Advanced alloys for engine applications

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Two new alloy systems have been developed and refined for use in advanced engines. The first is a composite system developed for light-weight high performance cylinder liners. Cylinder liners exert a major influence on engine performance, reliability, durability, and maintenance. Various combinations of non-metallic reinforcements and coatings have been used to improve the tribological performance of sleeves or surfaces used in compressors and internal combustion engines in four stroke, two stroke and rotary configurations. In this paper we report the use of a hybrid composite containing silicon carbide and graphite in an aluminium alloy matrix to improve the performance of various small engines and compressors. Material properties of the base material, as well as comparative dynamometer testing, are presented. The second involves

HYBRID COMPOSITES

Graphite reduces the coefficient of friction and minimises wear of loaded rubbing surfaces. Composites containing graphite particles have been shown to exhibit a lower friction coefficient and enhanced seizure resistance when sliding against cast iron, steel, and other composite surfaces under both non-lubricated (dry) and starved lubricated sliding conditions. Cast aluminium-graphite composites have unique microstructures the use of a common rare earth (cerium) to remarkably improve the high temperature performance of aluminium alloys. In the early 1980s, some promising research and development efforts focused on powder metallurgy revealed that aluminium alloys containing 4 wt% cerium exhibit high temperature mechanical properties exceeding those of the best commercial aluminium casting alloys currently in production. Cerium oxide is an abundant rare earth oxide that is often discarded during the refining of more valuable rare earths such as Nd and Dy. Therefore, the economics are compelling for cerium as an alloy additive. In this paper, we report select results obtained during an investigation of the castability of aluminium-cerium alloys and determine compositional modifications that may be required to ensure the compatibility of the alloy with near net shape casting methods such as advanced sand casting, die casting, permanent mould casting and squeeze casting. Al-Ce alloys were cast in binary composition of 6-16 wt% Ce. Commercially pure aluminium ingots were melted and held at approximately 785°C. Ternary and quaternary alloys with Si and Mg additions were also investigated. Test bars were cast to establish mechanical properties and step plates and hot tear moulds were used to determine sensitivity to solidification conditions and hot tearing sensitivity respectively. Finally, air cooled engine cylinder heads were cast in sand moulds to get a sense of castability in complicated shape castings. The use of these two alloys for piston/liner systems can yield significant improvements in engine durability and performance.

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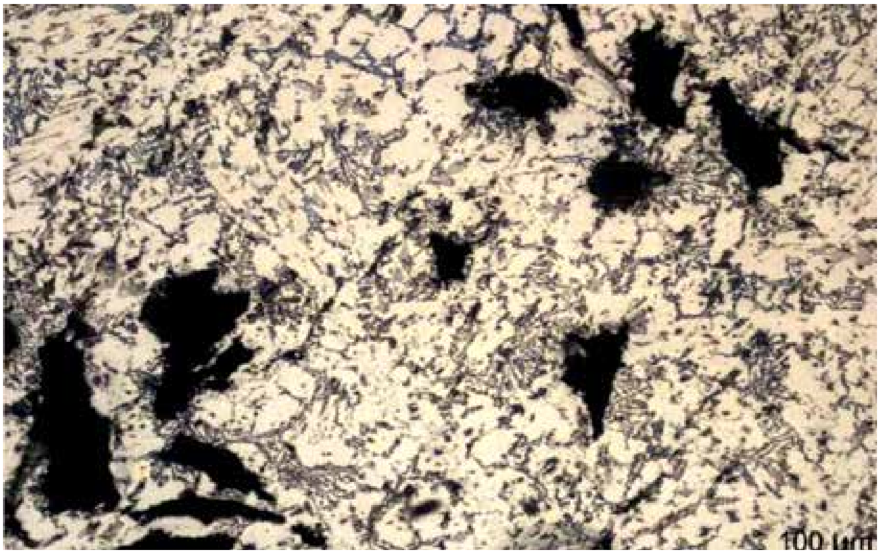
in which graphite particles are located in interdendritic regions along with the aluminium-silicon eutectic. See **Figure1**. With additions above two volume percentage graphite the alloy can run under boundary lubrication without seizing or galling. Cylinder liners and pistons of Al-Si-Gr alloys have been tested in small diesel and gasoline engines and have shown improved performance. In a two-stroke gasoline engine use of Al-Si-Gr liners showed improvement in power, reduction of specific fuel consumption and wear along with resistance to seizure.

Associated Engineering Company in Italy dispersed 4 vol% graphite particles in aluminium 18 percent silicon alloy. Liners of these alloys in two-stroke and four-stroke engines were evaluated in collaboration with Ferrari, Hiro, and Alfa Romeo for passenger and racing car applications. The power generated was improved by 10 percent, there was no significant liner wear and the pistons showed no sign of scuffing. Aluminium-graphite liners were fitted in Alfa Romeo racing cars which were victorious in the Formula 1975 World Championships.[1]

Later work concentrated on improving the distribution of graphite into the melt. Numerous attempts have been made to incorporate graphite flakes in aluminium alloys. Some of the earliest work performed by Badia and Rohat-

Figure1: Al-5Gr shown at 200X



gi[2] recognised the difficulty in mixing graphite particles into molten aluminium alloys due to the non-wetting nature of graphite by aluminium and the inherent density difference between the two phases. The poor wetting was overcome by nickel-coating the graphite particles prior to their incorporation by injection into the melt. Nickel provides a surface readily wet by aluminium and increases the density of the particle such that it is more easily drawn into the alloy mixture. Evidence for the wetting nature of nickel coatings on graphite surfaces was demonstrated by the sessile drop technique in which a drop of molten aluminium readily wet a planar nickel-coated graphite substrate.[3]

Initially the nickel coating protects the graphite particle and greatly reduces the amount of time required to incorporate the graphite particles into the aluminium alloy. Once the particle is wet by the molten aluminium alloy the nickel coating dissolves in aluminium and the graphite particle floats to the surface of the metal during mixing and during solidification in the casting. Homogeneous distribution of graphite in aluminium castings was, as a result, difficult to obtain.

Segregation of the graphite phase either during mixing and casting or solidification of the composite alloy continued to be a problem in the foundry. To ensure consistent quality of cast graphitic aluminium parts, the graphite phase must be in a stable suspension for the time necessary to ladle, transfer, pour, and solidify the alloy in the casting. The alloy that has been developed by Rohatgi for this work is a hybrid particulate reinforced aluminium alloy relying on the principle of hindered settling between two particle phases, one of which is denser and the other less dense than the melt. Although any particulate reinforcement with a density greater than that of aluminium would be suitable to stabilise a suspension of graphite particles, industrial activity has focused on a graphite–silicon carbide suspension due to the commercial availability of aluminium–silicon carbide composite materials. This modified structure is shown in **Figure2**. The dry sliding wear rate of the composites is better than either cast iron or an aluminium alloy like A356 and generally increases as the percentage of ceramic particles increases in the composite. These results are shown in **Figure3**.

Figure2: Al-10SiC-4Gr shown at 200X

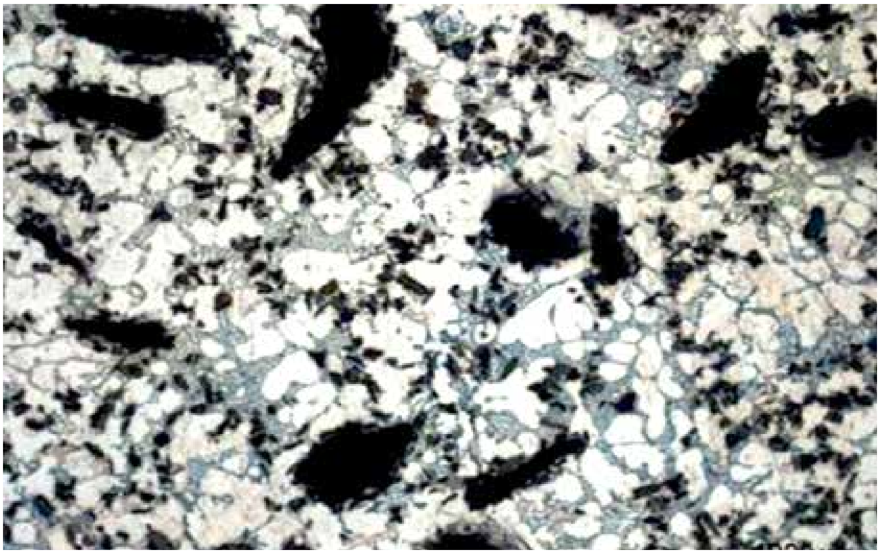
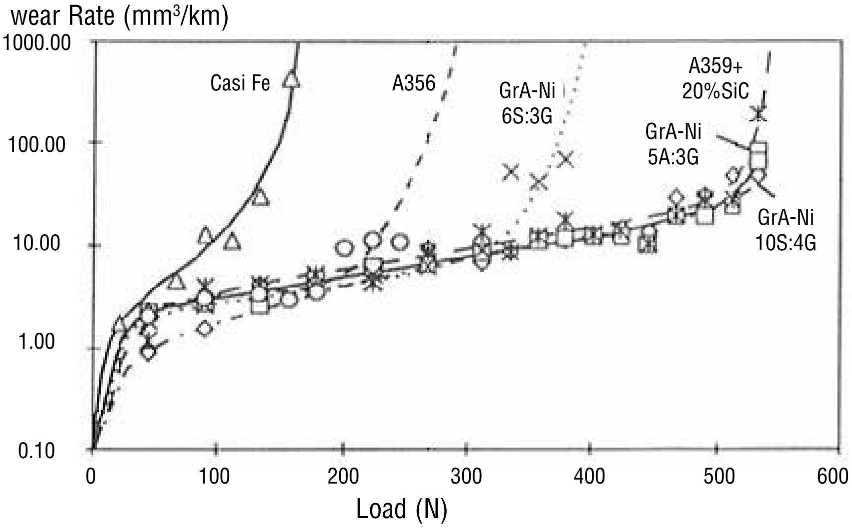


Figure3: Dry sliding wear of hybrid composite versus cast iron, A356 and Al-20 Volume SiC, from reference 4



Early developmental testing

Development work to replace iron sleeves in compressors with hybrid composite materials was completed prior to the current study. Customer testing confirmed a reduction in discharge air temperature by 50°F, a 65 percent reduction in oil bypass, and a reduction in horsepower draw of 25 percent.[5] All of these tests were conducted using the 10vol%SiC with 4vol%-

Graphite in a A359 base aluminium alloy. Other projects include a rotary engine rotor housing made from the same base alloy but with 25vol%SiC and 5%vol%-Graphite. That part is shown in **Figure4**. The customer reported a 20 percent improvement in power output at 6400 rpm when compared to coated 6061 rotors. The improved efficiency was attributed to lower thermal expansion of the material at engine operating temperatures.[6]

Figure4: Al-25SiC-5Gr rotor housing

Figure5: Pouring raw castings from hybrid composite material

Liner preparation and testing

Pre-alloyed A359 ingot containing 10 volume percent SiC and 4 volume percent nickel coated graphite was melted in a gas fired crucible under an argon cover gas at 1350°F. The argon cover gas was used in lieu of degassing. The alloy was not modified or grain refined. The metal was poured into sand moulds (**Figure5**) and naturally solidified. The castings were heat treated to a T6 condition, with a solution time of 8 hours at 1000°F followed by quenching in 180°F water and aged at 310°F for 4 hours.

The castings were subsequently machined using diamond tooling. Two Briggs and Stratton Animal engines with a 2.6875' bore and 2.2' stroke were tested to determine baseline properties. The Animal engine is a single-cylinder, carburetted four-stroke engine with 206cc displacement.

The cylinder liner in one of the engines was removed and a machined hybrid composite liner was press-fit into the block. The bore was honed after installation using a diamond hone.

Initial testing in the engine modified with the composite hybrid liner showed high piston ring wear using stock piston rings. New rings were acquired and coated with titanium nitride coating and used for the testing.

Side by side testing was done using a Dyno-Mite dynamometer. The engine using the hybrid composite liner showed a 1.5 percent higher peak torque and a 1.6 percent improvement in peak horsepower after normalising for initial engine conditions. See **Figure6**. Peak torque and peak horsepower occurred at slightly different rpm's in the two engines. In the engine with the stock liner, peak torque was recorded at 3700 rpm and peak horsepower at 5200-5500 rpm. In the engine with the composite liner, peak torque was recorded at 3400 rpm and peak horsepower at 5600-5700 rpm.

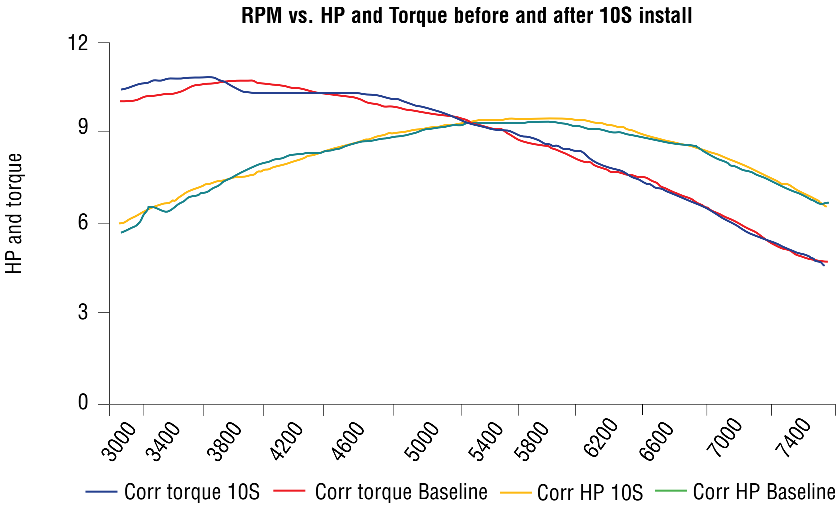
At 3300 rpm the engine with the composite liner showed a 4.4 percent improvement in torque and a 4.3 percent improvement in horsepower when compared to the engine with the stock liner.

The engine with the composite liner was run for a 10-hour durability cycle. Power increased as time was accumulated on the engine. Disassembly of the engine showed no signs of wear in the cylinder bore. The rings did show wear at the end gaps, most of the ring showed very little wear.

Ongoing work

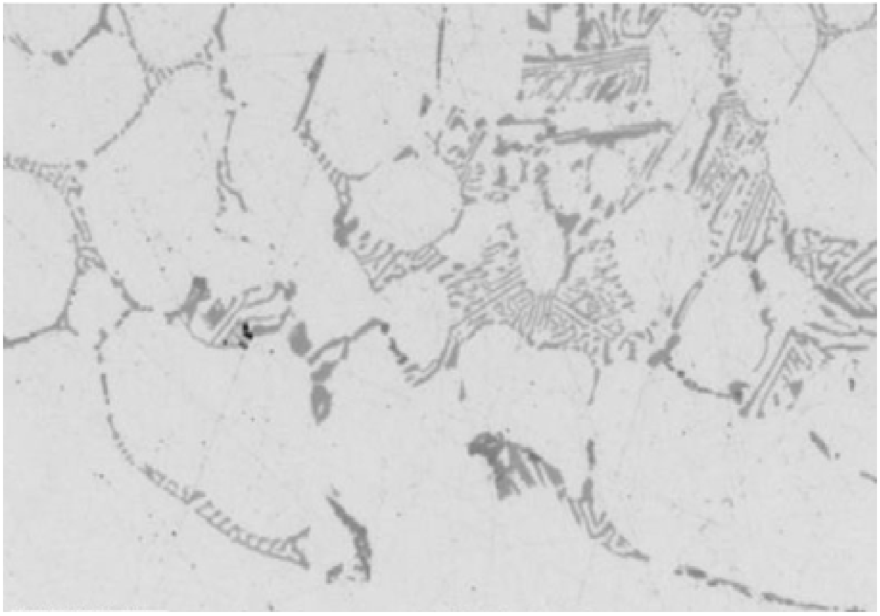
Liners are currently being tested in automotive engines of up to 380 HP. Initial results, comparing power output to engines using nikasil coated aluminium liners, show a 5 percent improvement in horsepower. Durability testing is underway, and inspection of the sleeves showed no wear after the initial testing, although some minor piston and ring wear was noted. The hybrid composites are being tested in other applications as well, including wrist pin inserts in pistons as a replacement for hard anodising of the wrist pin bores.

Figure6: Horsepower curves comparing standard cast iron and aluminium silicon carbide graphite liners



ALUMINIUM CERIUM ALLOYS

Figure7: As-cast microstructure of Al-6Ce alloy



The development of light alloys for high temperature applications has been the subject of considerable research.[7] Recent work has been focused on systems such as Al-Zr and Al-V which form stable L12 structure precipitates.[8] The alloys are strengthened by intermetallics which act as a creep-diffusion barrier at elevated temperatures.[7]

A new alloy system has been developed that uses cerium as a primary alloying element at near eutectic compositions. Additional alloying elements are used, primarily to assist in the development of room-temperature mechanical properties. The cerium in the alloy stabilises those properties at high temperatures (200-315°C). The primary intermetallic formed in the aluminium-rich region of the Al-Ce system is Al11Ce3.[9]

Microstructures typical of this alloy system are shown in **Figures7** and **8**. The as-cast microstructures show a very fine interconnected eutectic microstructure and the pure aluminium phase. The scale of the laths can be as small as 100nm and do not exhibit preferential direction at standard cooling rates. The intermetallics are trapped by the zero solubility of cerium in the aluminium matrix. This trapping prevents the system from minimising surface energy through diffusion, which blocks the alloys from traditional coarsening interactions.

Initial analysis of the Al-Ce system produced via a powder metallurgy followed by hot forging showed promising strengths at temperatures up to 343°C.[10] The casting characteristics of these alloys were unknown. A review of the phase diagram showed a promising eutectic composition at approximately [10] wt% cerium that suggested the alloy could be cast. **Figure9** depicts the Thermo-Calc calculated binary phase diagram of Al-Ce system.

Other authors have considered using cerium as an alloy addition for aluminium casting alloys. Shikun[11] reviewed the effect of additions of cerium of up to 4 wt% on the solidification range, solidification volume change and cast microstructure in an Al-4.5Cu alloy. Belov[12] studied the microstructure and mechanical properties of Al-Ce-Ni alloys containing up to 16 wt% Ce and 8 wt% Ni. He concluded that the casting characteristics of these alloys compared favourably with A356 type alloys and the high temperature mechanical properties were very good.

Casting trials

Preliminary casting trials were performed using a permanent mould that contained the standard ASTM B108 test bar geometry. This mould was heated using electrical cartridge heaters and could maintain a minimum set-point temperature to within 10°C. The casting alloys were prepared in 25 kg batches using P1520 ingot with the composition shown in **Table1**. Melting was done under nitrogen cover gas. Commercial cerium metal from Molycorp of better than 99 percent purity was added to achieve binary compositions of 6, 8, 10, 12 and 16 percent cerium. The alloy was not degassed and was poured into the mould heated to 400°C using a casting temperature of 750°C.

When considering casting characteristics of new alloys, comparisons are usually made to the Al-Si systems that contain 4.5-12 percent silicon. Silicon is added in excess to the amount required to form the strengthening phase of Mg2Si to improve alloy fluidity and to reduce the tendency to hot tear. When casting alloys containing 6 percent silicon or more at the indicated mould and metal temperatures, the

Figure8: As-Cast microstructure of Al-12Ce alloy

Figure9: Binary aluminium-cerium phase diagram as calculated using Thermo-Calc

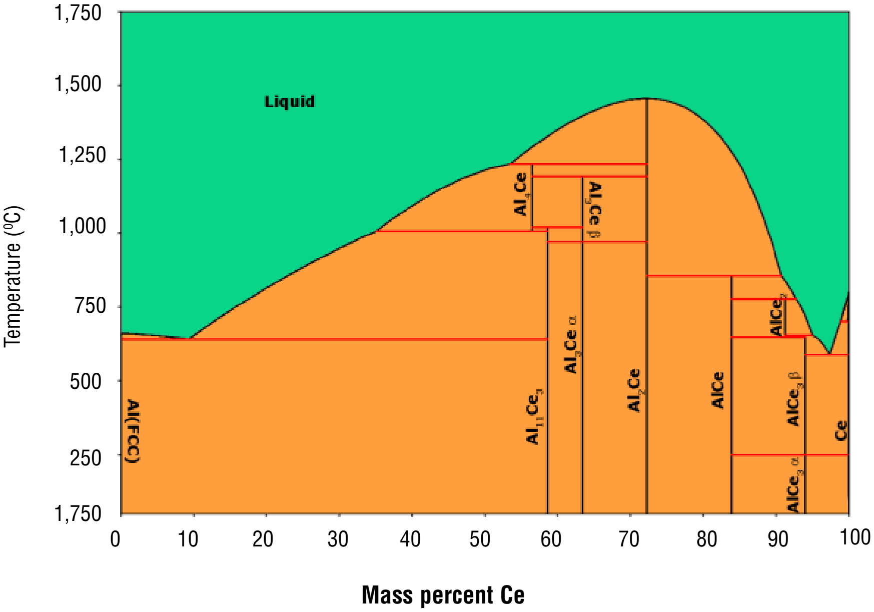


Table1: Weight percent composition of base alloy for Al-Ce development

	Si	Fe	Total Others	Aluminium
P1520	0.11	0.17	0.09	Remainder

test bar set easily fills and good test bars are produced. To fill consistently, alloys containing less silicon require additional superheat to either the mould or the metal. In comparison, for compositions of up to 10 percent cerium, the mould filled completely, and the production of sound bars was consistent with those produced with alloys containing 6 percent Si. At 12 percent cerium, mould-filling capability declined, and the metal temperature was adjusted upwards by 25°C to achieve complete fill. At 16 percent cerium, the mould did not fill completely at a mould temperature of 425°C and a casting temperature of 775°C. This is a result of the rapidly increasing melting temperature above the eutectic point for the alloy. None of the test bars showed any evidence of hot tearing.

Since the casting characteristics of the binary system were acceptable, a complicated cylinder head was cast using an 8 percent Ce binary alloy. The casting poured successfully and was inspected for hot tears or other defects. Except for some minor mis-runs attributable to a lower melt superheat than is currently used to produce this head, the casting passed all other inspection criteria including dye penetrant and x-ray inspection. The as-cast head is shown in **Figure10**.

In general, Al-Ce alloys near the eutectic composition had good to excellent casting characteristics. However, the room temperature mechanical properties were not high enough for many commercial applications nor did the alloys have a positive response to standard T6 type heat treatments. The strength peaks at the eutectic composition of ~12 percent at 163 MPa tensile, 58 MPa yield, and 13.5 percent elongation.

Figure10: An air-cooled cylinder head cast in Al-Ce8 alloy

Table2: As cast mechanical properties (MPa)

	Tensile	Yield	%E
Al-8Ce-4Mg	189	107	3
Al-8Ce-7Mg	195	151	2
Al-8Ce-10Mg	227	186	1

Table3: As cast mechanical properties after temperature exposure (MPa)

	Temp	Time (hours)	Tensile	Yield	%E	
Al-8Ce-10Mg	260°C	0.5	137	130	4	
	260°C	336	137	97	5	
	315°C	0.5	97	55	20	
	315°C	216	172	159	1	Tested at 25°C
	260°C	336	159	138	1	Tested at 25°C

Twenty additional alloys were produced using Al-8Ce as a base composition with additives of Si, Mg, Cu, Zn, Ni, Ti, Mn, or Fe. Except for Mg, the addition of these alloying elements in excess of 1 percent reduced die filling capability even though many of the alloys had improved mechanical properties. For ternary Al-Ce-Mg alloys, yield strength increased with increasing magnesium levels without a noticeable reduction in castability up to the tested level of 10 percent magnesium. Mechanical properties for three of these alloys are shown in **Table2**.

Preliminary work has been completed to develop mechanical properties after long-term high temperature exposure.

After exposure at 260°C for 336 hours and measured at room temperature, the Al-8Ce-10Mg-F alloy had a yield strength of 138 MPa, 31 percent higher than 354.0-T61 after 100 hours of exposure. In the Al-Mg-Ce ternary system, the mechanical properties show substantial recovery at room temperature after high temperature exposure. The available data is shown in **Table3**.

The calculated Al-Ce phase diagram shows no solid solubility for cerium in the aluminium matrix. This lack of solubility renders the Al11Ce3 intermetallic stable at elevated temperature as illustrated by the property diagrams in **Figure11**. The precipitates in other common alloy systems dissolve at lower temperatures than the Al11Ce3 resulting in less strength maintained at elevated temperatures.

The binary Al-Ce alloys have high ductility despite high intermetallic content. ALC-100 is Al-6Ce, ALC-200 is Al-8Ce, AlC-300 is Al-10Ce, ALC-400 is Al-12Ce and ALC-500 is Al-16Ce. This is illustrated in **Figure12**. The retention of ductility is probably related to the scale of the intermetallic which can be a small as 100nm. Mg does not significantly affect the thermodynamics or phase constitution of the Al-Ce binary system, but instead strengthens the matrix phase by forming intermetallic Al-Mg precipitates and metastable clusters. These precipitates improve tensile and yield strength in the ternary alloy, but reduce the elongation.

The entire family of Al-Ce alloys retains a higher percentage of tensile and yield strength at high temperature when compared to other casting alloys.[13] This is attributed to the stability of the Al11Ce3 intermetallic and the load sharing between it and the aluminium matrix. These relationships are displayed graphically in **Figure13**.

Economic considerations

Cerium is the most abundant rare earth. With the current price of metallic cerium

Figure11: Phase solubility in aluminium alloys

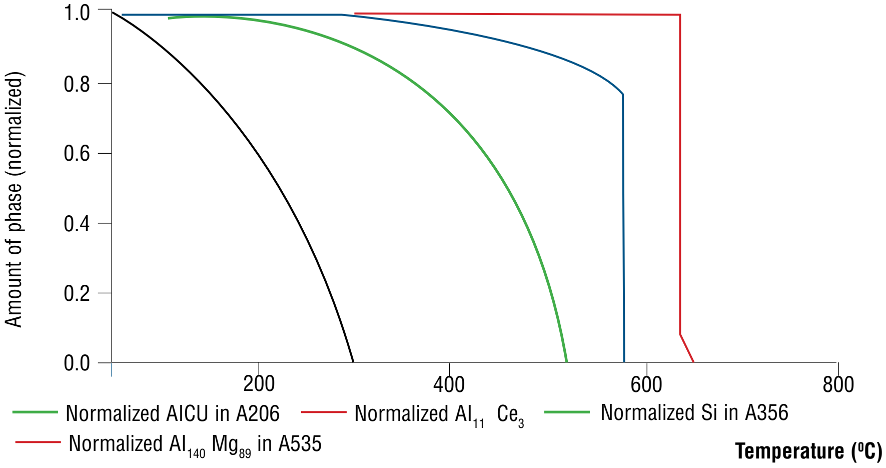


Figure12: Elongation vs mass fraction of intermetallic

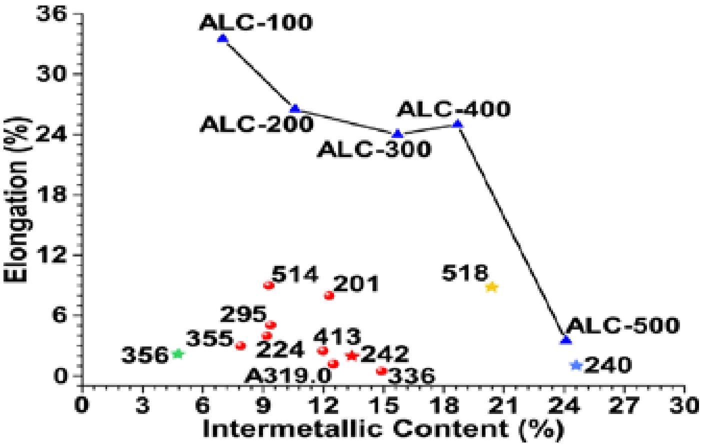
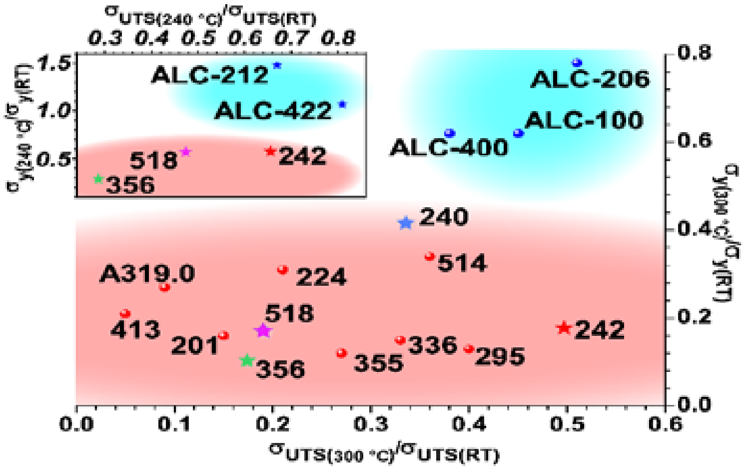
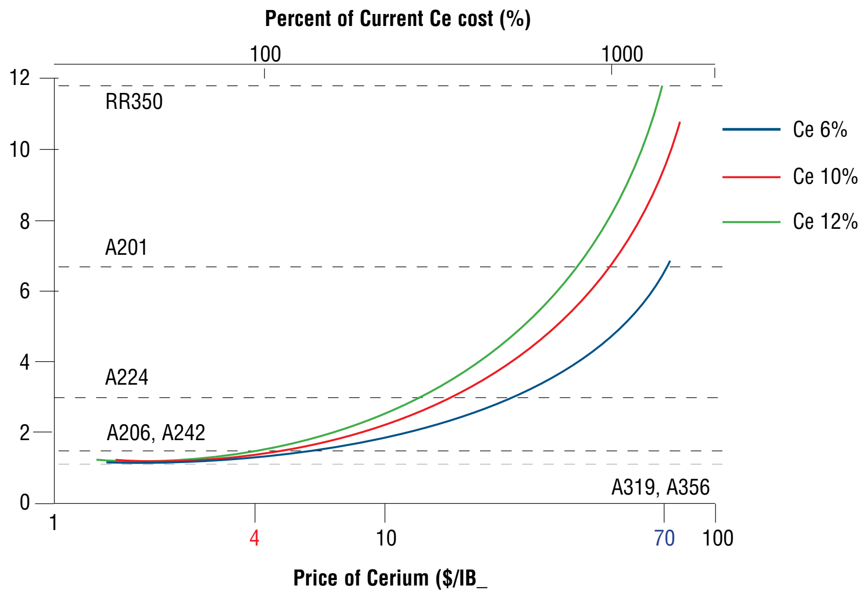


Figure13: Graph of yield and tensile maintenance at 240 and 300°C



in the $4-5/lb range, the use of cerium as an alloying element is economically feasible for high-volume production. The as-alloyed cost of Al-Ce material is competitive with other high-performance aluminium alloy systems. A graphical comparison is given in **Figure14**.

Figure13: Graph of yield and tensile maintenance at 240 and 300°C



Conclusions

Cylinder liners produced from hybrid metal matrix composites show a general improvement in engine operation as evidenced by higher power levels. This improvement stems from reduced frictional losses in the piston/ring/liner system. The amount of improvement will depend on operating and lubrication conditions. Side by side testing of the engines in this study demonstrated torque and horsepower improvements with engines using the hybrid composite liners when compared with standard cast iron liners. The thermal outputs of the engines changed because of the difference in the thermal conductivity of the liner.

The excellent castability of Al-Ce alloys has been demonstrated. All of the data and experience to date indicate that Al-Ce or Al-Ce-Mg have castability equivalent to 300 series alloys. These alloys retain a higher percentage of their mechanical properties at temperature due to a unique intermetallic that retains its strength to near the melting point of the material. The combination of castability, cost and high temperature mechanical properties make this alloy a unique solution to powertrain alloy needs.

The combination of an Al-Ce piston and a hybrid composite liner can improve the operating performance of the internal combustion engine through reduced frictional losses and capabilities at higher operating temperatures.

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