

The UPAL process: a direct method of preparing cast aluminium alloy–graphite particle composites

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A direct method of preparing cast aluminium alloy–graphite particle composites using uncoated graphite particles is reported. The method consists of introducing and dispersing uncoated but suitably pretreated graphite particles in aluminium alloy melts, and casting the resulting composite melts in suitable permanent moulds. The optical pretreatment required for the dispersion of the uncoated graphite particles in aluminium alloy melts consists of heating the graphite particles to 400° C in air for 1 h just prior to their dispersion in the melts. The effects of alloying elements such as Si, Cu and Mg on the dispersability of pretreated graphite in molten aluminium have also been reported. It was found that additions of about 0.5% Mg or 5% Si significantly improve the dispersability of graphite particles in aluminium alloy melts as indicated by the high recoveries of graphite in the castings of these composites. It was also possible to disperse upto 3% graphite in LM 13 alloy melts and retain the graphite particles in a well distributed fashion in the castings using the pre-heat-treated graphite particles. The observations in this study have been related to the information presently available on wetting between graphite and molten aluminium in the presence of different elements and our own thermogravimetric analysis studies on graphite particles. Physical and mechanical properties of LM 13–3% graphite composite made using pre-heat-treated graphite powder, were found to be adequate for many applications, including pistons which have been successfully used in internal combustion engines.

1. Introduction

In recent years considerable attention has been given to the preparation and study of the properties of cast aluminium alloy–graphite particle composites [1–12]. Aluminium alloy–graphite particle composites are excellent bearing materials and it has been reported that they compare well with many copper alloys including brasses and bronzes [5, 10]. Pistons and cylinder liners made using aluminium alloys containing dispersed graphite particles have been successfully used in internal combustion engines [13–15].

The major difficulty in the preparation of cast aluminium alloy–graphite particle composites by

a liquid metallurgy process is the apparent non-wettability of graphite by liquid aluminium alloys and hence the rejection of graphite particles by the melt. The contact angle of aluminium with graphite is 160° and it is reported to remain unwettable between the melting point of aluminium [16] and 1080° C.

Attempts have been made to solve the problem of non-wetting between graphite and molten aluminium through several approaches: (a) adding metal (copper or nickel) coated graphite powder in molten aluminium alloy [1–4] using the vortex, gas injection or pellet technique, (b) the addition of uncoated graphite particles with the aid of

TABLE I Recoveries of uncoated and unheat-treated graphite particles in castings of different base alloys

Base alloy	Chemical composition of base alloy	Percentage recovery of graphite in castings
LM-0	99.5% pure Al	1.66
LM-4	Al-4 Wt% Cu-6 wt% Si	16.6
LM-6	Al-12 wt% Si	26.0
LM-13	Al-12 wt% Si-1.5 wt% Cu-1.5 wt% Ni-1.5 wt% Mg	32.0
LM-28	Al-20 wt% Si-1.8 wt% Cu-1.5 wt% Ni-1.5 wt% Mg	16.0
LM-29	Al-25 wt% Si-5 wt% Cu-13 wt% Ni-1.3 wt% Mg	2.0

Note: Quantity of graphite added: 3 wt%.

Graphite particle size used: - 200 + 300 mesh.

ultrasonics and simultaneous additions of surface and interfacial active elements [5] (c) adding uncoated graphite particles into vigorously agitated molten alloy kept between the liquidus and solidus temperatures [17].

All these methods of preparing cast aluminium-graphite particle composites are cumbersome, since they require either a regular supply of metal coated graphite particles or very high-power ultrasonic probes. Hence a programme was initiated to develop a simple and more direct method of preparing cast aluminium-graphite particle composites without resorting either to metal coating or ultrasonic vibrations.

In this paper a new process, namely the "UPAL process" is described for the preparation of cast aluminium alloy-graphite particle composites by adding uncoated graphite particles above the liquidus temperature (without the use of ultrasonics). The effect of alloying elements such as Si, Cu and Mg on the dispersability of uncoated but pre-heat-treated graphite particles in aluminium (99.5% pure) melt has been investigated. The degassing characteristics of LM13 alloy-graphite particle composites made using uncoated graphite particles, have also been studied and reported in this paper. Limited physical and mechanical properties of cast LM 13-graphite particle composites made using uncoated graphite powder have also been reported.

2. Experimental procedure

The apparatus used and the vortex method [6] procedure employed for dispersing graphite particles are quite similar to our earlier method [3]. However, in this investigation, uncoated but pre-heat-treated graphite particles were added to the melts above their liquidus temperature (UPAL process).

3. Results and discussions

In the initial stages several trials were carried out to introduce and disperse uncoated and untreated (as-sieved, fresh) graphite powder in various aluminium alloy melts. The results of these experiments are shown in Table I. In the majority of the trials carried out, most of the graphite particles added to the melt were totally rejected. Similar rejection of uncoated and untreated graphite by aluminium alloy melt has been reported by Patton [12], Badia and Rohatgi [1], Gorbunov *et al.* [5], Mehrabian and Flemings [17] and Badia *et al.* [2]. In a few cases it was possible to recover very small quantities (< 32%) of the graphite particles in the melts and cast the composites. However, even in these castings the graphite was present in agglomerated forms and the castings contained gas holes. Segregation of graphite particles was also observed near the top surfaces of these castings, apparently due to the gas bubbles associated with graphite particles.

Results of these trials with uncoated and unheat-treated graphite particles suggested that the rejection of graphite particles in most of the trials, and their presence in the agglomerated form in a few castings, may be related to the presence of volatile substances and other adsorbed gases in the graphite particles. The expulsion of volatile matter and adsorbed gases from graphite particles when they are heat-treated was in fact confirmed by thermogravimetric analysis (TGA). TGA of graphite powder used in this study for preparing composites was carried out in a CO₂ atmosphere at a heating rate of 5° C min⁻¹. The CO₂ atmosphere was used to prevent oxidation of graphite. The expulsion of volatile matter from the graphite powder was of the order of 0.45 wt% of the original graphite (Fig. 1). TGA was also carried out in air to find out the required temperature and

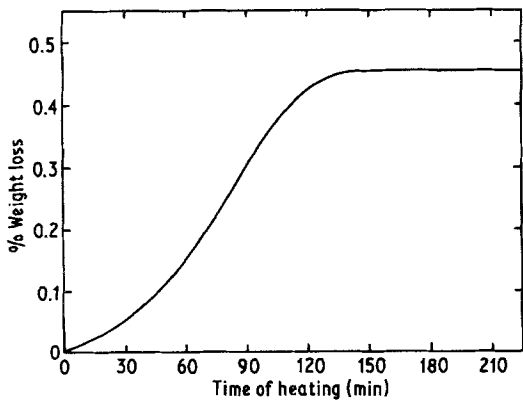


Figure 1 Isothermal heating of graphite powder in CO_2 at 400°C .

time for which the graphite particles should be heated to expel all the volatile matter and adsorbed gases before adding the graphite powder to the aluminium alloy melts. TGA isotherms at different temperatures shown in Fig. 2 indicate that it would be possible to remove most of the volatile substances and adsorbed gases present in the graphite particles by heating the graphite particles to 400°C for about 30 min when the amount of graphite is about 5 g and the graphite bed height is about 3 mm. Fig. 2 also shows that the time required to remove all the volatile substances

and gases can be less than 30 min if the heating temperature exceeds 400°C . However, severe oxidation of graphite powder was noticed at higher activation temperatures. Therefore, 400°C was selected as the optimum temperature for expelling the volatile substances and adsorbed gases.

A second set of experiments (fabrication of composites) was carried out with uncoated but pre-heat-treated graphite powder (heated to 400°C for 1 h just prior to their dispersion in the melt). Recoveries of graphite particles in various aluminium alloy melts, including the standard piston alloy (LM 13), are shown in Table II. A comparison of Table II with Table I shows that dispersability and recovery of graphite particles in all the aluminium alloy castings are significantly higher if the graphite particles are pre-heat-treated to 400°C for 1 h just prior to their dispersion in the aluminium alloy melts. Further it was observed that recoveries of graphite particles in the castings (made using pre-heat-treated graphite particles) made under identical conditions were different in different base alloy compositions. Hence, a systematic study was undertaken to investigate the effect of alloying elements on the dispersability and recovery of graphite in 99.5% pure aluminium.

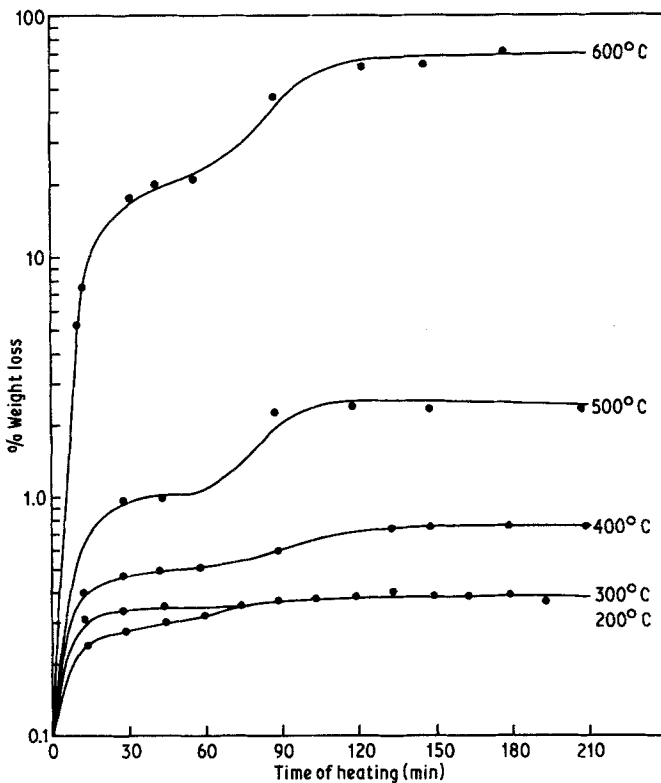


Figure 2 Isothermal heating of graphite powder in air at different temperatures.

TABLE II Recoveries of uncoated, pre-heat-treated graphite particles in castings of different base alloys

Base alloy	Percentage recovery of graphite in the casting	Base alloy	Percentage recovery of graphite in the casting	Commercial base alloys	Percentage recovery of graphite in the casting
Al-0 wt% Cu	20	Al-0.5 wt% Si	20	LM 4	66
Al-1.1 wt% Cu	25	Al-1.0 wt% Si	33	LM 6	98
Al-2.1 wt% Cu	48	Al-2.2 wt% Si	60	LM 13	98
Al-3.3 wt% Cu	54	Al-2.9 wt% Si	71	LM 28	70
Al-4.0 wt% Cu	95	Al-3.5 wt% Si	81	LM 29	60
Al-4.5 wt% Cu	96	Al-5.1 wt% Si	90	(with 5 wt% Cu)	
Al-5.0 wt% Cu	79	Al-6.3 wt% Si	96		
Al-6.2 wt% Cu	79	Al-8.0 wt% Si	96		
Al-8.0 wt% Cu	—	Al-10.3 wt% Si	96		
Al-9.7 wt% Cu	66	Al-12 wt% Si	98		
		Al-16 wt% Si	96		
		Al-18 wt% Si	97		

Note: Quantity of graphite added: 3 wt%.
 Graphite particle size: — 200, + 300 mesh.
 Pretreatment to graphite particles: 1 h heating in air at 400°C.
 Melt degassed with dry N₂ gas prior to graphite dispersion.
 Melt temperature at the start of graphite dispersion: 780°C.

3.1. Effect of alloy composition on dispersability and recovery of graphite in aluminium melts and solidified castings

Recovery of graphite particles in aluminium melt (99.5% pure) at 740°C is very poor (< 20%). This could be attributed to a high contact angle (130°) between aluminium and graphite and consequently to the poor wettability [18]. Even at melt temperatures of 800°C and longer stirring times (7 to 8 min), no improvement in the recovery of graphite in the castings was observed. This could be further attributed to the fact that the contact angle remains high, between 110° to 130° even up to a temperature of 1000°C regardless of the time of contact of the melt with graphite [18] (Fig. 3). Apparently, this is the reason why, in the present investigation, it was not found possible to disperse considerable amounts of pre-heat-treated graphite particles in aluminium melts (99.5% pure) at melt temperatures ranging from 670 to 820°C.

3.1.1. Effect of silicon additions to pure aluminium on the recovery of graphite particles in aluminium melts

Recovery of uncoated pretreated graphite particles in aluminium melts gradually increases with increasing additions of silicon from 20% at 0.5% Si to 98% at 12% Si. The beneficial effects of silicon in increasing the recovery of graphite could be attributed to decreased surface tension of the

molten aluminium due to additions of silicon. It has been reported [19] that the surface tension of aluminium decreases with the addition of silicon at a rate of 0.66 N m⁻¹ per 1 wt% Si. Wetting of graphite by aluminium is promoted by a decrease in the surface tension and apparently this makes the dispersion and retention of graphite easier in aluminium-silicon alloy melts. It was further observed that recoveries of graphite particles were

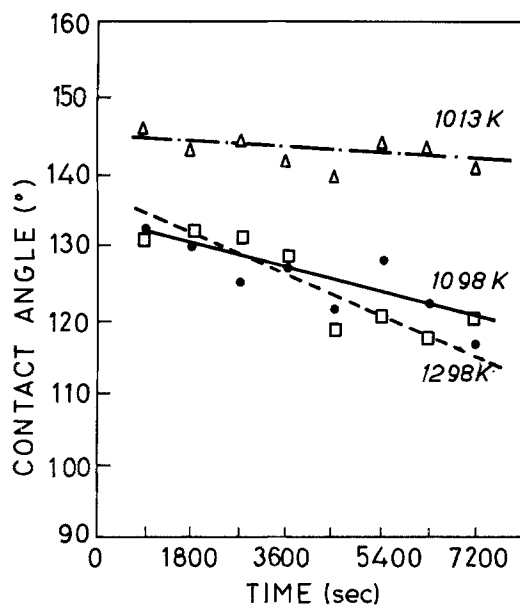


Figure 3 Time dependence of contact angle for 99.99% pure Al-graphite system [18].

quite high even when the silicon content was higher than 12 wt%.

3.1.2. Effect of copper additions on the recovery of graphite particles in aluminium melts

Additions of copper up to 4.5 wt% improve the recovery of uncoated but heat-treated graphite particles in castings. However, a report by Kohler [20], on the wetting of Al_2O_3 by aluminium indicates that the contact angle between Al_2O_3 and Al decreases with the addition of copper up to a certain level. Contact angles of Al, Al–1 wt% Cu and Al–5.6 wt% Cu alloys with Al_2O_3 have been reported to be 88° , 76° and 134° , respectively, indicating the adverse effect of 5.6 wt% Cu and the beneficial effect of 1 wt% Cu on wettability. Apparently, similar phenomena take place on wetting of graphite by Al–Cu alloys.

3.1.3. Effect of magnesium addition on the recovery of graphite particles in aluminium melts

Magnesium (added to the surface of the melt along with graphite powder) has been found to be the most important alloying element affecting the dispersion and recovery of uncoated and pretreated graphite in aluminium and aluminium alloy castings (Table III). This could be due to the fact that the surface tension of magnesium is $552 \times 10^{-5} \text{ N cm}^{-1}$ compared to a value of $825 \times 10^{-5} \text{ N cm}^{-1}$ for molten aluminium. The contact angle of aluminium with graphite at its melting point decreases from 160 to 145° C with addition of 1.39 wt% Mg and further decreases to 115° C with the addition of 9.98 wt% Mg [21]. At the same Mg levels and at higher melt temperatures the contact angle is expected to be still lower. Additions of as low as 1 wt% Mg on the surface of the melts could result in very high magnesium concentrations on the

melt surfaces, improving the wettability between aluminium and graphite powder due to a decrease in contact angle, and thereby improving the recovery of graphite particles in the castings from as low as 20% to as high as 70% in the case of pure aluminium.

3.1.4. Effect of iron in aluminium melts on the dispersability of graphite

No systematic experiments were carried out to investigate the effect of iron on the dispersability of graphite in aluminium, since iron contents greater than 0.8 wt% are considered undesirable in most aluminium alloys. However, when the iron content as an impurity was high in aluminium melts, or when the iron content of the aluminium melt increased due to accidental dissolution of the stirrer blade, the dispersability of graphite particles became much better. Presence of small quantities of iron in aluminium melts is known to improve its wettability with graphite [22], and apparently this is the reason for improved recoveries of graphite in the presence of iron.

The major objective of the present investigation was to introduce graphite particles into LM 13 alloy by the simplest technique, since LM 13 is a widely used alloy in piston applications. The experiments on the effect of alloying aluminium indicated that it should be possible to disperse upto 3 wt% uncoated but pre-treated graphite particles in LM 13. Hence, further experiments were conducted to identify the conditions necessary to obtain desired recoveries of graphite particles in LM 13 alloy melts and to achieve a uniform dispersion of graphite particles in the castings.

It was found that (Table II), upto 3 wt% graphite can be dispersed in LM 13 alloy. Although no direct measurements of contact angle between LM 13 alloy melt and graphite are available, the fact that it has been possible to disperse large quantities of graphite particles in LM 13 alloy melts in this study, suggests that there is good wettability. This indicates that elements such as silicon, magnesium and copper, which improve the wettability when present alone in the binary systems, are also able to improve the wettability when they are present together in proportions found in LM 13 alloys.

Experiments were also carried out to study the graphite recovery on remelting and degassing of LM 13 alloy–graphite composite melts made using

TABLE III Effect of magnesium addition on the recoveries of graphite in different aluminium alloys

Base alloy	Percentage recovery in castings	
	Without Mg addition	With Mg addition
LM 0	20	70
LM 4	66	93
LM 28	70	87
LM 29 (with 5 wt% Cu)	60	80

Note: Experimental conditions: as given in Table II.

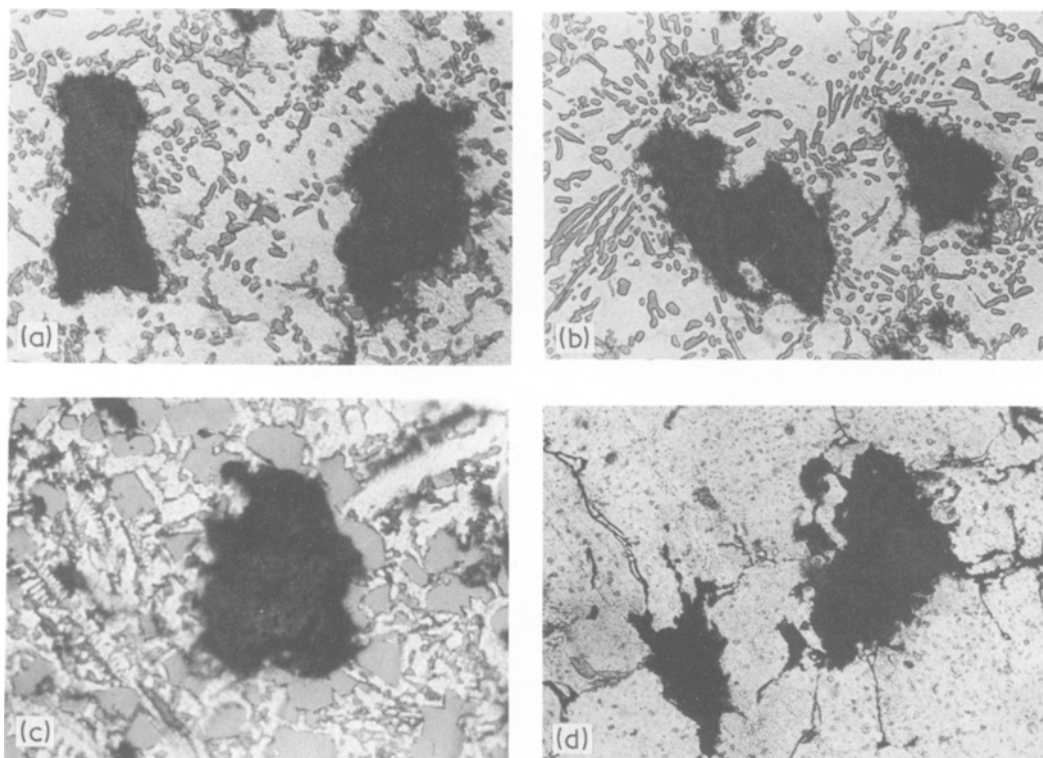


Figure 4 Typical microphotographs of aluminium alloy-graphite particle composites: (a) Al-12 wt% Si-1.5 wt% Ni-1.5 wt% Cu-1.5 wt% Mg-3 wt% graphite (X400), (b) Al-11.5 wt% Si-3 wt% graphite (X400), (c) Al-18 wt% Si-5 wt% Cu-1.5 wt% Ni-1.5 wt% Mg-3 wt% graphite (X400) and (d) Al-4.5 wt% Cu-3 wt% graphite (X400).

pre-heat-treated graphite particles. These experiments were carried out keeping in mind that industry may find it necessary to remelt and degas these composites (for example re-using runners and risers from castings).

3.2. Degassing of aluminium alloy-graphite particle composite melts

Several trials were carried out to degas the aluminium alloy melts before and after dispersing pre-heat-treated graphite particles using both dry N_2 gas and hexachloroethane degasser tablets. It was possible to degas the aluminium alloy melts using dry N_2 gas either before or after dispersing the pre-heat-treated graphite particles without significant loss of graphite particles. Hexachloroethane degasser tablets can also be used to degas the aluminium alloy melt only before the dispersion of graphite particles. However, hexachloroethane cannot be used to degas the melt after the dispersion of graphite since it leads to total rejection of dispersed graphite particles. The chlorine gas from hexachloroethane apparently alters the wetting behaviour [23-25] between the

suspended graphite particles and the aluminium alloy melts, resulting in the total rejection of dispersed graphite particles.

3.3. Microstructure, physical and mechanical properties of LM 13-3 wt%-graphite particle composites made using uncoated graphite particles

Fig. 4 shows microstructures of aluminium alloys containing dispersed graphite particles (uncoated and pre-heat-treated). No pores or voids are visible at these magnifications at the graphite-metal interface, indicating good wetting between the graphite particle surface and the metal matrix.

TABLE IV Mechanical properties of LM 13 alloy containing different percentages of pre-heat-treated graphite particles

Percentage graphite	Density ($g\ cm^{-3}$)	UTS ($N\ mm^{-2}$)	Percentage elongation	Hardness BHN*
0	2.72	207	0.50	105
1	2.69	195	0.44	97
2	2.62	164	0.40	93
3	2.60	161	0.37	92

* BHN: Brinell hardness number.

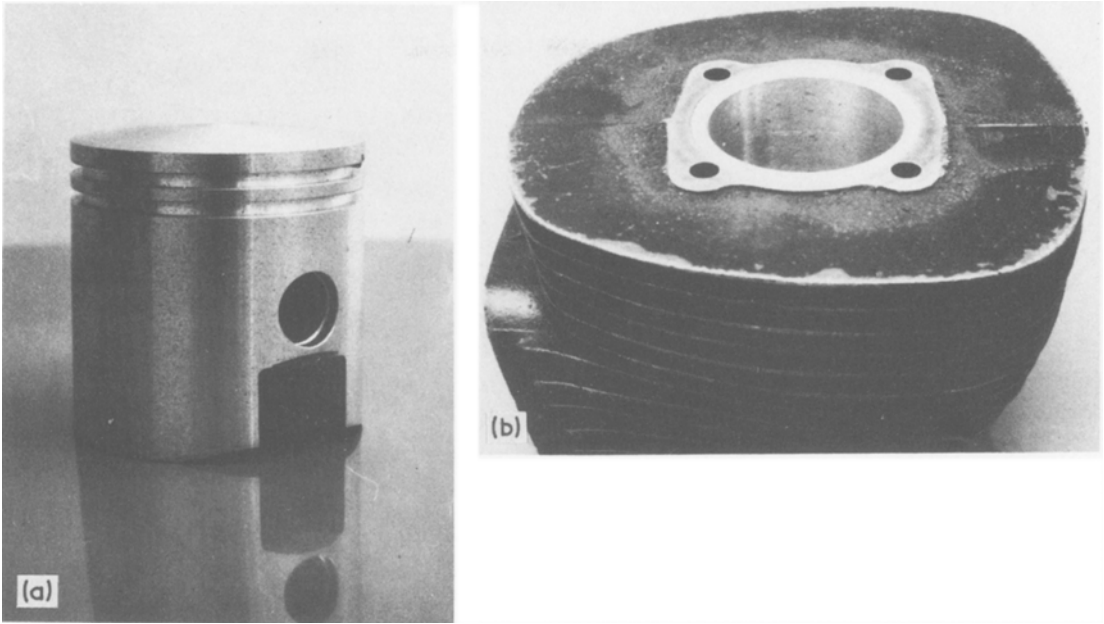


Figure 5 Photographs of a two-stroke petrol engine (a) Al-Si-graphite piston and (b) Al-Si-graphite liner inserted in a cast iron cylinder block.

From Table IV it is clear that density, ultimate tensile strength (UTS), hardness and percentage elongation of LM 13 alloy progressively decrease with the increasing additions of uncoated graphite particles, in a manner similar to the decrease in the properties of aluminium alloys made using copper or nickel coated graphite particles. However, the mechanical properties of aluminium alloys containing up to 3 wt% graphite are found to be adequate for many tribological applications. In fact, triboelements such as pistons, cylinder liners (Fig. 5) and bearings made of different aluminium alloy-graphite particle composites using the present process have been successfully used in internal combustion engines [13, 15].

4. Conclusions

(1) It was not possible in the present investigation to disperse more than 0.2 wt% graphite in 99.5% pure aluminium melts when uncoated and unheat-treated graphite particles were stirred in aluminium melts up to melt temperatures of 800° C.

(2) Additions of alloying elements such as Si and/or magnesium to aluminium melts and preheating of graphite particles to 400° C for 1 h in air, aids the dispersion of graphite particles in aluminium alloy melts, and significantly increases the recoveries of graphite particles in the castings.

(3) Apparently, preheating the graphite particles to 400° C for 1 h in air removes the adsorbed gases and volatile substances (as confirmed by TGA investigations), thereby improving the wettability between the graphite particles and the aluminium alloy melts.

(4) It is possible to disperse up to 3 wt% of uncoated but pre-heat-treated (heated to 400° C in air for 1 h) graphite particles (average size 50 μm) in Al-13 wt% Si-1.5 wt% Cu-1.5 wt% Mg-1.5 wt% Ni (LM 13) alloy melts by the vortex method, and cast into a variety of shapes including bearings and pistons.

(5) Mechanical properties of LM 13-3 wt% graphite composites made by the process of the present investigation were found to be adequate for several applications including pistons which were successfully used in internal combustion engines.

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