Options for Nanoreinforced Cast Al–Si Alloys with TiO_2 Nanoparticles

A.Y. Shash, I.S. El-Mahallawi and A.E. Amer

Abstract This study presents a new concept of refining and enhancing the properties of cast aluminium alloys by adding nanoparticles. In this work the effect of adding titanium dioxide (TiO_2) nano-particles (40 nm) to the aluminum cast alloy A356 as a base metal matrix was investigated. Titanium dioxide nano-powders were stirred into the A356 matrix with different fraction ratios ranging from (0, 1, 2, 3, 4, 5 %) by weight at variable stirring speeds ranging from (270, 800, 1500, 2150 rpm) in both the semisolid (600 °C) and liquid state (700 °C) using a constant stirring time of one minute. The cast microstructure exhibited change of grains from dendritic to spherical shape when increasing stirring speed. The fracture surface showed the presence of nanoparticles at the interdendritic spacing of the fracture surface and was confirmed with EDXS analysis of these particles. The results of the study showed that the mechanical properties (strength, elongation and hardness) for the nanoreinforced castings using TiO_2 were enhanced for the castings made in the semi-solid state (600 °C) with 3 % weight% of TiO_2 at 1500 rpm stirring speed.

Keywords Nanoreinforced castings · Semisolid casting · Hypoeutectic aluminium alloys

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1 Introduction

Al–Si alloys are used for several automotive applications and for various applications in the aerospace industry due to their outstanding properties such as high castability, abrasion resistance and excellent strength to weight ratio. The Al–Si alloys in particular are greatly known for their rapidly advancing influence in the aircraft, aerospace and automotive industries. Intensive efforts were made to understand the modifications of these alloys caused by adding Na, Sr or Sb [1–4]. The addition of certain elements, such as calcium, sodium, strontium, and antimony, to hypoeutectic aluminum-silicon alloys results in a finer lamellar or fibrous eutectic network [4]. Gruzleski et al. [2] discussed the techniques commonly used in the foundry, and showed that the addition of P to the melt results in modified hypereutectic Al–Si alloys, with both coarse and unmodified eutectic silicon surrounding the refined primary silicon. Though Na and Sr are used to achieve refinement of the eutectic silicon, a combined effect does not happen at the same time with P due to chemical incompatibility of phosphors with the other modifying chemicals such as strontium and sodium. This has been explained [2] to result from the formation of strontium phosphide or sodium phosphide upon the addition of strontium or sodium to phosphorus pre-refined alloys. Other investigations have shown that adding rare earth elements would result in modification and refinement of the primary and eutectic silicon particles [5, 6].

The mechanical properties of the A356 alloy, not only, depend on the dendritic structures, but also on the sizes and morphologies of the eutectic Si particles [7, 8]. The eutectic Si of untreated A356 presents a coarse plate-like structure, which will deteriorate the mechanical properties (especially the ductility) of the alloy. While, the mechanical properties of the hypereutectic Al–Si alloys are highly affected by the morphology, size, and distribution of both primary Si particles (PSPs) and eutectic silicon. The morphology of silicon particles is dependent on the solidification rate; as under normal casting conditions PSPs are very coarse and show star-like and other irregular shapes. Therefore, to improve the mechanical properties of the hypo and hypereutectic Al–Si alloys, size, distribution, and the morphology of PSPs and eutectic silicon should be controlled, as well as the refining of the aluminium dendrites [2, 3].

The use of ceramic particles to improve the yield and ultimate strength (UTS) of cast Al alloys has been considered by many researchers [9–15]. Prospects of using nanoparticles as refining and reinforcement agents to gain improved performance of Al–Si cast alloys by adding Al_2O_3 and TiO_2 particles have gained significant interest recently [16–22].

Rohatgi et al. [11] have predicted the significant role of producing Al–Si ceramic composites for bearings, pistons, cylinder liners, etc. leading to savings in material and energy. Previous trials to modify the structure and enhance the mechanical properties of A356 via reinforcement with ceramic micro-sized particles, such as Al_2O_3 [12], SiC [13, 14] and TiC [15] did not result a breakthrough in casting modification, though a small number of engineering cast products entered the market [23].

It has been shown that enhanced as-cast properties of Al–Si alloys are obtained by treating the melt with nano-sized particles [16–22]. Introducing Al_2O_3 nanoparticles to the (A356) cast alloy in the semi-solid state with mechanical stirring has a beneficial effect on improving strength–ductility relationship in these alloys [16, 17]. This is attributed to the modification of the dendritic columnar structure into a smaller and equiaxed globular grain arrangement, resulting from semi-solid casting conditions. Moreover, the enhanced viscosity of the semi-solid processing would serve to improve the ceramic particle/melt wettability and entrap or capture the reinforcement material physically. The addition of ceramic particles to aluminium alloys raises the viscosity very quickly [24] providing suitable conditions for particle capture. Moreover the Al_2O_3 nanoparticles possess appropriate properties that are compatible with the Al alloy's relatively high thermal conductivity and thermal expansion coefficients that affect its role as a nanodispersion for reinforcement in the Al alloy matrix [16–19].

For most applications, a homogeneous distribution of the particles is desirable in order to maximize the mechanical properties. In order to achieve a good homogeneous distribution of the particles in the matrix, the process parameters related with the stir casting method must be considered, the stirring speed and stirring time are key parameters. There is some debate in the literature about the appropriate stirring speeds, while one study [25] has investigated stirring speeds within the range of 500, 600 and 700 rpm and the stirring times in the range of 5, 10 and 15 min, another study [26] has used higher stirring speeds in the range 1000–1500 rpm.

Haizhi [23] has presented an overview of Al–Si based alloys for engine applications where it was shown that fatigue failure and wear caused by surface delamination are the most important causes for failure or end of life of engine parts. The main causes according to the analysis presented by Haizhi Ye [23] are the size and shapes (morphology) of the Primary Si Particles (PSPs). Also, these materials have low specific gravity that makes their properties particularly superior in strength and modulus to many traditional engineering materials. Therefore, the aim of this work is to compare the effect of adding three different nanoparticles as reinforcements (Al_2O_3, TiO_2 and ZrO_2) on the microstructure, the mechanical properties and the wear behavior of A356 aluminum alloy cast from the semi-solid state, in order to evaluate the options for using nanoparticles dispersion for the production of semi-solid cast A356 alloy with improved properties.

2 Experimental Work

2.1 Material Preparation

Titanium dioxide (TiO_2) ceramic particles of 40 nm particle size were added as reinforcement materials to the A356 alloy with the chemical composition illustrated in Table 1. A charge of 1 kg of aluminum alloy A356 was placed in a crucible furnace, and then heated to the required temperature (640 °C). The addition of the

Table 1 Chemical composition (in wt%) of A356 cast Al–Si

Alloy	Chemical composition (wt%)							
	Al	Si	Mg	Fe	Cu	Pb	Zn	Mn
A356	Bal.	7.44	0.3	0.27	0.02	0.022	0.01	Nil

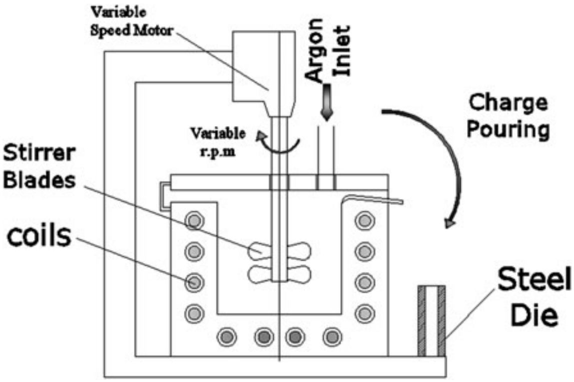

Fig. 1 Furnace used for preparing the castings

nanoparticles was made either at 710 °C or 640 °C in the liquid or semisolid state, respectively, by direct immersion of small packages of TiO_2 nanoparticles wrapped in aluminum foil with simultaneous mechanical stirring of the melt. The melting and casting conditions are fully presented in previous works [16–18]. In the case of the liquid state, the melt was brought to 700 °C when the addition was made, then stirred and poured. While in the case of the semisolid state, the temperature of the melt was brought down to 600 °C before pouring. The nanoparticles were added, while the melt was stirred mechanically at varied stirring speeds of (270, 800, 1500, 2150 rpm), and using the melting unit illustrated in Fig. 1. The stirring was carried out mechanically using a four blade impeller. The TiO_2 nanoparticles were preheated to 400 °C, to avoid entering the sintering stage. After completion of stirring and mixing, the alloys were poured in preheated steel moulds at 300 °C. Table 2 summarizes the different casting conditions used in this work.

Table 2 Casting conditions used in this work

No.	TiO_2 weight%	Temperature (°C)	Stirring speed (rpm)
1	0	600	1500
2	1	600	1500
3	2	600	1500
4	3	600	1500
5	5	600	1500
6	3	600	270
7	3	600	800
8	3	600	2150
9	3	700	1500

2.2 Mechanical Testing

The mechanical properties, mainly tensile strength, ductility, and hardness were determined in the as-cast conditions for the investigated material. The tensile tests were conducted on round tension test specimens of diameter 5.02 mm and gauge length 25.2 mm using a universal testing machine according to DIN 50125. The hardness tests were conducted on Rockwell hardness testing machine using a $\left(\frac{1}{16}\right)$ diameter hardened steel ball and a 62.5 kg applied load.

2.3 Microstructure and SEM Analysis

The microstructure examination was carried out using a OLYMPUS DP12 optical metallurgical microscope equipped with a high-resolution digital camera for investigating the microstructure. The surface topography and fracture characteristics were studied using Scanning Electron Microscope (SEM) to understand the fracture mechanism and to detect the favorable sites for particle incorporation by using JSM-5410 Scanning Electron Microscope with a high-resolution of 3.5 nm, equipped with an energy dispersive X-ray spectrometer (EDXS).

2.4 Wear Test for the TiO_2 Nanoreinforced Alloy

A PLINT TE 79 Multi Axial Tribometer Machine was used for measuring the friction force; friction coefficient and wear rate for the manufactured materials. A standard specimen with diameter of 8 and 20 mm length as a computerized Pin on disc machine used for friction & wear testing of materials is loaded vertically downwards onto the horizontal disc. The wear tests were then performed for the A356 cast material with the following parameters: velocity = 0.8 m/s, time = 1200 s and load = 10 N. The differences in the weight of the samples were taken as an indication of the wear resistance of the material.

3 Results and Discussion

3.1 Mechanical Properties

3.1.1 Effect of Nanoparticles Addition

Figure 2 presents the mechanical properties (ultimate tensile strength (UTS), elongation% and hardness) of the produced castings with TiO_2 nanoparticles reinforcement.

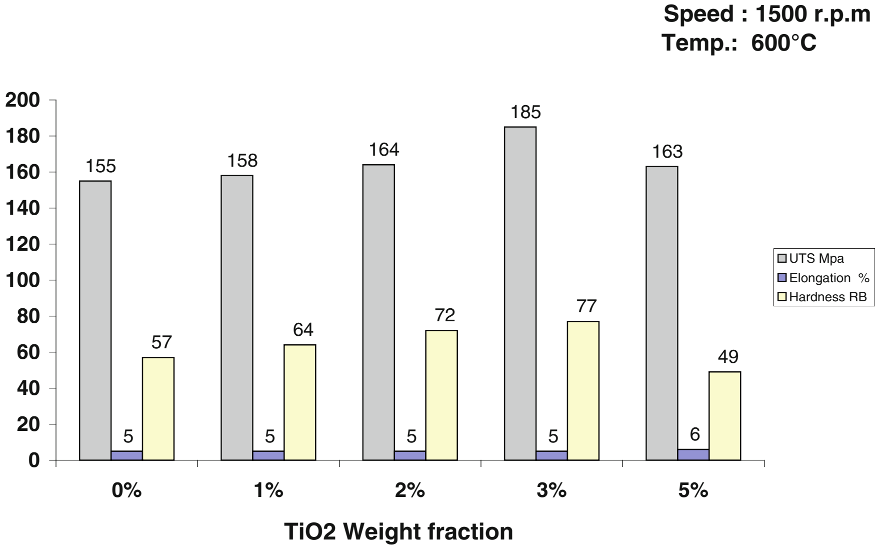

Fig. 2 The effect of TiO_2 nanoparticles% on the UTS, hardness and ductility using 1500 rpm stirring speed at semi-solid state (600 °C)

Figure 2 shows that as the weight% of the TiO_2 nanoparticles increases up to 3 %, the UTS increases until reaching 185 MPa. Beyond this weight%, the UTS decreases with increase in the wt% of the TiO_2 nanoparticles. The ductility reaches its maximum with 3 wt% TiO_2 nanoparticles added, and then drops to a minimum value with 5 wt% TiO_2 nanoparticles added. The hardness reaches its minimum value of 49 HRB with the addition of 5 wt% TiO_2 nanoparticles, which means that the material becomes softer and this is supported by the drop in the strength.

The previous results show that the inclusion of 2–3 wt% nanoparticles increases the tensile strength of the nanoreinforced A356 alloy, as well as its ductility. Beyond this limit all properties drop. The observed increase in the strength of the A356 nanoreinforced alloys suggests a misfit effect in the lattice parameter of the matrix phase. This would be a result of cooling induced changes caused by the difference between the coefficients of thermal expansion between the primary phase (Al or Si) and the nanoparticles), resulting in an increase in the hardness of the first. The coefficients of thermal expansion are: (22.2×10^{-6} m/m K for Al, 3×10^{-6} m/m K for Si, 9×10^{-6} m/m K for TiO_2 nanoparticles). Additionally, enhanced dislocation generation and reduced sub grain size owing to the presence of the nanoparticles may be contributing to the increased hardness of the aluminum phase. The increase in the hardness is also due not only to the mismatch in thermal expansion, but also the mismatch in elastic moduli of the nanoparticles. The addition of the nanoparticles also results in a constraint in the plastic flow of the matrix. The matrix could flow only with the movement of the nanoparticles or over the particles during plastic deformation. The matrix gets constrained considerably to the plastic deformation because of smaller inter-particle distance and this results in higher degree of improvement in the flow stress.

Rapid quenching from the melt or solid state reaction have been identified as processing routes for obtaining nanostructured materials leading to two phase nanostructures, however, it is highly desirable to obtain such nanostructures directly in bulk form, e.g. through casting [27]. The current work focuses on the properties of nanodispersed A356 alloys obtained by rheocasting, which is a challenging production method for producing nanodispersed alloys. The potential for nanodispersed materials for being a high-tech material has been explored [28, 29] and it has been shown that the addition of nano-oxides results in improvements in the hardness, the tensile strength and the ductility of stir cast aluminium. This has been explained by the tendency of the oxide nanoparticles to agglomerate on the grain boundaries in columnar structures, whereas these oxide nanoparticles are more likely to disperse uniformly along the equaxied structures resulting from stirring.

3.1.2 Effect of Stirring Speed

Figure 3 shows that as the stirring speed of nano TiO_2 reinforced casting increases to 1500 rpm, the UTS increases to reach 185 MPa. Beyond this stirring speed, the UTS decreases as the stirring speed increases possibly due to increase in internal

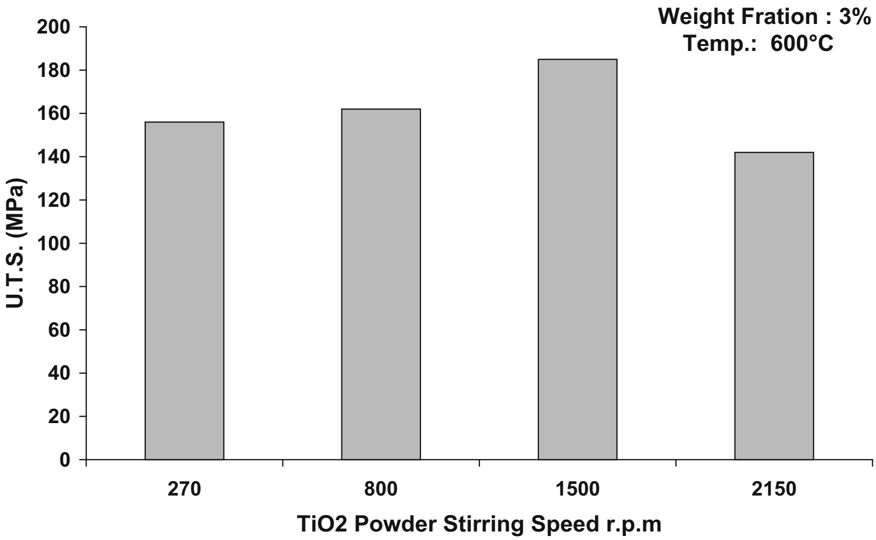

Fig. 3 The effect of stirring speed on the UTS of 3 wt% TiO_2 nanoreinforced alloy at 600 °C

porosity [18] and cooling of the semi-solid slurry, as explained before. When increasing stirring speed beyond 850 rpm the ductility starts to increase. The ductility increases slightly at the stirring speed of 1500 rpm. At 2150 rpm stirring speed, the ductility reaches its minimum value; possibly due to the high porosity [18] content created in the composite. Again, the hardness at this stirring speed decreases after reaching its maximum value at 1500 rpm.

3.1.3 Effect of Casting Temperature

From Fig. 4, it is clear that the UTS reaches the maximum value for the semi-solid casting at 600 °C. As explained before, the beneficial role of the semi-solid state (mushy zone) in obtaining homogeneous distribution of the nanoparticles in the A356 matrix leads to better reinforcement of the matrix. The good reinforcement leads to higher UTS and higher ductility with a high hardness.

The improved strength and ductility exhibited by the nano-composites fabricated by the semi-solid method over that fabricated by liquid metallurgy (700 °C) method may be attributed to the high effective viscosity of the metal slurry that prevents particles from settling, floating, or agglomerating. This leads to better distribution of the ceramic phase and hence better mechanical properties.

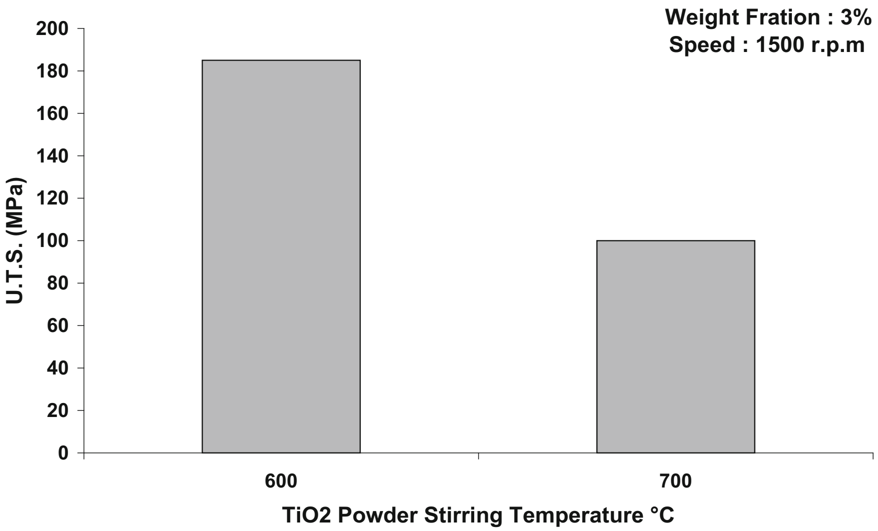

Fig. 4 The effect of stirring temperature on the UTS of MMC with 3 wt% fraction of TiO_2 nano particles at 1500 rpm stirring speed

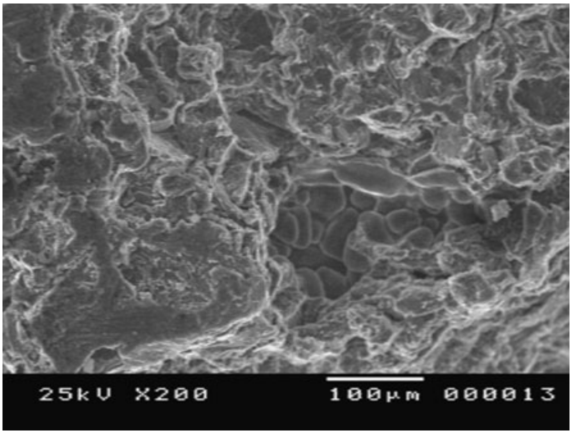

Fig. 5 The (SEM) of the fracture surface specimen reinforced with 3 wt% TiO_2 nanoparticles

3.2 *Microstructural Evolution*

Figure 5 illustrates the brittle fracture surface of the specimen of the A356 alloy reinforced with 3 wt% TiO_2 which showed the optimum mechanical properties. It was difficult to detect TiO_2 nanoparticles; possibly due to the absence of agglomerated particles which could appear clearly.

3.3 *Wear Test Results*

The average-wear results of A356 samples reinforced with 0, 1, 2, 3 and 5 weight% TiO_2 nanoparticles are shown in Table 3. It can be seen from Table 3 that the addition of 1 weight% of nanoparticles resulted in a significant drop in friction coefficient, unaccompanied by any improvement in terms of weight loss. Increasing nanoparticles up to 5 % resulted in deterioration in wear resistance in terms of friction coefficient and weight loss, as also included from a previous research work [29, 30].

Table 3 The average wear results of A356 samples reinforced with 0, 1, 2, 3 and 5 weight% TiO_2 nanopowder

Sample no.	Additions	Weight loss (mg)	Friction coefficient
1	A356	3.6	0.38
2	A356 + 1 % TiO_2	4.0	0.36
3	A356 + 2 % TiO_2	4.2	0.39
4	A356 + 3 % TiO_2	4.6	0.41
5	A356 + 5 % TiO_2	5.1	0.44

The results show that the addition of 1 weight% nanoparticles did not produce a significant change in the wear resistance of the hypo-eutectic alloy A356, though there was a reduction in the friction coefficient. The fact that the wear resistance deteriorated after adding 2, 3 and 5 weight% nanoparticles (though the hardness and strength increased) may be attributed to microstructural effects as well as the high load used in the test [30, 31].

4 Conclusion

- The castings made by adding nano-sized dispersoids using the semi-solid route exhibited better mechanical properties when compared with those prepared by liquid metallurgy route.
- The stirring speed has a significant effect on the mechanical properties of the nano-dispersed castings. Increasing stirring speed to more than 1500 rpm causes a reduction in the tensile strength. The alloy stirred with 1500 rpm exhibits the highest tensile strength and elongation%.
- The A356 matrix alloy reinforced with 3 % weight of TiO_2 at the conditions of 1500 rpm stirring speed at the semi solid state temperature 600 °C has the highest mechanical properties.
- Analysis using scanning electron microscopy (SEM) at high magnification shows evidence for the possibility of incorporating and entrapping nano-sized particles within the interdendritic interface developing during the solidification of the dispersed alloys.
- The introduction of varying amounts of nanosized particles to the A356 alloy did not produce a significant change on the wear resistance of the tested hypo-eutectic alloy A356 material with 1 % nanoparticles and resulted in deterioration after adding 2, 3 and 5 % nanoparticles, though a drop in the friction coefficient occurred at 1 % addition.

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