

# Effect of ZrSiO<sub>4</sub> Addition on Mechanical Properties of ASTM ZA-27 Alloy

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### **ABSTRACT**

This work aims to study the ability of improving the properties of ASTM ZA-27 by reinforcin with ZrSiO<sub>4</sub> particles of size 45-100  $\mu$ m and ranging of 0.5, 1, 2 and 3% by weight .The liquid metallurgy technique was used to fabricate the composite material by the Gravity Die Casting (GDC) method. Tests showed that the adding of zircon helps to increase the mechanical properties and the addition of 1% has achieved the highest tensile strength. This percentage of addition is use to produce the composite materials by a new method of casting which is New Rheocasting (NRC). The manufacturing of the material by the NRC process helped to improve the mechanical properties of the ZA-27 alloy. Solution treatment, for the material produced by the two methods, was performed at 320°C for a duration time of 3 hrs, and then artificially aged at 150 °C for 2hrs. The composite material responded to the treatment and gives an increase in the mechanical properties.

Keyword; ZA-27, Gravity Die Casting, New Rheocasting, wear rate.

#### 1. Introduction

The higher aluminum content of zinc alloys give several distinct advantages over the traditional zinc alloys, Including higher strength, superior wear resistance, superior creep resistance. However, when wear resistant properties are needed, ZA-27 has demonstrated extraordinary performance [1-4]. The attractive properties of the ZA-27 alloy have inspired researchers to reinforce them with ceramic dispersions in order to obtain much more enhanced mechanical and tribological properties. The reinforcement of the alloy with graphite and SiC has shown improvement in the mechanical and wear properties. MMCs based on ZA-27 matrix are being increasingly applied as light-weight and wear resistant materials [5-6]. In the real casting condition, the ZA alloys have the typical denderitic structure, which size depends on the applied casting process.

The cooling speed imposes strong influence on the structure fineness, during the cooling in the mould. The consequences of the dendritic structure are manifested , primarily , in the lower ductility of the casted alloy ,as well as in relatively high inhomogenety of mechanical properties .The second important problem is related to high aluminum zinc alloys and it refers to dimensional instability , which is cause by presence of metastable phase [6]. K. H. W. Seah et al [7] studied the mechanical properties of ZA-27 alloy with graphite particulate composites containing graphite. The results showed that as graphite content was increased, there were significant increases in the ductility, ultimate tensile strength and compressive strength while there was a significant decrease in the hardness. D. R. Somashekar et al added zircon particles range from 1-5% .The study revealed improvements in ultimate tensile strength and yield strength with 28% and 18% respectivily with the addition of 5% ZrSiO<sub>4</sub> [8].

### 2. Experimental Work

Matrix material used in this research was ZA-27 (table 1).



Table (1): Chemical analyses for ASTM ZA-27

Elements (wt %) Material	Al%	Cu%	Mg%	Fe%	Cd%	Pb%	Zn %
Nominal Chemical Composition	25-28	2-2.5	0.01-0.02	0.1	0.003	0.004	Rem
Actual chemical Composition	27.16	2.35	0.013	0.087	0.0013	.0011	Rem

Procedure of preparing ZA-27 consisted of melting pure aluminum firstly in an electrical furnace using graphite crucible with 5Kg capacity. At approximately 700°C, master alloys (to control Cu and Mg wt %) were added respectively. Electrolytic Zinc was added gradually with decreasing melting temperature to reduce or prevent zinc evaporation. When the temperature approach 570°C, molten metal was poured in steel mould for gravity die casting. Melting procedure for NRC was mainly like GDC, except, the pouring temperature was 532°C and when the stainless steel (AISI 304) mould temperature reached 410°C, it was suddenly water cooled [9]. Reinforcement particles ZrSiO<sub>4</sub> of size 45-100μm and of contents ranging from 0-3% by weight were added to the molten matrix alloy (ZA-27).

Moulds of 12x6x6 cm dimensions were employed for the two casting processes. For homogenous distribution of the reinforcement particles stirring was made using stainless steel electrical stirrer, at 400-500 rpm for 5-8 min. A chromel-Alumel thermocouple (K-type) covered by a hastalloy was used to measure temperature variation during solidification. For NRC and to increase the contact area between molten metal and mould-wall the mold was inclined with an angle of  $75^{\circ}$ , to give a good opportunity for crystals formation on the wall and increasing the distance the metal flows will help in increasing the possibility of separating the freezing crystals from the mould wall [10]. When the temperature of molten was approximately  $532^{\circ}$ C, it poured on the wall of the inclined mould and then when temperature of semi-solid reached to 410  $^{\circ}$ C the mould was water cooled (quenched). Solution treatment was done at  $320^{\circ}$ C and holding 3 hrs for homogenization. Water quenching was used from  $320^{\circ}$ C and then specimens were artificially aged at  $150^{\circ}$ C for 2hrs then air-cooled [11, 12]. Optical microscope was used to determine the volume fraction of the phases present in addition to  $\alpha$  - Al grain size and dendrites arm space. The grain size was measured by lineal intercept technique. Volume fraction program was used to calculate the percentage of white ( $\alpha$ -Al phase) and black (eutectoid) areas in the digital image by using Scion Image computer program. Three tensile test specimens were tested for matrix alloys and each percentage of addition before and after heat treatment (age hardening). Brinell hardness was used, employing a ball 2.5mm in diameter and a load of 31.25 kgf.

### 3. Results and Discussion

### - GDC ZA -27 Alloy

The microstructure of GDC specimen was completely dendrite from wall toward the center. X-ray diffraction test showed that the structure of the as cast ZA-27 alloy consists of four phases  $\alpha$ ,  $\beta$ ,  $\epsilon$  and  $\eta$ . The first solidified Al rich  $\alpha$  phase appears as core of the dendrite, which is surrounded by the decomposed Zn rich  $\beta$  phase (Fig.3).

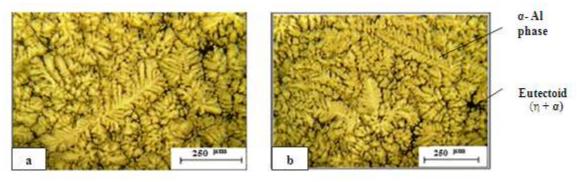
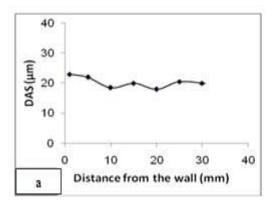


Fig (3): Microstructure of GDC ZA- 27 alloy: a- 2mm from the wall, b- 30 mm from the wall

On other hand in the interdendritic region there are eutectoid  $\eta$ ,  $\alpha$  phases and  $\varepsilon$  metastable epsilon phase CuZn<sub>5</sub> [4] . Limited variation was shown in the measuring of Denderitic Arm Spacing (DAS) from wall to center of the casting with



an average equal to 20 μm, while the average volume fraction for primary α- Al phase varied from 0.58 at the wall to 0.67 at the center of the casting with an average of 0.64 (Fig.4).



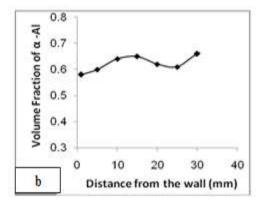


Fig (4): a- Variation in DAS b- Variation in volume fraction of  $\infty$ -Al

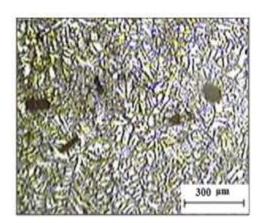
This increment in volume fraction from the wall to the center is due to the richness of the last solidified liquid with the alloying elements of the low melting temperature which leads to their behavior as nuclei for the  $\alpha$ - Al phase and hence the increase in the volume fraction. Also, the high cooling rate at the wall lead to increase in the volume fraction of the eutectoid phase [10]. The ultimate tensile strength, yield strength, elongation and hardness measured from the wall to center of the casting of the GDC ZA- 27 alloy were 320MPa, 295MPa, 2.8% and 96HB respectively (Table 2).

Table (2): Mechanical properties of GDC ZA- 27 alloy

Properties  Materials	Tensile strength (MPa)	Yield stress (MPa)	Elongation (%)	Hardness (HB)
Nominal mechanical properties ZA- 27	310-325	280	2.4	90-110
Actual mechanical properties ZA - 27	320	295	2.8	96

### GDC ZA-27 / ZrSiO<sub>4</sub> Composite

Microscopic examination of GDC ZA-27 reinforced with 1% ZrSiO<sub>4</sub> showed that this addition has no effect on the dendrite structure nor on dendrite arm spacing (DAS) or average volume fraction for primary α- Al phase where, they were 22 µm and 0.63 respectively (Figs. 5&6).



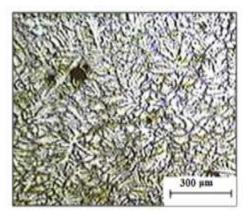
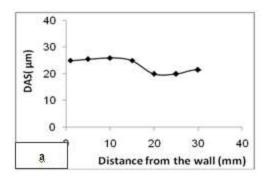


Fig (5): Microstructure of ZA- 27 / 1% ZrSiO<sub>4</sub>: a- 2mm from the wall, b- 30 mm from the wall





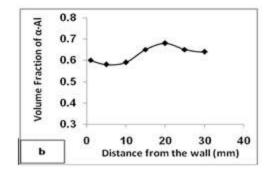


Fig (6): a-Variation in DAS, b- Variation in volume fraction of ∞-Al

As well there is no effect on the present phases. Tensile test of reinforced GDC ZA-27 alloy showed an increase in the yield strength, ultimate tensile strength for all percentage of  $ZrSiO_4$  added compared with the unreinforced alloy. Results in table (3) indicate that the 1% addition of  $ZrSiO_4$  has the maximum effect where yield strength increases to 355 MPa with an average increment of 20.3%.

**Properties** Tensile Yield stress Elongation strength (MPa) (%) (MPa) Materials ZA- 27 320 295 2.8 0.5% ZrSiO<sub>4</sub> / ZA- 27 335 315 1.8 1% ZrSiO<sub>4</sub> / ZA -27 370 355 1.6 2% ZrSiO<sub>4</sub> / ZA- 27 360 343 1.5 3% ZrSiO<sub>4</sub> / ZA -27 340 310 1.3

Table (3): Mechanical properties of GDC ZA- 27 / ZrSiO<sub>4</sub> composites

Tensile strength also increases by an amount of 50 MPa to reach 370 MPa, i.e. the percentage of increase is 15.6%, while the elongation is reduced by 42.8%. Increasing the percentage of reinforcement particles to 3% causes pronounced reduction in strength (both yield and tensile) as compared with that of 1% due to agglomeration of ZrSiO<sub>4</sub> particles. The hardness was increased with 3% addition to reach 135HB at 2mm from the wall to about 109HB at the center with average 123HB. For 1% addition the hardness was 109HB and 90HB from the wall to the center respectively with an average of 106HB. For the 2% addition, the average values reach 116HB, and with 0.5% addition average values reach 102HB. 3% addition showed increase in hardness reaching to 28%, and with 1% of addition 10.5% as compared with ZA-27 alloy.

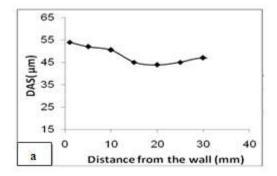
### Solution Treatment and Age Hardening of GDC ZA- 27

To determine whether precipitation hardening has an effect on the properties of GDC ZA-27 alloy and to determine the best time for aging that would achieve the best wetting between  $ZrSiO_4$  and matrix alloy, the alloy was solution treated at  $320^{\circ}C$  for 3hrs to homogenize it. This was followed by water quenching then artificial aging at  $150^{\circ}C$  for different aging times (1-4 hrs) then air cooled .It was shown that the best aging time is 2 hrs where maximum hardness of 121HB is obtained compared to other periods of time , so this value of time was adopted for all aging processes. After aging, the fine zinc and aluminum lamella, formed in the former beta region around the alpha cores, were partly replaced by a mixture of much coarser particles .The epsilon phase had diminution entirely and the copper was concentrated into a large number of the stable  $\tau$ - phase, AlCuZn. It has been shown that the growth which occurs on aging ZA-27 alloy is due to the gradual conversion of the epsilon metastable phase  $CuZn_5$  to a stable copper rich intermetallic  $\tau$ - phase which is closer to equilibrium. The  $\tau$ - phase is isomorphouse and has a deformed structure based on an ordered body centered cubic lattice , so it has increased the mechanical properties, it consists of 53.98 wt% Cu ,15.89 wt% Zn and 30.13 wt% Al. The effect of the heat treatment on the structure (solution treatment) has produced an f.c.c solid solution, which ,on quenching and aging ,decompose to give a mixture of zinc ( $\eta$ ) and aluminum ( $\alpha$ ) grain [6].

The microstructure examination of the heat treated GDC ZA-27 alloy showed an increase in the dendrite arm spacing (DAS) equal to 49  $\mu$ m compared to that of 20  $\mu$ m before heat treatment. Also average volume fraction for  $\alpha$ - Al phase was



increased to 0.85 after heat treatment while it was 0.64 before heat treatment. Figure (7) shows the effect of the heat treatment on DAS and volume fraction of  $\alpha$ - Al phase respectively.



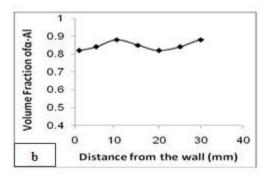


Fig (7): a- Variation of DAS with the distance, b- Variation of volume fraction of ∞-Al with the distance

It was found that these changes have a noticeable effect on mechanical properties, where the increase in volume fraction for  $\alpha$ - Al phase is accompanied with a reduction in mechanical properties, but the emergence of a new phase ( $\tau$ -AlCuZn) after the aging process hinders dislocation motion with an pronounced increase in the properties [6]. Heat treatment caused a slight increase in hardness along the cross section to reach 104 HB as compared to 96HB before heat treatment, yield strength and tensile strength increased by an amount of 85 MPa and 70 MPa respectively and the percentage of increment is 28.8%, 21.8% with almost no change in elongation percentage.

#### Solution Treatment and Age Hardening of GDC ZA- 27/ ZrSiO<sub>4</sub>

The solution treatment and the aging process of MMCS didn't affect the behavior of the  $\alpha$ - phase volume fraction and DAS resulted when compared with the ZA-27 after heat treatment which equal 0.82 and 54µm respectively at 1% ZrSiO<sub>4</sub>. The addition of ZrSiO<sub>4</sub> with any percentage increases hardness of GDC ZA-27. With 3% addition the hardness has an average of 132HB while with 1% addition hardness equals to 121HB and with 2% addition average value reaches 127HB, and with 0.5% addition average value reaches 111HB. 3% addition shows an increase in hardness reaches to 7.3%, and with 1% of addition reaching 14% as compared with composite before heat treatment. The results of tensile test indicate that yield strength, ultimate tensile strength increase after heat treatment (table-4).

Tensile Yield stress **Properties** strength (MPa) Elongation (MPa) (%) Material ZA -27 380 2.5 390 0.5% ZrSiO<sub>4</sub> /ZA - 27400 390 1.6 425 400 1% ZrSiO<sub>4</sub> /ZA - 271.4 2% ZrSiO<sub>4</sub> /ZA- 27 420 395 1.3 3% ZrSiO<sub>4</sub> /ZA -27 415 385 1.2

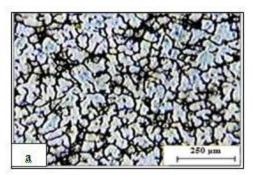
Table (4): Mechanical properties of ZA- 27 / ZrSiO<sub>4</sub> composite after heat treatment

The ultimate tensile strength increases to reach 425 MPa at 1%  $ZrSiO_4$  in comparison with GDC ZA- 27 /1%  $ZrSiO_4$  before heat treatment which was 370 MPa. While, the yield strength increases to reach 400 MPa in comparison with GDC ZA- 27 /1%  $ZrSiO_4$  before heat treatment which was 355 MPa with drop in the elongation to 1.4%. X – Ray diffraction analysis showed the appearance of  $\tau$ - AlCuZn phase after heat treatment in addition to the phases present before heat treatment which are  $\alpha$ - Al,  $\beta$ -Zn,  $\eta$  - Zn,  $\varepsilon$  – CuZn<sub>5</sub>  $\tau$ - AlCuZn phase may be the reason why mechanical properties increase after heat treatment.

#### - NRC ZA -27 Allov

Since the structure of GDC ZA-27 alloy is dendrite, another casting process was suggested which was NRC using an inclined mould at an angle of 75.° The NRC aims to increase significantly the grains population and change shape of the  $\alpha$ -phase dendrites to a semi-globular one. Microstructure examination (fig. 8).





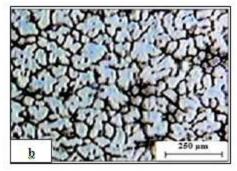
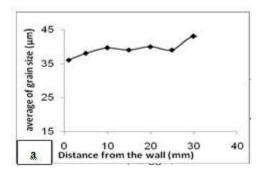


Fig. (8): Microstructure of NRC ZA -27 alloy a- 2mm from the wall b-30 mm from the wall

Shows the disappearing of the dendrite to a great extent. The primary Al rich  $\alpha$ -phase has a shape close to the equiaxed grain surrounded by eutectoid with an average grain size equal to 36  $\mu$ m near the wall ,increases to 44  $\mu$ m at center with an average equal to 39  $\mu$ m with very limited variation along the cross section ,which would give a positive effect on the isotropic properties . The average volume fraction for primary Al rich  $\alpha$ - phase was 0.58 as compared with 0.64 for GDC ZA-27 alloy, but with uniformity of the volume fraction distribution which is attributed to the NRC with its consistency along the cross section (fig. 9).



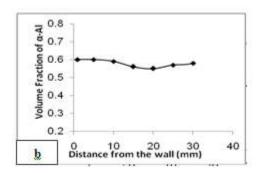


Fig. (9): a- Variation in grain size, b- Variation in volume fraction of ∞-Al

In addition to microstructure change from dendrite shape to equiaxed grain, volume fraction of eutectic increased causing an improvement in mechanical properties. The hardness of ZA-27 alloy resulting from NRC is higher than that resulting from GDC and increases to reach 107HB due to the increase in volume fraction of eutectic and grain refinement of  $\alpha$ - Al phase. Also yield and tensile strength increase to reach 340 MPa and 360 MPa respectively with a less increase in elongation (3%) compared to that resulting from GDC (table -5).

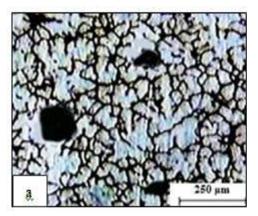
Table (5): Mechanical properties of ZA- 27 / ZrSiO<sub>4</sub>composite by GDC& NRC

Properties			
	Tensile	Yield	Elongation
	strength	stress	(%)
Materials	(MPa)	(MPa)	
ZA- 27 GDC	320	295	2.8
1% ZrSiO <sub>4</sub> / ZA- 27 GDC	370	355	1.6
NRC ZA- 27	360	340	3
1% ZrSiO <sub>4</sub> /NRC ZA -27	390	380	2.8

### NRC ZA-27/ZrSiO<sub>4</sub> Composite

From the previous discussion, it is shown, that the best percentage of reinforcement particle addition is 1%, so this percentage is used in manufacturing MMCS by NRC method in order to combine the effect of both equaxid refinement and  $ZrSiO_4$  addition. Figure (10) shows that the microstructure is equiaxed with average grain size equal to 36 $\mu$ m.





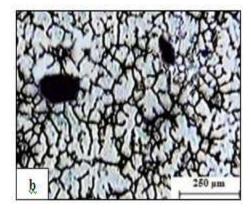


Fig. (10): Microstructure of NRC ZA- 27 / ZrSiO<sub>4</sub> a- 2mm from the wall, b-30 mm from the wall

The grain size increases as expected toward the center of the casting and preserve values very near to the NRC ZA-27, which means that the stirring has no effect on the resulting microstructure, while the average volume fraction for primary  $\alpha$ - Al phase is 0.56 which is approximately the same as NRC ZA-27. The MMCS by NRC showed an increase in the hardness in comparison to that produced by GDC with an average equal to116HB. The results of tensile test, show increase in yield stress from 355MPa to 380MPa, and increase in ultimate tensile strength from 370MPa to 390MPa, with increase in elongation to 2.8% (table-5).

When using the NRC process to preparer a composite with an addition of 1%, the tensile strength was 390 MPa and the yield strength was 380MPa which was in compliance with the results of the compocast process from the aspect of the tensile strength but the NRC process gave an increase of 70MPa (22.5%) on the value of the yield strength .

It should be indicated that an addition of 1% by the compocast process which consequently lead to additional costs due to the increase of the addition percentage. On the other hand, when comparing (at the same addition percentage) between the two methods, it can be found that the NRC process gave an increase in the tensile strength to reach 390MPa, in comparison to 350MPa by the compocasting process, as well as, an increase in the yield strength by the NRC to reach 380MPa against 270MPa by the compocast process.

### Solution Treatment and Age Hardening of NRC ZA- 27

Solution heat treatment and age hardened of NRC ZA- 27alloy show an increase in grain size of the primary  $\alpha$ - Al phase along the cross section of casting to reach 63 $\mu$ m in comparison to 39 $\mu$ m befor heat treatment (fig. 11).

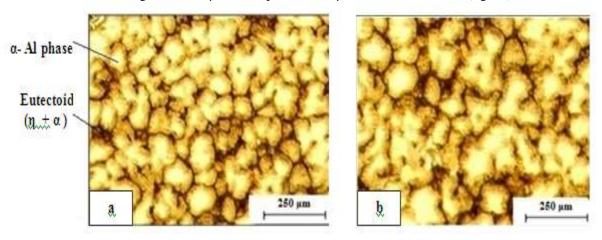
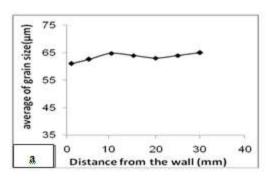


Fig. (11): Microstructure of NRC ZA- 27 after heat treatment a- 2mm from the wall b-30 mm from the wall

The volume fraction of the primary  $\alpha$ - Al phase was 0.73 (2mm from the wall) to 0.79 at the center with an average equals to 0.79 .This increase is at the expense of the decrease in the volume fraction of the eutictoid (fig. 12).





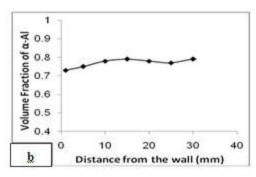


Fig. (12): a- Variation in grain size after heat treatment ,b. Variation in volume fraction of ∞-Al

It has been shown that the growth which occurs on aging ZA-27 alloy is due to the gradual conversion of the metastable  $\varepsilon$ -CuZn<sub>5</sub> to stable copper rich intermetallic  $\tau$ - phase AlCuZn [6]. A little increment was observed in hardness value after heat treatment to reach 114HB, while yield and tensile strength increase to 410 MPa and 425 MPa respectively with small increase in elongation (table-6).

Table (6): Mechanical properties of ZA- 27 / ZrSiO<sub>4</sub>composite after heat treatment

Properties  Materials	Tensile strength (MPa)	Yield stress (MPa)	Elongation (%)
ZA- 27 / GDC	390	380	2.5
1% ZrSiO <sub>4</sub> / ZA -27 GDC	425	400	1.4
ZA- 27 / NRC	425	410	2.6
1% ZrSiO <sub>4</sub> / ZA 27 NRC	445	420	2.4

### Solution Treatment and Age Hardening of NRC ZA- 27 / ZrSiO<sub>4</sub> Composite

Heat treatment of NRC ZA-27 alloy reinforced with 1% ZrSiO<sub>4</sub> caused an increase in average grain size to reach 60  $\mu$ m compared to 36  $\mu$ m before heat treatment (fig. 13) with an increase in average volume fraction for  $\alpha$ - Al phase to 0.79 while it was 0.56 before heat treatment.

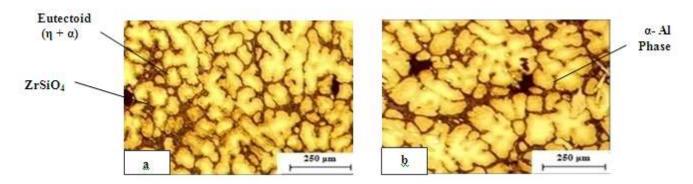


Fig. (13): Microstructure of NRC ZA 27 / 1%  $ZrSiO_4$  a- 2mm from the wall b- 30 mm from the wall after heat treatment

Hardness was increased along cross section from 121HB to 131HB. Tensile strength was increased from 425 MPa to 445 MPa and yield strength from 400 MPa to 420 MPa as compared with GDC ZA-27/1%  $ZrSiO_4$  after heat treatment while elongation reached 2.4 % (table-6). The stable intermetalic copper – rich phase  $\tau$ -AlCuZn appeared in all specimens tested by X-ray diffraction after heat treatment, which indicates that the mentioned phase is one reason for the increasing in mechanical properties.



### **CONCLUSIONS**

- 1. MMCs of ZA-27 reinforced with ZrSiO<sub>4</sub> particles can be manufactured by NRC in addition to GDC process.
- 2. Equaxid grain with an average grain size of  $39~\mu m$  is obtained from NRC compared to the denderitic microstructure resulting from GDC.
- 3. NRC increases the eutectoid volume fraction by 16.6% with decrease in α- Al volume fraction by 9.3%.
- 4. NRC increases the mechanical properties of ZA-27 alloy by 12.5%, 15.2% and 11.5% for tensile, yield strength and hardness respectively compared to that resulting from GDC process.
- 5. The appearance of  $\tau$  AlCuZn phase is the reason for increasing the mechanical properties after heat treatment.
- 6. The aging time for 2 hrs of ZA-27/1% ZrSiO<sub>4</sub> gives higher hardness reaching 121HB.

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