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METALLURGICAL BACKGROUND TO THE DEVELOPMENT OF CREEP RESISTANT GRAVITY CASTING MAGNESIUM ALLOYS

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Abstract

Magnesium alloys, being the lightest structural metallic materials, are very attractive in automotive and aerospace industries. New alloys are required that would resist the increasingly onerous operating environment and that would provide more complex components with increased lifetime and reduced maintenance cost. The desire to achieve weight reduction of large powertrain components used by the automotive and aerospace industries has resulted in the development of new gravity casting alloys that provide a good combination of service properties and cost. The present paper addresses physical metallurgy principles that enabled to develop new alloys designated MRI 201S, MRI 202S and MRI 203S. New alloys are designed for applications up to 250-300°C and have excellent mechanical properties, corrosion behavior and creep resistance in T6 condition. In addition, paper will also highlight some practical applications that illustrate the capabilities of the newly developed alloys.

Introduction

Magnesium is one of the most promising lightweight metals, which can play the vital role in the automotive and the aerospace industries enabling mass savings and consequently fuel economy and reduction of CO_2 emission. However, to use magnesium in automotive powertrain components, which represent a significant portion of the weight of vehicles there is a need for alloys with improved performance at higher operating temperature. Recently several creep resistant die casting alloys were developed [1-3]. However, for particularly large and heavy components, for example, engine block, high-pressure die casting is not the best production method. In fact, most of such parts are being produced by sand casting and gravity die casting or by low-pressure sand and gravity die casting.

All creep resistant, gravity casting magnesium alloys contain zirconium and consequently are aluminum free. Zirconium is a unique grain refiner of magnesium. It also benefits corrosion resistance of the alloy and contributes to prevention of porosity in castings [1,4]. However, zirconium can serve as a powerful grain refiner of magnesium only if the molten metal is saturated with soluble Zr at high temperature range of 750-800°C. This leads to strong oxidation of the molten metal and loss of magnesium and expensive alloying elements such as Y, Gd, Dy, Yb, Nd etc. In addition, the existing technology of alloy preparation is based on single batch process with the use of small crucibles up to 300-400 kg. The process efficiency is relatively low due to the need to retain a significant amount of heel in the crucible in order to prevent the entrapment of settled inclusions and excessive Zr compounds in the castings. Thus, the preparation process and the use of expensive alloying elements results in relatively high cost of commercial creep resistant gravity casting alloys both in ingot form and in final castings. Therefore, those alloys are mainly designated for the production of high performance complicated castings, which are used in the aerospace industry and for luxury and racing vehicles. In such applications, the performance is of prime importance, while cost is regarded as a secondary factor.

The research activities in the field of gravity casting alloys were very limited since the 1980’s when Magnesium Electron Ltd has developed WE43 and WE54 alloys [1, 5]. These alloys exhibit excellent creep and corrosion resistance and are considered as the best performance high temperature Mg alloys. Unfortunately, the extremely high cost of WE alloys enables their use only in specific applications that can afford such high cost. In addition, it is not easy to handle both WE alloys during melt processing due to their oxidation tendency and necessity of special mold gassing techniques. Currently the largest portion of gravity casting applications is covered by ZE41 alloy and partially by EZ33 alloy [1,6,7], which have moderate strength and creep resistance, combined with good castability. Although these alloys exhibit poor corrosion resistance (especially in marine environment), they are still widely used as a preferable material in various helicopter transmission applications. The significant gap, which exists between high performance and extremely high cost of WE43 alloy and the moderate cost but limited creep resistance and poor corrosion properties of ZE41 and EZ33 alloys, was recognized in the last 3 years. This situation stimulated the new activities in the development of high temperature magnesium alloys for sand and permanent mold casting applications [8-11].

Physico-metallurgical considerations

The development of magnesium alloys for high temperature applications is a very comprehensive process, which requires an understanding of the basic principles and mechanisms affecting strengthening and creep behavior of alloys. The strategy of gravity casting alloys development is significantly different to that for high-pressure die casting alloys. The major mechanisms, which affect the properties of high-pressure die casting alloys, are solid solution strengthening due to selective alloying elements and grain boundary strengthening due to rapid cooling under solidification. The stable intermetallics have a eutectic nature precipitating under solidification process and are relatively coarse. On the other hand, the major mechanisms that affect properties of heat resistant gravity casting alloys are precipitation hardening and grain boundary strengthening. In general, alloying principles for the development of creep resistant magnesium alloys for gravity casting applications after T6 heat treatment can be reduced to the following rules.

The main alloying elements should have a wide range of solid solubility in magnesium, which decreases sharply at room temperature. This factor is very important to provide a marked response to aging. Solubility limits for binary magnesium alloys can be found in [1].

Solutes should have a low diffusion coefficient, to provide strong interatomic bonds and to form solid solution, which has no response to aging over service conditions. For enhanced elevated temperature properties, alloying elements should form thermally stable intermetallic compounds that have the coherency with the matrix and are effective obstacles against deformation and strengthen grain boundaries. The melting point of the precipitate is a good indication of its thermal stability.

The first precipitates to nucleate are very often metastable and coherent with the matrix providing excellent precipitation hardening. As aging progresses, metastable precipitates are transformed into stable equilibrium phases. The morphology of the precipitates including their shape and interparticle spacing affect both ambient strength and creep resistance. Based on the data listed in [1] and taken into consideration the availability and commercial attractiveness of the alloying elements, some of them such as Nd, Ce-based mish metal, Y, Gd and Ca seem to be most promising for the development of new alloys. Cerium based mishmetal is the cheapest alloying alternative. However, due to very limited solubility of Ce and particularly La in solid magnesium the above mixture cannot provide significant response to aging. Among other four elements listed above, Nd should be considered as the main alloying element due to optimal combination of enhanced solid solubility, availability and cost. Yttrium and particularly gadolinium have the highest solubility in magnesium. However, they are relatively expensive and Gd has also a great atomic weight that requires its higher weight additions in order to obtain the same atomic percent of Gd compared to Y and Nd.

Zinc content should be limited to 0.3-0.8% as zinc combines with RE elements and yttrium to form stable eutectic intermetallics thereby nullifying the contribution of yttrium and RE elements to precipitation hardening.

As it was already mentioned grain refinement is considered as a very important tool at the development of gravity casting alloys. It is well known and documented that Zr has a grain refining effect when added to magnesium leading to the greater casting integrity and improved mechanical properties [1,4,5-7]. The soluble Zr fraction mostly provides the fine grain size obtained in Zr contained alloys [4,12]. Mg-Zr alloys have more consistent properties through thin and thick sections and are not prone to through-wall porosity, which can cause lubricant leakage [1,3,4].

In comparison to Mg-Al alloys, all Mg-Zr alloys have the tendency to be intrinsically high purity material. This is due to the highly reactive nature of zirconium, which ensures all common impurities found in magnesium alloy melts are precipitated as separate compounds. Those compounds are settled down before any zirconium dissolves in molten magnesium (the maximum solubility of zirconium in molten magnesium is 0.6%). This leads to the fact that content of impurities such as Si, Cu, Fe and Ni is invariably below 50 ppm and typically in the range 10-20 ppm. The most practical elements compatible with Zr are Zn, Y, Ag and rare earth elements (La, Ce, Pr and Nd).

Heat treatment is a very important factor for obtaining a required combination of service properties. It should be selected a based on compromise between mechanical properties requirements and commercially acceptable holding time at solid solution treatment and particularly at aging. Solid solution treatment should be performed at the highest practicable temperature to dissolve coarse eutectic intermetallic phases formed during casting process. Practically the solid solution treatment is conducted at the temperatures about 20-30°C below the solidus temperature of the alloy. The most challenge is usually associated with selection of the temperature and time of aging because these parameters significantly affect the final properties.

In addition to their influence on mechanical properties and creep behavior, alloying elements should provide good castability (increased fluidity, low susceptibility to cracking, reduced porosity and greater casting integrity) combined with improved corrosion resistance and affordable cost. In fact, the development of practical alloys is usually a compromise between the required performance and the affordable cost. Thus, the main challenge is to find the optimum combination of the above factors. This issue was addressed by DSM and VW in the attempt to develop new creep-resistant magnesium alloys for sand casting and gravity die casting applications.

Properties and performance of new MRI's alloys

Extensive research that was initiated and carried out by DSM and VW led to the development of three creep resistant alloys designated MRI 201S, MRI 202S and MRI 203S. All of these alloys are well suitable for sand and gravity die casting applications and for related low-pressure alternatives. New alloys have to be used only in the T6 condition to realize the precipitation hardening mechanism and generate the optimum combination of ambient strength, ductility and creep properties. The typical microstructures of MRI 202S and MRI 203S alloys in as cast and T6 conditions are shown in Figs.1 and 2.

In as cast condition both alloys show more or less continuous network of degenerate $Mg_{12}RE$ eutectic in the grain boundaries and between the magnesium dendrite arms. Solid solution heat treatment followed by aging results in significant dissolution of eutectic intermetallics in the alloy MRI 202S while the microstructure of MRI 203S does not experience the transformations that are visible under optical and scanning electron microscopes. This difference should be attributed to the fact that Nd in MRI 202S has better solid solubility in Mg compared to cerium based mishmetall, which is used for alloying MRI 203S.

Typical mechanical properties of new MRI alloys at room and elevated temperatures are shown in Table 1 in comparison with commercial alloys WE43, ZE41 and EZ33. It is evident that alloy MRI 201S-T6 exhibits a combination of properties similar to that of WE43-T6 alloy. Thus, based on the chemical composition of both alloys, one can consider MRI 201S as a low cost replacement of WE43 alloy.

The alloy MRI 202S is a creep resistant alloy with moderate strength and good corrosion resistance. It outperforms all common sand casting alloys, except for WE43 and WE54 alloys in creep and corrosion resistance.

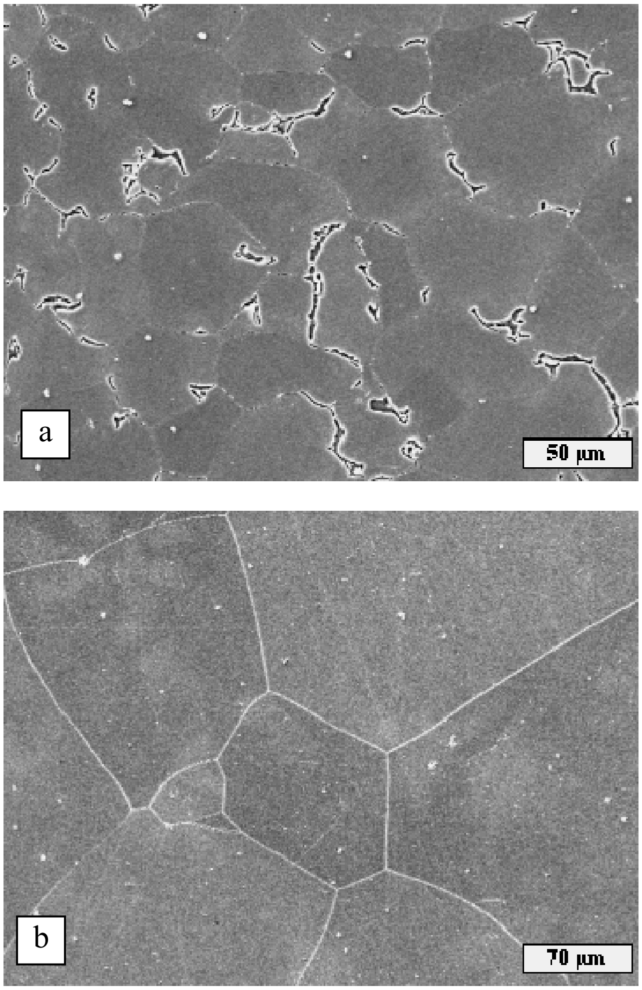

Fig.1. The microstructure of MRI202S in as cast (a) and T6 (b) conditions

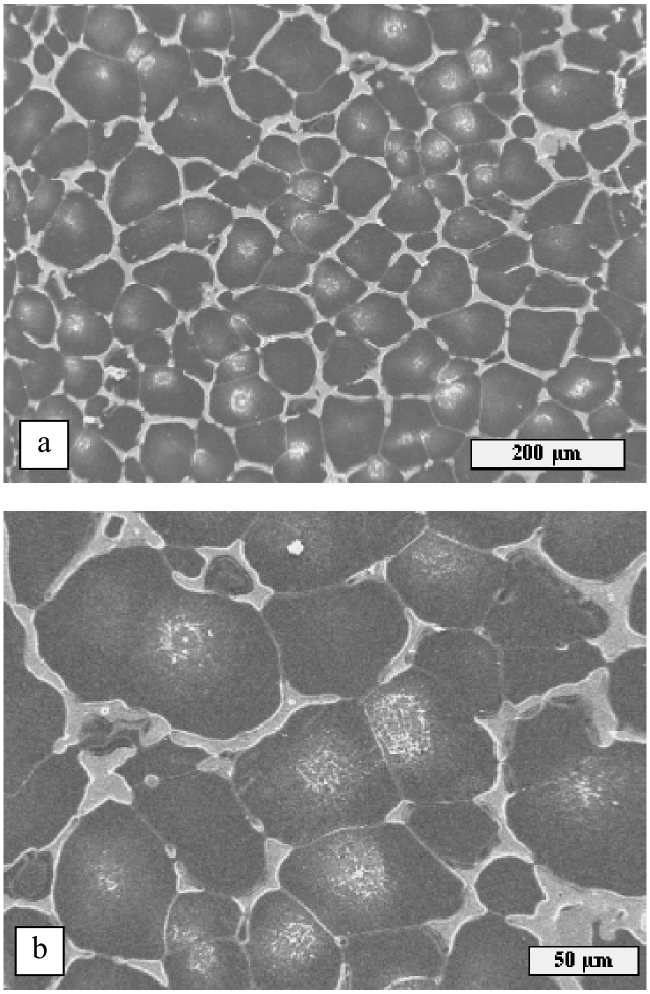

Fig.2. The microstructure of MRI203S in as cast (a) and T6 (b) conditions

The alloy MRI 203S is a low strength gravity-casting alloy, which exhibits creep and corrosion resistance superior to those of EZ33 and ZE41A alloys. Since the production cost of MRI 203S is considered similar to that of ZE41A and EZ33 alloys, this new alloy can be used as a high performance substitution for EZ33 and ZE41A alloys.

Fig.3 demonstrates elevated temperature tensile properties of MRI 201S and MRI 202S alloys. Both alloys exhibit excellent strength retention at temperatures up to 250°C (maximum temperature at which the properties were tested). In contrast to this, the aluminum alloy A319.0-T6 (AlSi6Cu3.5), which is commonly used as sand casting alloy for crankcase manufacturing, showed significant loss in strength at temperatures higher than 150°C.

As can be seen from Fig. 4, all new MRI alloys also outperform the alloy A319.0 in creep strength at the temperature range of 150-200°C.

In addition to tensile creep behavior, it is very important for powertrain applications to estimate the relaxation effects that may occur under compressive loads especially at bolts area. Table 2 illustrates results of bolt load retention tests obtained on MRI 202S and MRI 203S alloys at 175 and 200°C and initial load of 70 MPa. The ratio of the load at finishing the test after returning to room temperature, P_F to the initial load at room temperature P_0 was taken as a measure of bolt load retention behavior of alloys. For comparison, table2 also shows the results obtained on die cast alloy A380 and results for sand-cast alloy A319 reported by Beetles et. al [9]. Based on the data shown in Table 2 one can conclude that new alloys outperform the above aluminum alloys in bolt load retention behavior.

According to experience with WE54 [1, 5] one of the important requirements to high temperature alloys for crank-case and gearbox applications is their long-term stability at temperatures up to 200°C, particularly around 150°C. For example, that alloy WE54 showed significant degradation in room temperature ductility (less than 2%) after long-term (beyond 1000h) exposure at 150°C. Therefore special treatment was carried out with MRI alloys in order to verify their susceptibility to embrittlement under long-term exposure at elevated temperatures.

Tables 3 and 4 illustrate the effect of long-term exposure at 150°C and 200°C for 1000 hours on the tensile properties of MRI 201S and MRI 202S at room temperature and 175°C. Analysis of the results obtained shows that both alloys are not prone to embrittlement after long-term exposure. Both alloys exhibit excellent strength retention at 175°C also after long-term exposure at 150-200°C

Table 1. Typical Mechanical Properties of New MRI's Alloys compared with commercial alloys

Properties	MRI 201S T6	MRI 202S T6	MRI 203S T6	WE43 T6	ZE41 T5	EZ33 T5
TYS (MPa)						
at 20 °C	170	150	125	180	140	100
at 150 °C	170	145	120	178	120	95
at 175 °C	165	140	115	175	110	89
UTS (MPa)						
at 20 °C	260	250	210	260	220	165
at 150 °C	245	220	190	210	170	150
at 175 °C	240	215	180	205	150	140
Elongation (%)						
at 20 °C	6	7	4	6	5	3
at 150 °C	11	15	8	7	22	9
at 175 °C	12	16	12	11	25	16
CYS (MPa)						
at 20 °C	190	145	125	190	140	97
at 150 °C	190	140	120	185	115	95
at 175 °C	185	136	113	185	110	90
Fatigue strength (MPa) (1) at 20 °C	110	95	-	100	95	-
Corrosion Rate (2) (mg/cm2/day)	0.10	0.12	0.14	0.10	3.1	1.4
Stress [MPa] to produce 0.2% creep strain						
at 175 °C	185	155	110	190	70	75
at 200 °C	160	100	70	160	50	65
at 250 °C	75	40	30	60	20	27

(1) Rotating bending 5x10 ^{7}Cycles

(2) 200hr. Salt Spray Test (ASTM Standard B-117)

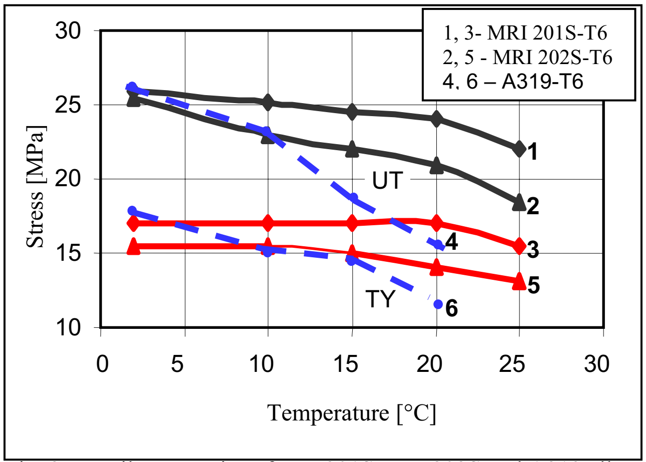

Fig. 3. Tensile properties of MRI201S, MRI202S and A319 alloys vs. temperature.

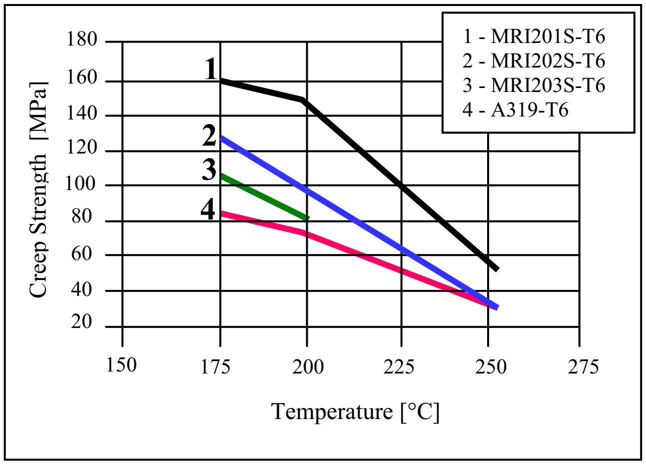

Fig.4. Creep Strength* of MRI Alloys in comparison with A319.
***** *The Strength to produce 0.1% creep strain for 100h*

In addition, it should be noted that new MRI alloys develop their excellent mechanical properties after accelerated T6 heat treatment, which includes aging time that is significantly shorter than typical aging time over 16-48 hours used for common gravity casting alloys [6,7].

Table 2. Bolt Load Retention properties of MRI alloys compared to commercial aluminum alloys

Alloy	Percentage of retained stress at room temperature after 100 h testing at elevated temperatures (P_F/P_0*100%)	
	175^{O}C / 70 MPa	200^{O}C / 70 MPa
MRI 202S-T6	97	81
MRI 203S-T6	90	76
A319-T6	76	-
A380 (die cast)	82	72

Table 3. Effect of long-term exposure for 1000 h at elevated temperatures on tensile properties of MRI 201S-T6 and MRI 202S-T6 tested at room temperature

Alloy	Exposure temperature [°C]	TYS [MPa]	UTS [MPa]	E [%]
MRI 201S	20	170±7	260±10	6±1
	150	170±9	165±8	6±1
	200	165±8	162±10	6±1
MRI 202S	20	150±5	250±9	7±1
	150	146±8	250±7	7±1
	200	139±7	242±8	7±1
MRI 203S	20	125±8	210±9	4±2
	150	120±6	210±11	4±1
	200	118±5	205±6	3±1

From practical point of view, it is very important that MRI's newly developed alloys also exhibit excellent castability, pressure tightness and weldability. This was illustrated by several successful casting trials of various engine blocks and cylinder head covers. For example, Fig.5 demonstrates cylinder head that was produced by low-pressure sand casting from the alloy MRI 201S

Table 4. Effect of long-term exposure for 1000h at elevated temperatures on tensile properties of MRI 201S-T6 and MRI 202S tested at 175°C.

Alloy	Exposure temperature [°C]	TYS [MPa]	UTS [MPa]	E [%]
MRI 201S	20	164±3	240±8	12±1
	150	163±4	242±7	11±2
	200	162±5	240±9	11±2
MRI 202S	20	140±3	230±9	16±1
	150	138±6	228±8	17±1
	200	136±5	232±6	16±2
MRI 203S	20	115±7	180±11	12±3
	150	110±5	175±7	13±2
	200	112±4	172±9	12±4

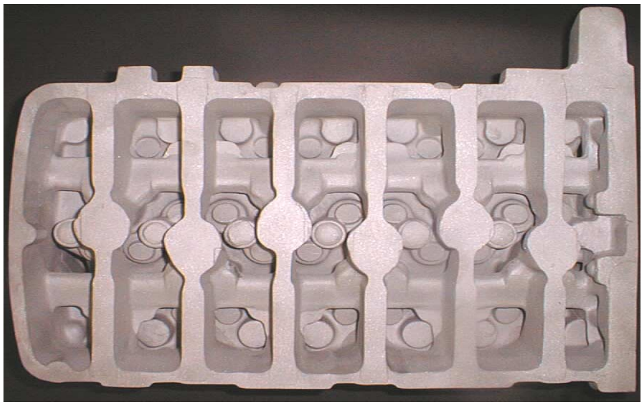

Fig.5. The 17 kg cylinder head VR6-4V sand casting in MRI 201S

Automotive and aircraft producers always require from new materials the highest performance combined with the affordable cost. As can be seen from Table 5, the alloys MRI 201S and WE43 exhibit practically similar performance in terms of strength, creep behavior and corrosion resistance.

Two other new alloys exhibit lower performance compared to WE43 alloy but significantly outperform ZE41 and EZ33 alloys. However, if the cost is also taken into consideration, it is clearly evident that all the newly developed alloys provide the best combination of properties in terms of value to cost (Fig.6)

Table 5. Combined rating of MRI's alloys compared to commercial alloys

		Creep resistance	TYS at 150 ^{O}C	Corrosion resistance	Performance Score	Cost	Total score
Alloy	Weight	10	7	9		10	
MRI 201S	Score	10	9	10		4	
	W x S	100	63	90	253	40	293
MRI 202S	Score	9	8	10			
	W x S	90	56	90	236	70	306
MRI 203S	Score	8	5	9		9	
	W x S	80	35	81	196	90	286
WE43	Score	10	10	10		2	
	W x S	100	70	90	260	20	280
ZE41	Score	6	6	3		10	
	W x S	60	42	27	129	100	229
EZ33	Score	7	4	5		9	
	W x S	70	28	45	143	90	223

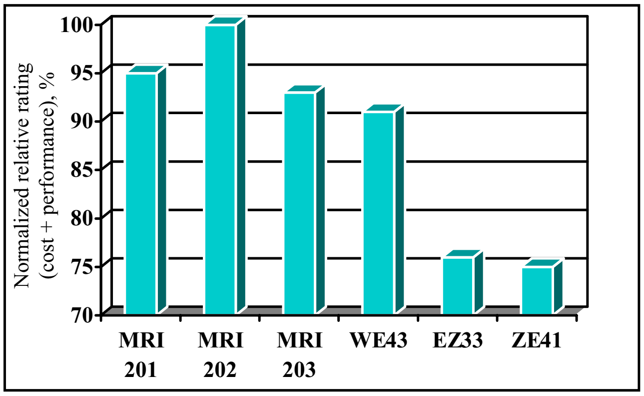

Fig.6. Normalized relative rating (cost +performance) of MRI's alloys compared to commercial alloys

Conclusions

The general physical metallurgy principles underlying the development of gravity casting creep resistant alloys were outlined and discussed. Based on the above principles three new alloys were developed. These alloys designated MRI 201S, MRI 202S and MRI 203S represent a higher-performing, more economical alternative to existing gravity casting magnesium alloys. The results obtained on separately cast samples and real components indicate that new alloys exhibit excellent high-temperature properties and corrosion resistance combined with affordable cost. The excellent castability, pressure tightness and dimensional stability of new alloys were manifested by the production of different powertrain components such as cylinder heads, crankcases, intake manifolds, oil pumps, etc.

The components made of new alloys can be produced by various methods such as sand and gravity die casting; low-pressure sand and gravity die casting as well as squeeze casting.

References

1. J.F. King, "Development of Practical High Temperature Magnesium Casting Alloys", Magnesium alloys and their applications, ed. K.U. Kainer (Weinheim, Germany: Wiley-VCH Verlag GmbH, 2000), pp.14-22.

2. A.Luo "Recent magnesium alloy development for automotive powertrain applications", Materials science Forum. Magnesium alloys 2003,Osaka. January 2003, pp.57-66.

3. B.Bronfin et al, "Development of new magnesium alloys for advanced applications", Magnesium alloys and their applications, ed. K.U. Kainer (Weinheim, Germany: Wiley-VCH Verlag GmbH, 2004), pp.55-61.

4. E.F. Emley, Principles of Magnesium Technology, Pergamon, Oxford, 1966.

5. J.F.King, P.Lyon, K.Savage,"Influence of rare earth elements and minor additions on properties and performance of magnesium-yttrium alloys in critical aerospace applications", Proceedings of 59th World Magnesium Conference, Montreal, May 19-21, 2002, pp.15-22.

6. J.Polmear," Grades and Alloys", Magnesium and Magnesium Alloys, ASM Specialty Handbook, ASM International, 1999,pp.12-25

7. W.Unsworth "The role of rare earth elements in the development of magnesium alloys", Int. J. of Materials and product technology, 1989, v.4, pp.359-378.

8. B.Bronfin et al," High temperature resistant magnesium alloys", US Patent 6,767,506.

9. C.J.Beetles et al," AMC-SC1: A new magnesium alloy suitable for powertrain applications", SAE technical paper 2003-01-1365.

10. B.Bronfin et al," High temperature Mg alloys for Sand and Permanent Mold Casting Applications", SAE technical paper 2003-01-1365.

11. P.Lyon and T.Wilks, "Elekron 21- A new aerospace magnesium alloy", Proceedings of 61st Annual World magnesium Conference, New Orleans, May 9-12,2004, pp.109-118.

12. Ma Qian et al, "Effect of soluble and insoluble zirconium on the grain refinement of magnesium alloys ",Material Science Forum. Magnesium Alloys 2003,Osaka ,January 2003, pp.593-598.