

## Enhancement the Mechanical Properties of Aluminum Casting Alloys (A356) by Adding Nanorods Structures from Zinc Oxide

Qasim ZS<sup>1\*</sup>, Jabbar MA<sup>1</sup> and Hassan JJ<sup>2</sup>

<sup>1</sup>Department of Mechanical, Engineering College, Basra University, Iraq

<sup>2</sup>Department of Physics, Science College, Basra University, Iraq

### Abstract

The improvement of the mechanical properties such as tensile strength, hardness, and ductility were studied by a new and developed technique in the additions field (ZnO nanorods additions) under as-cast condition. Different melting temperatures, holding times, and ZnO nanorods amount were used and the refining of the microstructures and comparison of the obtained results with heat treatment conditions were also investigated in this paper. The results showed that the network of eutectic silicon particles is agglomerated, refined, and less angular after adding of ZnO nanorods to A356 aluminum casting alloys with quick solidification by water. Good enhancement in ultimate tensile strength and elongation with slightly increasing in the hardness were observed and they reached 222 MPa, 35%, and 78 HB respectively. Moreover, ZnO nanorods additions to A356 aluminum casting alloys give the possibility to improve the ultimate tensile strength, elongation, and hardness without heat treatment. Furthermore, the optimal melting and holding temperature for the present work is 700°C with holding time of 3 hours.

**Keywords:** Nanorods zinc oxide; A356 aluminum casting alloys; Microwave assisted hydrothermal route

### Introduction

Aluminum-silicon alloys are one of the most preferred used foundry alloys in different industries because they introduce excellent properties, A356 aluminum casting alloys are one of Al-Si alloys and widely used in automotive and aircraft due to the superior properties such as low density, high strength to weight ratio, high corrosion resistance, good impact resistance, good thermal conductivity, excellent castability and high wear resistance etc. [1]. In aluminum casting industry, the 3xx.x series alloys are widely used. The primary alloying element in the 3xx.x series alloys is silicon, where the addition of the silicon leads to increase fluidity and strength. The high hardness of the primary silicon phase lead to reducing machinability of aluminum alloys, thus generally the silicon content in aluminum alloy will not exceed the eutectic point (silicon content 12.6%) to avoid formation of the hard-primary silicon phase [2]. Zinc oxide is a multi-functional material because of the unique chemical and physical properties such as high electro-chemical coupling coefficient, high chemical stability, radiation absorption and high photo-stability. The variety methods for ZnO production were studied and the most common and cost effectiveness method is microwave assisted hydrothermal route [3-7].

The mechanical properties can be enhanced by controlling of addition materials, alloying elements, casting process parameters, solidification rates, heat treatments, etc. consequently, Zhang et al. [8] studied the effects of Scandium (Sc) addition as alloying elements on the as-cast Al-Si alloys microstructure. The results clarified that by scandium modification, the eutectic Si altered from plate-like and coarse structure to branched with fibrous shape, these changes involve increasing of volume fraction of the primary  $\alpha$ -Al phase monotonically with increasing of Sc content in the casting. Song Mousheng et al. [9] investigated the properties and microstructures of electrolytic (A356) cast alloys for low cycles fatigue with different Ti contents. They were concluded that the high Ti content make the alloys to have better grain refinement, the stronger capacity for cyclic hardening, the higher yield and tensile strengths as compared with those of unmodified alloys.

Casari et al. [10] studied the influence of trace additions of Nickel or

Vanadium on the ultimate tensile strength and elongation of unmodified (A356) alloys. In as-cast condition and sand cast of (A356) alloys, the ultimate tensile strength and yield strength were reduced by (37% and 87%), respectively, while the contrary gained with the V additions which lead to increasing ultimate tensile strength and yield strength by (25% and 42%) because of the effect of solid solution strengthening. The sand cast (A356) alloys that containing V showed after T6 heat treatment little better mechanical properties ( $\approx 18\%$ ) as compared to those in (A356) reference alloy. Nowak et al. [11] concerned with the effect of inoculation of (Niobium-Boron) from point of view the grains refinement on (Al-Si) alloys of binary (Al-xSi) (where  $x=1-10$  wt.%) to avoid possible effects of other alloying elements. The results were that the developed formed niobium borides make the grain refiner of (Nb-B) refine the binary (Al-xSi) alloys effectively where this addition lead to refine the eutectic phase as well as the primary ( $\alpha$ -Al) grains.

Kaiser et al. [12] investigated the mechanical properties and microstructure of Al-6Si-0.3Mg alloys with scandium (0.2 to 0.6 wt%). They found that the addition of scandium lead to refining the dendrite grain and increasing the hardness of aged (Al-6Si-0.3Mg) alloys, inhibition of softening effects has been observed during this investigation where all of these results the mechanical properties were improved. Birol et al. [13] employed the (Al-5Ti-1B) and (Al-3B) as grain refiners to conclude the potential of B additions and study their effects on the mechanical properties. They found that the average grain size of the (Al7Si0.3Mg) grain refined alloys were ( $156 \pm 29 \mu\text{m}$ ) and ( $465 \pm 102 \mu\text{m}$ ), respectively, and secondary dendrite arm spacing (SDAS) values were very similar ( $30 \pm 5 \mu\text{m}$ ). The two types of castings show very identical ultimate tensile strength, hardness, and yield

\*Corresponding author: Qasim ZS, Mechanical Department, Engineering College, Basra University, Iraq, Tel: 9647832160691; E-mail: [zaid.cpecc@gmail.com](mailto:zaid.cpecc@gmail.com)

Received January 05, 2017; Accepted March 24, 2017; Published April 03, 2017

Citation: Qasim ZS, Jabbar MA, Hassan JJ (2017) Enhancement the Mechanical Properties of Aluminum Casting Alloys (A356) by Adding Nanorods Structures from Zinc Oxide. J Material Sci Eng 6: 328. doi: [10.4172/2169-0022.1000328](https://doi.org/10.4172/2169-0022.1000328)

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values, despite of the difference between the grain size which prove that the mechanical properties of aluminum castings are controlled by the SDAS instead of the grain size.

Jabeera et al. [14] clarified the effect of zinc oxide nanoparticles on the aluminum zinc alloy sacrificial anode. They discovered that ZnO nanoparticles have effective activation for the sacrificial anodes and they suitable for reinforcing aluminum alloy anodes, substantially improvement of the metallurgical properties of the anodes were occurred because of reinforcing anodes with the nanoparticles which causing substantial reduction in the self-corrosion value. Shin et al. [15] investigated influence of refining on microstructure of (A356) aluminum alloys by using an exothermic chemical reaction called aluminothermic between (A356) alloy and zinc oxide nanoparticles (ZnO, ~20 nm in size) and the results showed improvement in the mechanical properties.

## Experimental Procedures

### Chemical composition analysis

In the present work, several A356 aluminum casting alloys from different vehicles wheels were purchased from local market. The chemical compositions of those alloys analyzed by materials spectrometer analyzer device and the results tabulated in Table 1 [16].

### Preparation of ZnO nanorods

The powders of ZnO nanorods were prepared from Hexamine (Hexamethylenetetramine  $C_6H_{12}N_4$ ) with Zinc nitrite hexahydrate ( $Zn(NO_2)_2 \cdot 6H_2O$ ) as following steps: (1) mixing (10 gm) from each of Hexamine and Zinc nitrite hexahydrate with (100 ml) from distilled water separately in two glass beakers. (2) Stirring glass beakers by hot plat device up to 800 rpm to ensure that the solutions are fully mixed. (3) Put (350 ml) from distilled water in a beaker which placed inside electrical microwave oven, and setting it up to temperature range (85°C-90°C). (4) Inject (6 ml) per (5 min) from both of Hexamine and

Zinc nitrite hexahydrate separately in the becker that positioned inside the microwave for (2-2.5 hrs.). (5) ZnO nanorods formed from the mixture of Hexamine, Zinc nitrite hexahydrate and distilled water, the mixture must be exposure to high temperature by hot plat device for (30-60 min) to remove impurities from the resulting ZnO nanorods (diameter=50-200 nm, length=1-2  $\mu m$ , purity=99%, and color=milky).

### Casting process

The A356 aluminum casting alloys were cut to small pieces and melted inside a graphite crucible in electrical furnace and heated to 700°C, then adding ZnO nanorods powder with different amounts manually and mixing with A356 molten inside the graphite crucible and holding inside the furnace and finally pouring the molten in the mold manually by using handle and cooling it quickly by the water. The amount and media shown in Table 2 with holding time inside furnace for (0, 1, 2, and 3 h).

### Tensile and hardness tests

Two tests were carried out in this work to estimate the difference between the mechanical properties of A356 aluminum casting alloys before and after the addition of ZnO nanorods. The first test was tensile test to indicate the ultimate tensile strength and the elongation which carried out by using instron universal testing machine while the second test was the hardness by using brinell hardness test, more than 100 samples from A356 aluminum casting alloy with and without ZnO nanorods additions were tested in this work. The shapes and dimensions of tensile specimens were prepared according to ASTM E8 standard [17,18].

### Metallographic examinations

The metallographic samples were cut, grinded, and polished according to ASTM E3-11 standard [18] and etching them after polishing according to ASTM E407-99 standard [19] by using 2 mL HF, 3 mL HCl, 5 mL  $HNO_3$ , and 190 mL water solutions. The microstructural

Elements	Sample 1 (Wt%)	Sample 2 (Wt%)	Sample 3 (Wt%)	Sample 4 (Wt%)	Standard Values (Wt %) [16]
Si	7.55	7.575	7.515	7.465	6.5-7.5
Fe	0.099	0.115	0.12	0.105	0.5 Max
Cu	0.00795	0.0035	0.00215	0.0035	0.2 Max
Mn	0.00395	0.0061	0.004	0.00525	0.3 Max
Mg	0.31	0.22	0.275	0.295	0.2-0.6
Zn	>0.008	>0.008	>0.008	>0.008	0.1 Max
Ni	>0.005	>0.005	>0.005	>0.005	0.1 Max
Pb	>0.005	>0.0075	>0.0075	>0.0075	0.1 Max
Sn	>0.006	>0.006	>0.006	>0.006	0.1 Max
Ti	0.135	0.13	0.145	0.14	0.2 Max
Al	Remainder	Remainder	Remainder	Remainder	Remainder

Table 1: Chemical analysis of A356 aluminum casting alloys (Al-Si7Mg0.5) [16].

Added ZnO nanorods (gm)	A356 aluminum casting alloy melt (gm)	Quenching media
0.5	1000	Water
1	1000	Water
1.5	1000	Water
2	1000	Water
3	1000	Water
4	1000	Water
5	1000	Water
10	1000	Water
20	1000	Water

Table 2: Conditions of ZnO nanorods additions to A356 aluminium casting alloy melt.

examinations were carried out by using optical microscopy (Olympus) and field emission scanning electron microscopy (Zeiss-model supra 55 vp) to observe the effect of ZnO nanorods on the microstructure of A356 aluminum casting alloys.

## Results and Discussion

### Microstructures evolution

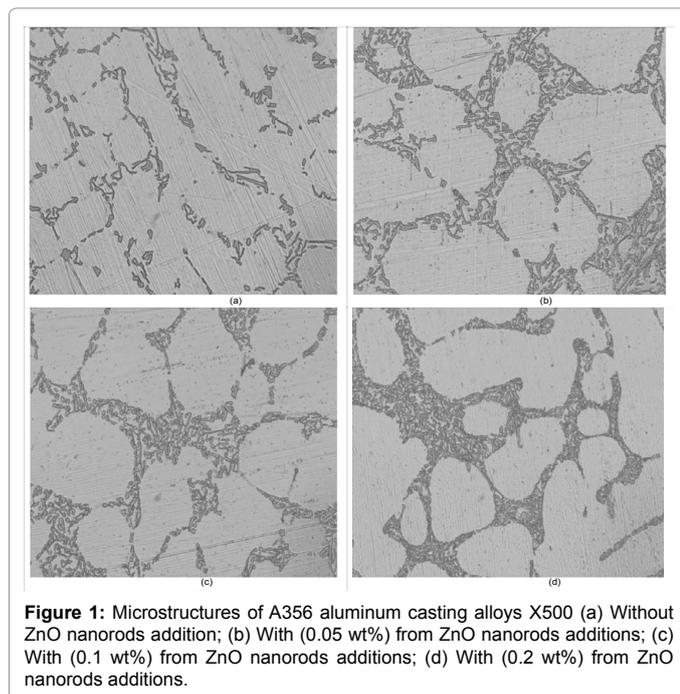
The optical microstructures of the A356 and refined A356 specimens under as cast condition are shown in Figure 1 which also shows the microstructure evolution by increasing the amount of ZnO nanorods additions. It can be seen that the addition of ZnO nanorods refined the structure significantly and changed the network of sharp eutectic Si particles with coarse  $\alpha$  (Al) primary dendrite into agglomerated network of spheroidized and less angular eutectic Si particles that uniformly distributed at the grain boundaries with fine  $\alpha$  (Al) primary. As illustrated in Table 2, the grain refinement of the microstructure starts effectively at 5% wt and above from ZnO nanorods that added to A356 alloy. Figure 2 shows clearly the structure of ZnO nanorods with the dimensions and Figure 2e and 2f shows the energy-dispersive x-ray spectroscopy in addition to the spheroidization evolution of eutectic Si in addition to the microstructural transformation in presence of these nanorods in Figure 2a-2d. It is clear that the agglomerated nanorods transformed to individual nanorods distributed uniformly in the matrix of A356 as shown in Figure 3 which showing the exact distribution of Al, Si, and Zn in the matrix of A356.

### Effect of ZnO nanorods content on A356

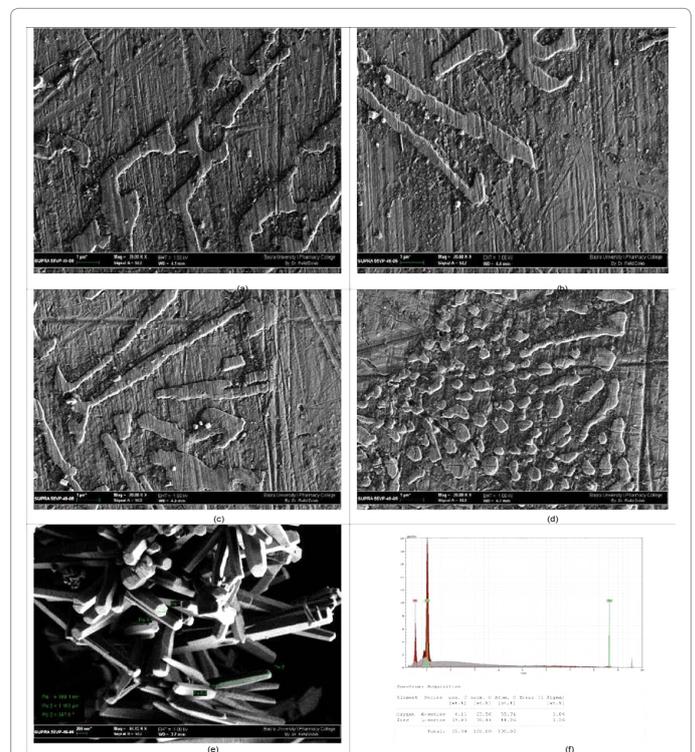
The chosen of nano-size addition by ZnO nanorods is attributed to the reactivity of the surface area, the surface area of the nanorods is more than the bulk one which lead to increase the number of reaction sites. ZnO nanorods were introduced in A356 molten as grain refiner and the mechanism of the refinement attributed to the two phenomena, the first theory involved restriction of the grain growth by the atoms of the solutes which diffused at the interface of the solid-liquid which lead to restricts the grain growth and decrease the grain size. In another

hand, the second theory is the inoculation which has been explained by increasing the heterogeneous nucleation sites for the primary grains of aluminum by introduce the master alloy to aluminum casting alloys [20].

Since the additions of ZnO nanoparticles were explained as comparable with the addition of Al-Ti-B master alloy [15], the refining phenomena could be ascribed to the nucleant particles and the segregation elements [21]. The decomposition of ZnO nanorods occurs after adding them to the A356 melt which lead to introduce the atoms of oxygen and zinc into the melt, oxygen atoms present as  $Al_2O_3$  particles as shown in Figure 2c and the restriction of primary aluminum growth by  $Al_2O_3$  particles due to the increasing of the oxygen content and formation of the  $Al_2O_3$  in the eutectic region is not the main cause for grain refinement and it can be considered to be suppression particles for restriction process. In another hand, the



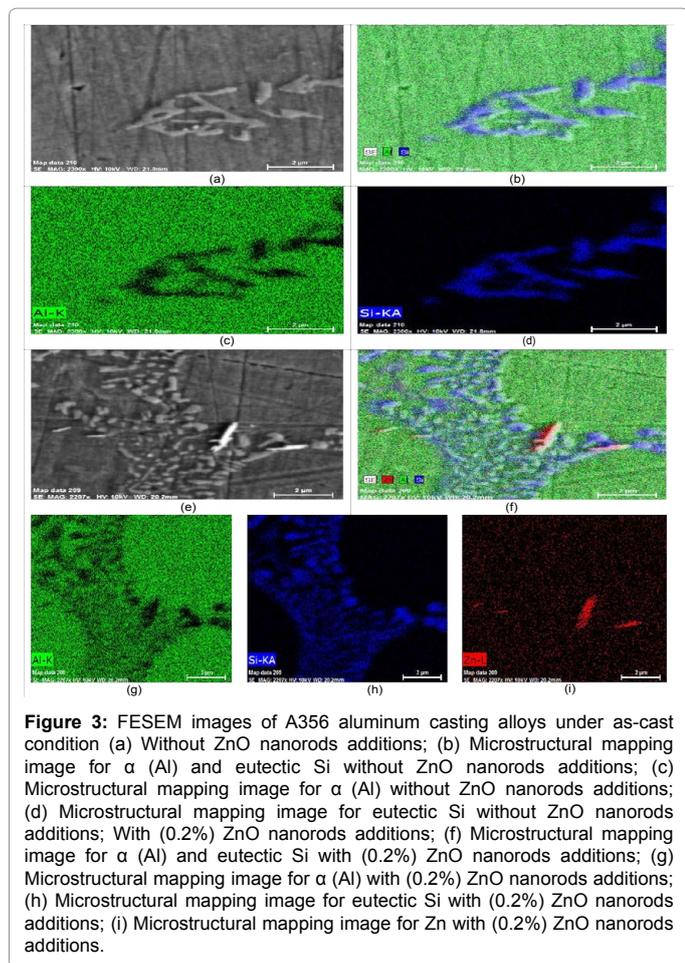
**Figure 1:** Microstructures of A356 aluminum casting alloys X500 (a) Without ZnO nanorods addition; (b) With (0.05 wt%) from ZnO nanorods additions; (c) With (0.1 wt%) from ZnO nanorods additions; (d) With (0.2 wt%) from ZnO nanorods additions.



**Figure 2:** FESEM images of A356 aluminum casting alloys under as-cast condition (a) Without ZnO nanorods additions; (b) With (0.05 wt%) from ZnO nanorods additions; (c) With (0.1 wt%) from ZnO nanorods additions; (d) With (0.2 wt%) from ZnO nanorods additions; (e) ZnO nanorods structure; (f) X-ray spectroscopy for ZnO nanorods.

Sample No.	Ultimate Tensile Stress (MPa)	Elongation % (mm/mm)	Hardness (HB)
1	185	14.53	74
2	183	14.73	75
3	183	13.33	74
4	185	15.73	74
5	180	13.33	74
6	185	15.53	75
7	183	13.53	75
8	185	15.06	74
9	184	14.4	74
10	181	14.33	74
Average	183.4	14.45	74.3

**Table 3:** A356 aluminum casting alloys without ZnO nanorods additions.



**Figure 3:** FESEM images of A356 aluminum casting alloys under as-cast condition (a) Without ZnO nanorods additions; (b) Microstructural mapping image for  $\alpha$  (Al) and eutectic Si without ZnO nanorods additions; (c) Microstructural mapping image for  $\alpha$  (Al) without ZnO nanorods additions; (d) Microstructural mapping image for eutectic Si without ZnO nanorods additions; (e) With (0.2%) ZnO nanorods additions; (f) Microstructural mapping image for  $\alpha$  (Al) and eutectic Si with (0.2%) ZnO nanorods additions; (g) Microstructural mapping image for  $\alpha$  (Al) with (0.2%) ZnO nanorods additions; (h) Microstructural mapping image for eutectic Si with (0.2%) ZnO nanorods additions; (i) Microstructural mapping image for Zn with (0.2%) ZnO nanorods additions.

effect of zinc atoms on the grain refinement attributed to the solutes effects and the heterogeneous inoculations. A356 casting alloys contain high levels from the segregation elements (solute), the levels will be increased by the presence of zinc which remained as solid solution after solidification because zinc has the greatest solid solubility in aluminum of all the elements. By increasing of solutes, the grain size will be decreased because the solutes atoms will diffuse and suppress the growth especially the columnar grains from primary aluminum. The increasing of nucleation sites by zinc atoms which expected to acting partially as nucleant for primary aluminum grains by undercooling lead to degreasing the grain size and spheroidized the eutectic silicon particles thereby the refinement is achieved.

### Mechanical properties enhancement

The ultimate tensile strength and the ductility for A356 under as-cast condition were improved significantly as shown in Tables 3-6 in addition to the slightly increasing in the hardness. As-cast A356 alloy has ultimate tensile strength about 183.4 MPa and by adding the ZnO nanorods, the highest ultimate tensile strength that obtained is 219 MPa because of the grain refinement of these additions which made the grain finer and spheroidized structure with agglomerated structure. The significant improvement in the ductility from 14.45% to 33.72% is attributed to the spheroidized grains, grain refinement, and the enhancement in the castability because of the ZnO nanorods additions which delayed the failure of the A356 alloy by make the grains have high resistance for the plastic deformation. The hardness of A356 alloys

Sample No.	Ultimate Tensile Stress (MPa)	Elongation % (mm/mm)	Hardness (HB)
1	205	20.8	74
2	206	20.73	75
3	207	21.33	74
4	210	21.66	74
5	205	20.01	75
6	200	19.2	75
7	198	19.53	75
8	197	19.4	74
9	205	20.86	76
10	207	21.01	74
Average	204	20.45	74.6

**Table 4:** A356 aluminum casting alloys with (0.05 wt%) ZnO nanorods additions.

Sample No.	Ultimate Tensile Stress (MPa)	Elongation % (mm/mm)	Hardness (HB)
1	209	20.8	75
2	214	25.46	75
3	212	24.86	75
4	213	25.13	76
5	210	21.33	74
6	211	22.2	75
7	213	25.4	76
8	211	23.4	75
9	212	24.73	76
10	210	24.01	75
Average	211.5	23.73	75.2

**Table 5:** A356 Aluminum casting alloys with (0.1 wt%) ZnO nanorods additions.

Sample No.	Ultimate Tensile Stress (MPa)	Elongation % (mm/mm)	Hardness (HB)
1	219	34.06	78
2	218	33.36	76
3	216	32.2	77
4	219	33.46	76
5	217	33.33	78
6	221	34.46	75
7	220	33.13	77
8	222	35	76
9	216	33.2	75
10	222	35	78
Average	219	33.72	76.6

**Table 6:** A356 Aluminum casting alloys with (0.2 wt%) ZnO nanorods additions.

have no significant effects when the ZnO nanorods were introduced, where the increment in hardness values were just from 74.6 HB to 76.6 HB because of the grain refinement which considered to be one of the most effective to strengthening mechanism.

### Conclusions

The enhancement of A356 aluminum casting alloys can be achieved by introduce nanoparticles (ZnO nanorods) because of the grain refinement and the mechanism of the refining can be compared with the addition of Al-Ti-B master alloy form, the refining mechanisms caused transformation in the network of sharp eutectic Si particles with coarse  $\alpha$  (Al) primary dendrite into agglomerated network of spheroidized and less angular eutectic Si particles that uniformly distributed at the grain boundaries with fine  $\alpha$  (Al) primary. The improvement of the mechanical properties that included ultimate tensile strength, elongation, and hardness are 183.4 MPa to 219 MPa, 14.45% to 33.72%, and 74.6 HB to 76.6 respectively for A356 aluminum casting alloys can

be achieved and comparable with mechanical properties of heat treated A356 alloys by (T7).

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