PRODUCTION OF ALUMINA/NI NANOCOMPOSITES BY HETEROGENEOUS PRECIPITATION METHOD AND PRESSURELESS SINTERING

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Abstract- In the present study, Al_2O_3/Ni composites with different Ni volume ratios (1, 3, 5vol.%) were prepared by the heterogeneous precipitation method by pressureless sintering at 1450-1550°C for 2h. The structural and mechanical properties of the composites were characterized by XRD, SEM and Vickers Indentation technique, respectively. Homogeneous microstructure could be obtained in all composites. The effects of Ni content and sintering temperature on densification and mechanical properties were analyzed.

Keywords- Alumina, Nanocomposite, Hardness, Microstructure.

I. INTRODUCTION

Alumina (Al_2O_3) possesses high mechanical properties like high hardness, abrasion resistance with chemical stability and it is very cost-effective material in the family of advanced ceramics. These properties make it an ideal material to perform in a variety of applications such as alumina-based wearing parts, biomaterials, armors. It wouldn't be wrong to consider alumina as the "workhorse material" of the structural ceramics. However, the applications of alumina are limited by the material's low tensile strength, fracture toughness, and low thermal shock resistance. To prevent catastrophic failure in service, designs must take into consideration its limitations [1]. In this direction, Al_2O_3 matrix composites have been widely explored since 1990's. Especially ceramic nanocomposites which contain sub-micron secondary phase particles dispersed in micron grain sized Al_2O_3 matrix is a favorable choice to enhance low mechanical properties [2]. On the basis of nanocomposite concept, Al_2O_3/metal nanocomposites have an important place and by producing this kind of composites, not only high mechanical properties but also other attractive properties such as magnetic, electric or optical can be obtained [3]. Mentioned high properties are especially related to the microstructure and its homogeneity. Hence it is critical to choose the most appropriate fabrication method. Compared to other methods such as mechanical mixing of Al_2O_3 with metallic powders or sol-gel, coating processes (like electroless plating, co-precipitation, and heterogeneous precipitation) have important advantages and so they are being investigated comprehensively in recent years. By employing coating methods both green density and sintering activity can be improved; also, the uniformity of different phases and mechanical properties of sintered body can be enhanced [4].

In this study, Al_2O_3 powders were coated with nano-sized nickel particles by using heterogeneous precipitation method. Guo Jun Li and his co-workers prepared Ni coated Al_2O_3 composites by using this method but they preferred hot pressing route (at 1300-1450°C with an applied pressure of 20 MPa) for sintering the nanocomposites which have different nickel contents (4, 6.5, 8.5vol.% and 10vol.%) [4,5]. We used pressureless sintering route and the composites were prepared by changing the nickel volume ratios as 1, 3, 5 vol.%. The main goal of this work is to densify Al_2O_3/Ni composites with homogeneous metal particle dispersion without using hot pressing sintering route. The effects of nickel content on density, microstructure, and hardness were investigated.

II. EXPERIMENTAL PROCEDURE

Al_2O_3/Ni powder mixture with different volume ratios of Ni (1, 3, 5vol.%) was prepared using an alumina powder (Almatis Calcined Alumina, Germany), appropriate amounts of $Ni(NO_3)_2.6H_2O$ (BDH Chemicals Ltd. Poole England, % 98 purity) and NH_4HCO_3 (Sigma-Aldrich, % 99 purity) as starting materials. The amount of nickel nitrate was adjusted according to the volume ratio of Ni in the final composite in every experiment. Al_2O_3, $Ni(NO_3)_2.6H_2O$ and 0.5wt% polyacrylic acid as a dispersant were first mixed in distilled water and ball milled for 24 hours with yttria-stabilized zirconia balls (ball: Al_2O_3 powder ratio of 10:1 by weight). The average particle size of Al_2O_3 powder after ball milling was measured as 500 nm. Then, NH_4HCO_3 solution of 1.0 M was added dropwise to the as prepared slurry under vigorous stirring. Precipitation reaction of Ni precursor is given by the following equation [6],

$$3Ni^{+2} + 6HCO_3^{-1} + H_2O \rightarrow NiCO_3 \cdot 2Ni(OH)_2 \cdot 2H_2O \downarrow + 5CO_2\uparrow$$

By using an excess amount of NH_4HCO_3 and by keeping the pH value of mixed solution between 8-9 during precipitation, above reaction could be

completed. The slurry was filtered and thoroughly washed with distilled water and ethanol. The precipitants were dried in air for 24 h and calcined in air at 550°C for 2h and reduced in a 90%Ar/10%H_2 atmosphere at 700°C for 4h. Calcining and reducing cycles were applied at 5°C/min heating rate then cooled down to room temperature in the furnace.
After reduction, nano Ni-coated Al_2O_3 composite powder was pressed as pellet form under the uniaxial pressure of 70 MPa, then cold-isostatically pressed under 90 MPa. Specimens were sintered at three different temperatures (1450-1500-1550°C) in a vertical tube furnace under 90%Ar/10%H_2 atmosphere. Sintering cycles were applied as 5°C/min heating rate and held 2h at sintering temperature then cooled down to room temperature in the furnace. Pure Al_2O_3 specimens were prepared by ball milling and pressing in similar conditions and sintering at 1450-1550°C for 2h in air.

X-ray diffraction (XRD) patterns were obtained at a scanning rate of 4°/min with a 2Θ range from 10° to 70 by a Bruker diffractometer. The bulk density measurements of the sintered samples were evaluated by the Archimedes' water replacement method. The samples, in pellet shape, were polished down to 0.5 µm to eliminate the effect of surface flaws on mechanical properties. Scanning electron microscope (SEM) (Philips XL30-FEG) was employed to characterize the polished surfaces.
Hardness was measured by an Instron® Wolpert Testor 2100 equipped with a diamond pyramid Vickers indenter. Loading time and load was selected as 10 s and 5 kg, respectively.

III. RESULTS AND DISCUSSION

Fig.1 shows XRD patterns of alumina powder, the powder mixtures and sintered Al_2O_3/Ni composite for 5vol.% Ni content at 1550°C. For comparison purposes, Fig. 1.a shows the XRD pattern of starting alumina powder. XRD results indicate that precipitated Ni precursor $NiCO_3$•$2Ni(OH)_2$•$2H_2O$ is an amorphous phase because no new peaks are present except for Al_2O_3 peaks (Fig. 1.b). After calcination at 550°C/2h in air, the amorphous phase was crystallized to nano-sized discrete NiO particles [4] (Fig. 1.c). By heat treatment at 700°C/4h in 90%Ar/10%H_2 atmosphere, NiO particles were all reduced to nano-sized Ni particles (Fig. 1.d). The calcination and reduction parameters were determined according to Guo-Jun Li and his co-workers study [7] and Sekino and his co-workers study [8], respectively. Finally, by sintering in reducing atmosphere Ni was kept in a metal form and Al_2O_3/Ni composites were produced (Fig. 1.e). Fig.2 is the XRD patterns of sintered Al_2O_3 and Al_2O_3/Ni composites with 1, 3 and 5 vol.% Ni content. It can be seen that when the volume ratio of Ni increases, Ni peaks become evident.

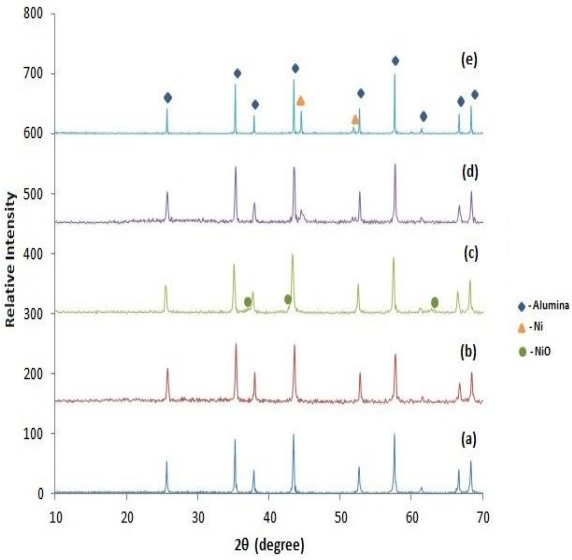


Fig.1. XRD patterns of the powder mixtures and sintered Al_2O_3/Ni composite with 5vol%Ni content. (a) monolithic alumina (b) uncalcined (c) calcined at 550°C/2h (d) reduced at 700°C/4h (e) sintered at 1550°C/2h.

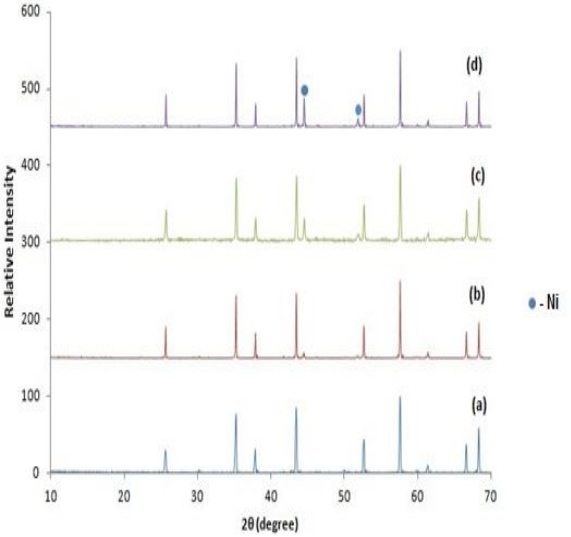


Fig.2. XRD patterns of the sintered Al_2O_3/Ni Composites with (a) monolithic alumina (b) 1vol.% Ni (c) 3vol.% Ni (d) 5vol.% Ni.

Fig.3 shows the variation of relative densities for Al_2O_3/Ni composites containing different Ni content. With increasing sintering temperature, the relative densities of composites enhance. When Ni content is lower (1 vol.%), the composites attain the highest relative densities of 98.2 % at 1550°C. When Ni content is higher (5 vol.%), the relative density is 97.1 % at 1550°C. The melting temperature of Ni is 1450°C and there is a liquid phase in the range of sintering temperature. Wetting ability of Ni to Al_2O_3 is poor in both liquid and solid state [4]. The nonwetting behavior of Ni hinders the densification of the microstructure, especially in higher Ni content because of the larger interface of Al_2O_3/Ni surfaces. Although pressureless sintering was applied, densification was acceptable.

Fig.4 presents the polished surface SEM-BSE images of the Al_2O_3/Ni composites with different Ni content sintered at 1450°C. Their densities decrease with increasing Ni content as 91, 88, 85%, respectively. Nickel has a higher atomic number than Al_2O_3 so Ni grains appear white and Al_2O_3 grains appear gray. It is seen that porosity increases in the microstructure with increasing Ni content. In all composites, homogeneous metal dispersion could be obtained. Metal grain sizes were calculated to be in the range of 150-500 nm from SEM images; however, for 5vol.% Ni content (NA5) particles exceeding 1 □m could also be seen.

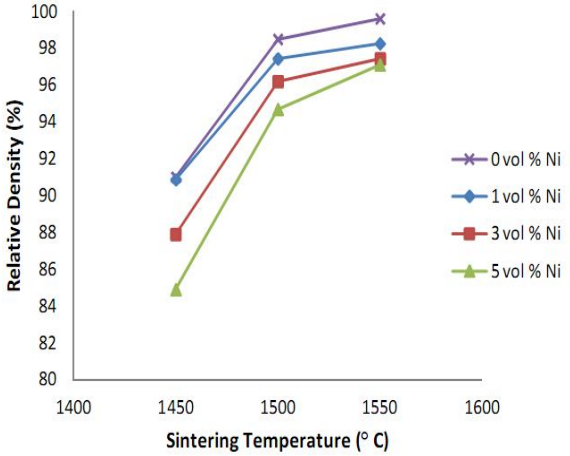
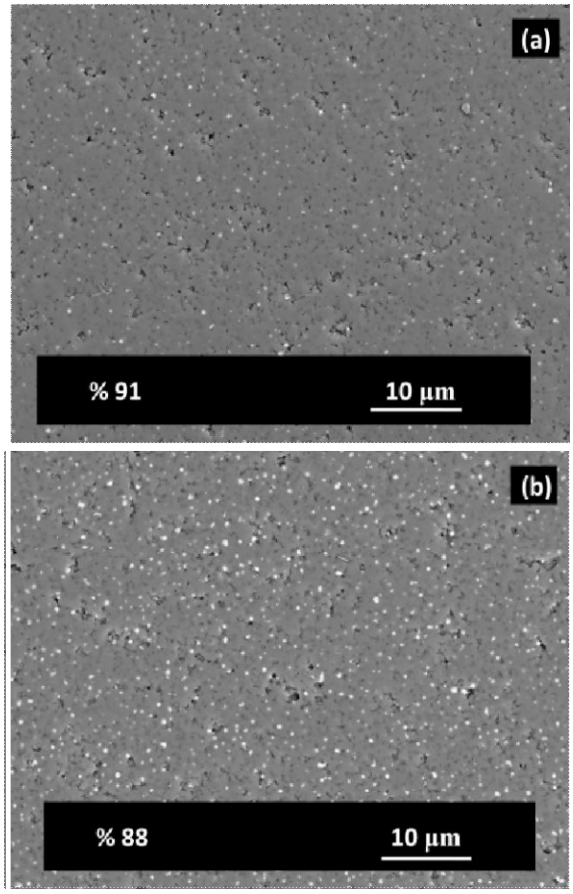


Fig.3. Relative densities vs. sintering temperature for pressureless sintered Al_2O_3/Ni composites.



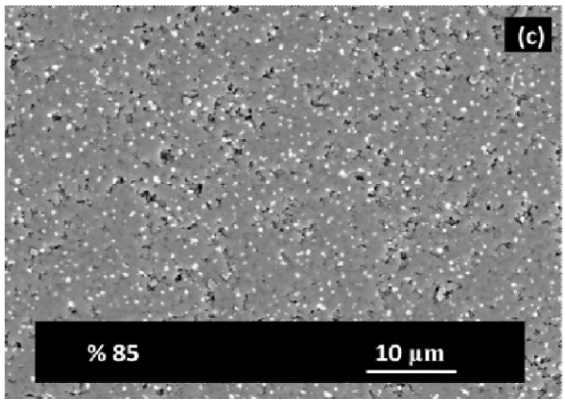


Fig.4. Polished surface SEM-BSE images of (a) 1vol.% Ni (b) 3vol.% Ni (c) 5vol.% Ni

Fig.5 shows the relation of hardness, sintering temperature, and Ni content. Al_2O_3/Ni composites present higher values at a high sintering temperature (1550°C). Al_2O_3/Ni composite with 1 vol.% Ni content is the hardest one at 1550°C (22.5GPa). An increase in Ni content and a decrease in relative density would reduce the hardness of the ceramic material according to the rule of mixtures. Hardness of the composite with 5vol.% Ni is measured to be 22.0 GPa. As predicted there is a decrease in hardness; however, this decrease is somewhat less than expected and within experimental variation. It appears that increase in Ni content does not have an adverse effect on the hardness of the material. It is proposed that in nano-sized metals dislocation slip is restricted and hardness is enhanced [9]. In our composites, the nickel size is above 100 nm but it appears that they are still small enough and do not reduce the hardness of the material and the decrease in hardness is attributed to the slightly lower density of the NA5.

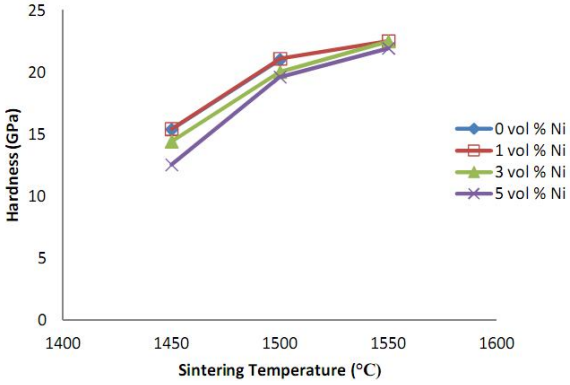


Fig.5. Relation of hardness, sintering temperature and Ni content.

CONCLUSIONS

In the present study, dense Al_2O_3/Ni composites with different nickel content (1, 3, 5 vol.% Ni) were prepared by heterogeneous precipitation method by pressureless sintering at 1550°C. Homogeneous microstructure could be obtained for all Ni ratios. It was observed that Ni content has an adverse effect on densification of Al2O3/Ni composites. On the other

hand, measurements showed that Ni content did not reduce the hardness of the material. It is concluded that if better densification could be achieved an increase in the hardness of the composite material is possible.

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