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Synthesis of ZrO₂ nanoparticle by combination of sol-gel auto-combustion method- irradiation technique, and preparation of Al-ZrO₂ metal matrix composites

ABSTRACT

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Nanocrystalline ZrO₂ with particle size of about 38 nm was directly synthesized by sol-gel auto-combustion method. The overall process involved three steps: formation of homogeneous sol at 50-55°C; formation of dried gel at 110°C, and combustion of the dried gel at 400°C. Experiments revealed that ZrO₂ dried gel derived from glycine (Fuel) and nitrate sol exhibited self propagating combustion at 400°C that it was ignited in air. The auto-combustion was considered as a heat-induced exothermic oxidation-reduction reaction between nitrate ions and carboxyl group. After auto-combustion, products were calcined at 650°C. ZrO₂ nano particle were incorporated into the A356 aluminum alloy by a mechanical stirred at 850°C and after that, cylindrical specimens were cast. After preparing the samples, mechanical properties were measured. The results of microstructure, compression and hardness tests indicated that addition of ZrO₂ nano particulates to aluminum matrix composites improved the mechanical properties. Also, Based on experiments, it was revealed that the presence of ZrO₂ reinforcement led to significant improvement in hardness and compressive strength.

Keywords: *ZrO₂; Nanostructure; Mechanical properties; Sol-Gel; Auto-Combustion; Ultrasonic.*

INTRODUCTION

Zirconium oxide (ZrO₂) has attracted considerable attention because of its diverse practical applications in fuel-cell technology [1], as a catalyst or catalyst support [2], oxygen sensor [3], protective coating for optical mirrors and filters [4], nanoelectronic devices, thermal-barrier coating [5], ceramic biomaterial [6], and thermo luminescence UV dosimeter [7]. ZrO₂ nanostructures are of significant current interest in preparing piezoelectric, electro optic, dielectric, and nanocomposite materials [8-10].

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ZrO₂ is classified as a wide band gap semiconductor and tends to become more conductive with increasing temperatures.

The crystal structure of ZrO₂ significantly influences its physical properties. Pure ZrO₂ exists in three polymorphic phases at different temperatures: monoclinic, tetragonal, and cubic. At very high temperature (>2370°C) the material has a cubic structure. From temperature 1150°C to 2370°C, ZrO₂ has a tetragonal structure. At low temperature (below 1150°C) the material transforms to the monoclinic structure which is a thermodynamically stable phase [11].

ZrO₂ powders with nanostructured particles have been synthesized by various techniques [12-15]. Hydrothermal route is one of the most extensively employed techniques in the synthesis of metal oxide nanostructures [16].

Aluminum matrix composites possess many advantages such as low specific density, high strength and good wear resistance with the development of some non-continuous reinforcement materials, whisker, fibers or particles. In particular, the aluminum matrix composites reinforced with particles, not only has good mechanical and wear properties, but also are economically viable [17-20].

There are many methods for fabrication of metal matrix composites (MMCs) such as powder metallurgy [21], squeeze casting [22-25], and compocasting [26-29]. For the metal matrix composites, molten metal mixing is a cost effective method while powder metallurgy is costly, and squeeze casting provides good infiltration quality of chopped performs [30, 31].

In this paper, we study the synthesis of ZrO₂ nanostructure by combination of sol-gel auto-combustion method and irradiation technique using zirconium (IV) nitrate as a precursor. Then, ZrO₂ nanopowder was stirred into the molten A356 aluminum alloy with a graphite stirrer at 850°C.

EXPERIMENTAL

Zirconium (IV) nitrate (Zr(NO₃)₄·3H₂O, Merck), glycine (Merck), NH₄OH (Merck) and Al powder (Merck) were used as raw materials. All the reagents were used without further purification. Deionized water was used for all experiments.

Aluminum (A356) was obtained from Kian Alloy Company, in Kashan of Iran as metal matrix of composites. The chemical analysis of Al alloy is given in Table 1.

Table 1. Chemical analyses of A356.

| Element | Mass Percent |
|---------|--------------|
| Al | 91.73 |
| Mn | 0.02 |
| Cu | 0.18 |
| Fe | 0.32 |
| Si | 7.23 |
| Mg | 0.38 |
| Zn | 0.05 |
| Ni | 0.02 |
| Ti | 0.01 |

Nanoparticles of ZrO₂ are prepared by sol-gel auto-combustion method. Appropriate amounts of analytical grade Zr(NO₃)₄·3H₂O are taken and mixed with glycine. The ratio of the nitrate to glycine is equal to 1:3. The mixture is then dissolved in deionized water. The addition of glycine helps the homogenous distribution and segregation of the metal ions. A small amount of ammonium hydroxide is added carefully to the solution to change the pH value to 7. The solution is continuously stirred using a magnetic stirrer. The resultant sol is poured in a platinum crucible and heated at 400°C.

The reinforced phases used to improve strength of ZrO₂ ceramics matrix in this research were aluminum alloy A356. The ZrO₂ powders were synthesized particle size of about 38nm. The structure of the ZrO₂ nano particle was monoclinic structure. Therefore, cast treatable alloy A356 was selected. The ZrO₂ powders were mixed homogeneously with 0.75 and 1.5 Vol. % and Al powder at room temperature. The mixture was then placed in a stainless steel mold and 20 MPa of pressure was used to form the ZrO₂ performs.

X-ray diffractometer (Model: XPERT-MPD, Philips) using Cu K α radiation ($\lambda=1.05406\text{\AA}$) with operated at 40 Kv and current of 40mA. The shapes and morphologies of nano

powder and Al/ZrO₂ composites were analyzed by Scanning Electron Microscopy (SEM- Philips XL30). The HF-Frequent 35 KHz, 240W/ Made in Germany was used as ultrasonic bath at room temperature.

For casting Al/ZrO₂ Composite, a resistance furnace equipped with a stirring system was used. After smelting the aluminum ingots, an amount given of keryolite was added to the molten Al alloy and the stirring was established for a few min. ZrO₂ nanopowder with 0.75 and 1.5 Vol. % were wrapped into the aluminum foils and added to the melt Al alloy to produce Al-ZrO₂ composite. The processing temperature have been chosen at 850°C. Stirring was continued for another 10 min for homogeneous dispersion and to prevent agglomeration of particulates. A metallic mold is used for casting.

The morphology of the composites were analyzed by scanning electron microscope (SEM, Oxford CAMSCAN-MV2300), equipped with X-ray mapping system and Specimens were polished and etched using Keller solution. The compression test was conducted in air at room temperature (Instron Universal Testing Machine-1195 machine) according to ASTM-E9. At least five specimens were tested for each casting conditions. After grinding and polishing, composite samples were tested using the Brinell method (The hard meter system DVRB-M model made by Eseyway Company-England) with a load of 306.56 N.

RESULTS AND DISCUSSION

The XRD patherns of the ZrO₂ nano particle is shown in **Figure 1**. The particle size of the samples has been calculated employing the Scherres equation:

$$D=K\lambda/\beta\text{Cos}\theta \quad (1)$$

Where θ is the angle between the incident and diffracted beams (degree), β , the full with half maximum (rad.), D, the particle size of the sample (nm) and λ is the wavelength of the X-ray. The results of XRD show at lower temperature the diffraction lines have confirmed the formation of single phase of monoclinic ZrO₂ nanostructure. The grain size of the prepared ZrO₂ is found to be about 38nm.

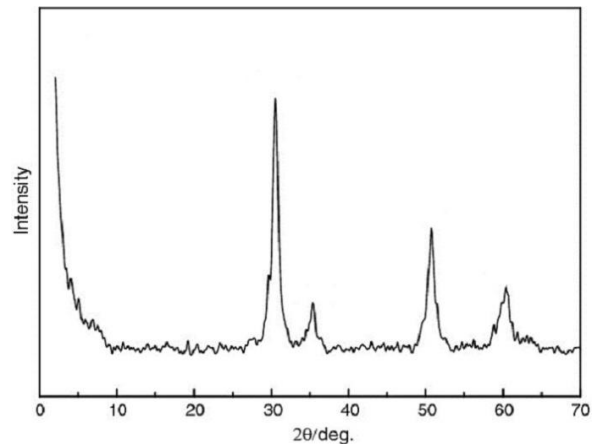


Fig. 1. The XRD pattern for ZrO₂ nano particles.

The structural morphology of the nano particles was investigated using SEM. **Figure 2** shows the SEM images of ZrO₂ nano particles.

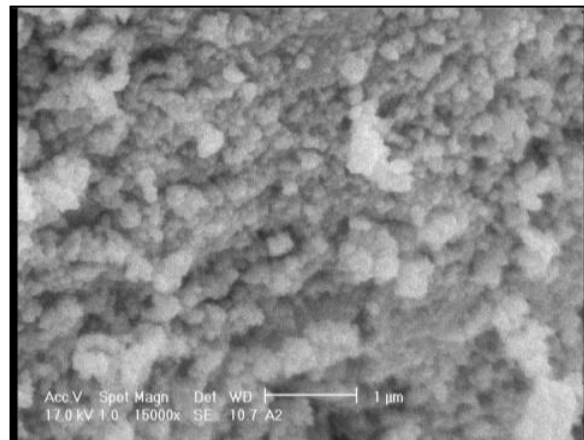


Fig. 2. SEM images of ZrO₂ nanoparticles.

The phase analyses of the A356/ZrO₂ composites were performed using X-ray diffraction pattern. The results of phase analyses of A356/ZrO₂ are shown in **Figure 3**.

Also, **Figure 3** shows the XRD peck of A356/ZrO₂ at 850°C. The composite had only monoclinic ZrO₂ peck with 0.75 Vol. %. Because of the stability of monoclinic ZrO₂ structure, casting with molten aluminum alloys with very short process, no other reaction product in the compositions was found.

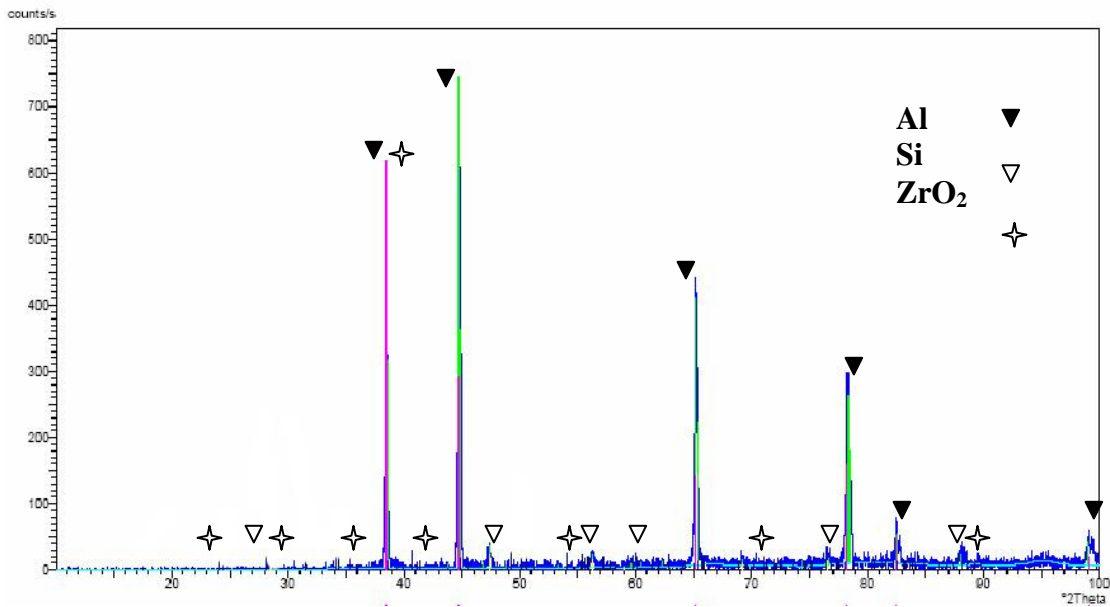


Fig. 3. X-ray diffraction pattern of A356/ZrO₂ composite at 850°C.

The morphology of the A356/ZrO₂ is shown in Figures 4 and 5. The black matrix is aluminum and the white spots represent ZrO₂ nano particles. And the grey part is porous base materials. The phases are indicated by arrows on

images. It should be noted that nano-sized ZrO₂ particles were well dispersed in the matrix of aluminum and just a partial agglomeration in composites with 0.75 and 1.5% content of ZrO₂ could be detected in Figures 4 and 5.

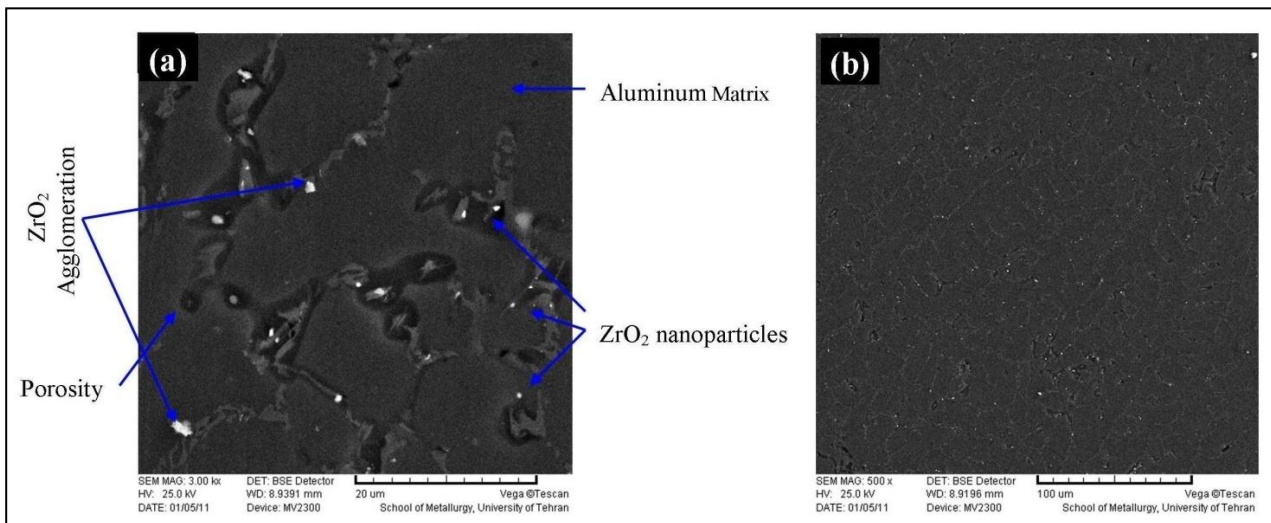


Fig. 4. SEM micrographs of Al356/ZrO₂ composite specimens with 0.75 vol. % ZrO₂ and prepared at 850°C at different magnifications: a) 3.00kX and b) 500X.

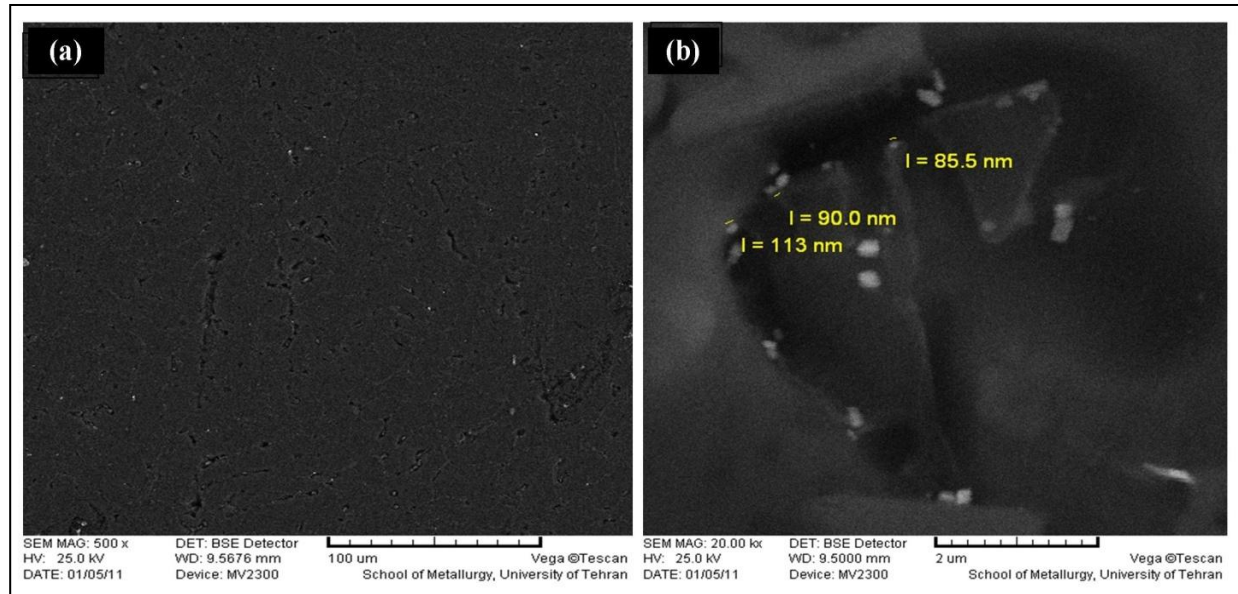


Fig.5. SEM micrographs of Al356/ZrO₂ composite specimens with 1.5 vol. % ZrO₂ and prepared at 850°C at different magnifications: a) 500X and b) 20.00kX.

Presence of ZrO₂ nano particles in Al356 alloy resulted in enhancement of mechanical properties such as hardness and compressive strength values. Considering that the hardness values of the ZrO₂ (for composites samples with 0.75 and 1.5 Vol. % of ZrO₂ are 58 and 50 BHN, respectively) is higher than the matrix alloy (45 BHN), improvement in hardness properties of composites would occur by presence of ZrO₂ nano particles. Also, with increasing the volume percent of ZrO₂ reinforcement particles, the values of the compressive strength (for composites samples with 0.75 and 1.5 Vol. % of ZrO₂ are 736 and 810 MPa, respectively) compared with unreinforced matrix alloy (700 MPa), increased. This enhancement seems to be related to work-hardening behavior. This could be because of elastic properties effects of ceramic particles and inhibition response of plastic deformation of matrix.

CONCLUSION

A nitrate-glycine gel was prepared from metal nitrates and fuel by a sol-gel auto-combustion process in order to synthesize ZrO₂. The well-crystalline ZrO₂ was produced when pH=7. So, it was necessary to adjust appropriate pH to produce pure ZrO₂. The grain sizes of the prepared nano

particles were found to be about 38 nm. The particles have been calcined at 650°C for 4 h. Then the product was placed in ultrasonic bath of n-propanol for 15 min. SEM results showed that the grains were regular sphere-shaped nano particles. The XRD data shows ZrO₂ nano powders have monoclinic structure.

Also aluminum alloy was successfully reinforced with monoclinic ZrO₂ nano powders having the grain size of about 38 nm, and A356/ZrO₂ composite were produced at 850°C. High hardness of ZrO₂ increases the hardness of Al-ZrO₂ composite. Also, the compressive strength of Al-ZrO₂ composite was increased comparing with unreinforced Al matrix.

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