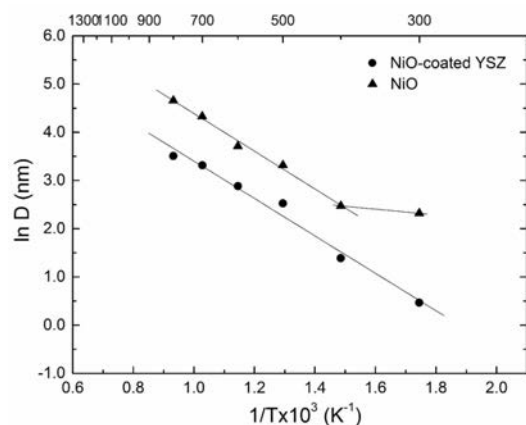


Fig. 4. Crystallite sizes of NiO as a function of calcination temperature.

particles. NiO crystallites were only 1.6 nm in size at 300 °C and slowly grew to 33.3 nm at 800 °C. A steady increase in crystallite size in the temperature range of 300 °~400 °C was attributed to the growth of the crystallites within small aggregates. The thermal decomposition of Ni precipitates and removal of volatiles result in highly porous and very fine crystallite aggregates. At this temperature region, these aggregates are densified into single crystallites [18].

The retarded growth of NiO has been reported in nano-crystalline NiO-coated Fe_2O_3 powder [11]. Also, the retardation of ZrO_2 growth has been observed in an ultrafine mixture of ZrO_2 and Al_2O_3 powders prepared by chemical methods [19]. In contrast, mechanically mixed powders were found to exhibit the same growth as observed in the powder containing no Al_2O_3 . In this study, the growth of NiO in the coated powder is different from that of chemically prepared powder mixtures. NiO crystallites decomposed from Ni precipitates are strongly bound to YSZ particles, and hence their growth will be restrained. As a result, a strain will be developed in NiO crystallites during the heat treatment. It should be noted that the underlying

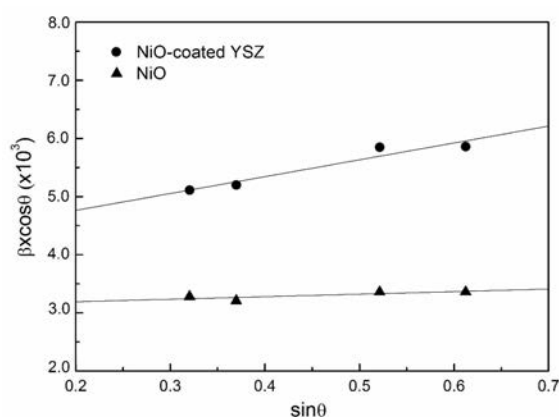


Fig. 5. Williamson-Hall plot for NiO and NiO-coated YSZ powders calcined at 600 °C.

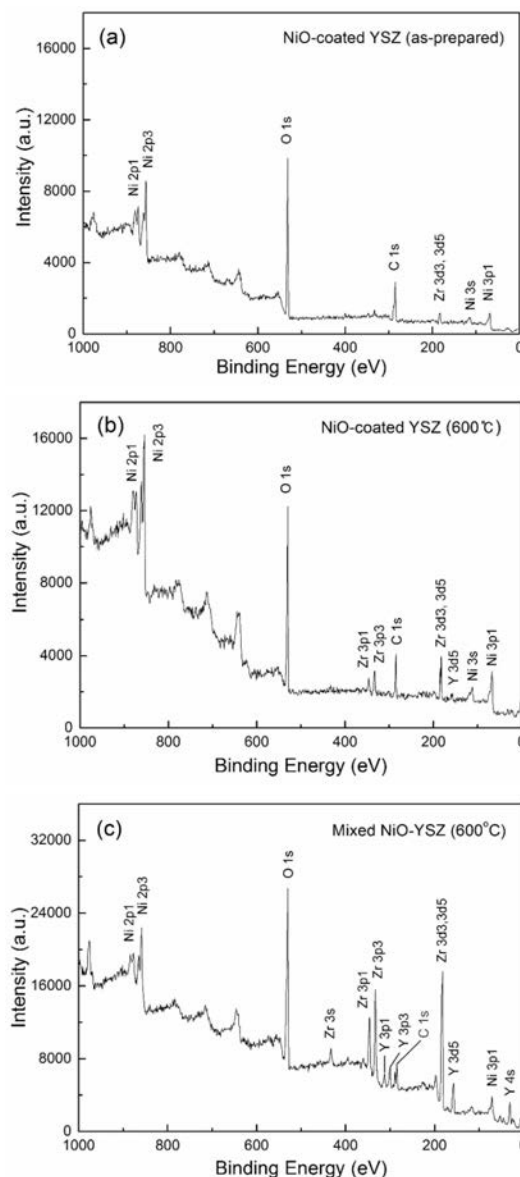


Fig. 6. XPS spectra of NiO-coated YSZ powders (as-prepared (a) and calcined at 600 °C (b)) and mechanically mixed NiO and YSZ powders (c).

Table 1. Chemical analysis of NiO-coated YSZ powder calcined at different temperatures by XPS.

Temperature (°C)	NiO wt% (vol%)	ZrO ₂ wt% (vol%)	Y ₂ O ₃ wt% (vol%)
300	93.4 (92.5)	5.4 (5.8)	1.3 (1.7)
600	80.9 (78.7)	15.7 (16.7)	3.5 (4.5)
800	64.1 (61.2)	31.0 (32.5)	4.9 (6.4)

YSZ particles do not affect the growth of NiO because their sizes remain unchanged at all calcination temperatures, as mentioned previously.

Fig. 5 shows the Williamson-Hall plot for NiO and NiO-coated YSZ powders calcined at 600 °C. NiO powder exhibits a straight line with no slope, suggesting that only crystallite size affects the peak broadening. Whereas, the coated powder shows a straight line with a slope and an intercept. This indicates that strain, as well as crystallite size, contributes to the peak broadening. Therefore, the retardation of NiO growth in the coated powder was associated with the strain developed in NiO crystallites.

In order to ascertain the presence of NiO coating, NiO-coated YSZ powder was analyzed with XPS. Figs. 6(a) and (b) are XPS spectra of as-prepared powder and the powder calcined at 600 °C, respectively. For comparison, XPS spectrum of a mechanical mixture of NiO and YSZ powders is shown in Fig. 6(c). Ni peaks in Fig. 6(a) suggests that YSZ particles were coated with Ni precipitates. A very weak Zr peak can be attributed to the coating thickness. Considering the detection depth of XPS (~10 nm), Zr peak can be detected if any portion of the coating layer is not uniform. More Zr peaks appeared in the powder calcined at 600 °C, indicating that a small portion of YSZ particle surfaces was exposed (Fig. 6(b)). In contrast, the powder mixture showed much stronger Zr and Y peaks compared with those for the coated powder because NiO and YSZ particles existed separately (Fig. 6(c)).

The appearance of Zr and Y peaks in the coated powder calcined at 600 °C can arise from an agglomeration of NiO nanoparticles. NiO nanoparticles grow and agglomerate with increasing temperature. As a result, the underlying YSZ particle surfaces become more exposed and thus more and stronger Zr and Y peaks are observed. Table 1 represents the surface analysis for the coated powder by XPS. YSZ particles were nearly coated with NiO, as indicated by 93.4 wt% (92.5 vol%) of NiO at 300 °C. As the calcination temperature increased to 800 °C, the amount of NiO was decreased to 64.1 wt% (61.2 vol%) with concurrently increasing the amounts of ZrO₂ and Y₂O₃.

Conclusions

NiO nanoparticle coating on YSZ particles was

prepared by precipitation using Ni(NO₃)₂·6H₂O and (NH₄)₂CO₃ as a precipitant. The coated powder was calcined in air at temperatures between 300 °C and 800 °C. NiO crystallites in single-phase NiO powder grew without any constraint during the heat treatment. However, their growth on YSZ particles was significantly retarded. NiO crystallite size for single-phase NiO powder rapidly increased from 10.1 nm at 300 °C to 105.6 nm at 800 °C, whereas that for the coated powder was only 1.6 nm at 300 °C and increased to 33.3 nm at 800 °C. The Williamson-Hall analysis suggested that the retardation of NiO growth was associated with the strain developed by strongly bound underlying YSZ particles. The results of XPS showed that NiO coating was initially continuous but became discontinuous with increasing calcination temperature. YSZ surfaces were found to be more exposed due to the agglomeration of NiO nanoparticles.

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