

Development of a Mg–RE based die-cast magnesium alloy for elevated applications

Xixi Dong^a, Lingyun Feng^a, Eric A. Nyberg^b, Shouxun Ji^{a,*}

^aBrunel Centre for Advanced Solidification Technology (BCAST), Brunel University London,
Uxbridge UB8 3PH, United Kingdom

^bTungsten Parts Wyoming, Laramie, Wyoming 82072, USA

*Corresponding author: Tel: +44 1895 266663; Fax: +44 1895 269758

E-mail address: shouxun.ji@brunel.ac.uk

Abstract

The development of magnesium (Mg) alloys capable of operating at the demanding working temperature of above 200 °C and the ability of using high pressure die casting for high-volume manufacturing are the most advanced development in manufacturing critical parts for internal combustion (IC) engines used in power tools. Here we introduce the development of a Mg–RE based die-cast Mg alloy for elevated applications in small IC engines. The developed Mg–RE based die-cast Mg alloy shows good ambient and high temperature strength, and it also has excellent high temperature creep resistance. In addition, the developed Mg–RE based die-cast Mg alloy shows good stiffness at elevated temperatures. Furthermore, the developed Mg–RE based die-cast Mg alloy exhibits good thermal conductivity at ambient and high temperatures, which is a key point that is normally neglected during the development of high temperature Mg alloys.

Key words: Magnesium alloy; Die casting; Elevated application; Mechanical properties

1. Introduction

Magnesium alloys have a great potential for structural applications in industries due to their significant weight savings, thus improving fuel economy and lessening environmental impact [1]. The development of magnesium (Mg) alloys capable of operating at the demanding working temperature of above 200 °C and the ability of using high pressure die casting (HPDC) for high-volume manufacturing are the most advanced development in manufacturing critical parts for internal combustion (IC) engines used in power tools, for light-weighting, noise reduction, damping and use comfort [2–4].

In the early stage of development of die-cast Mg alloys for high temperature applications, significant amount of Al was used for the improvement of die castability, and a group of Mg–Al

based die-cast alloys were developed [5,6]. Representative alloys are the widely used AZ91 AM50 and AM60 alloys, the Mg–Al–Si alloys (AS21X, AS31, AS41) [7,8], the Mg–Al–Ca alloy (AX51, AX52) [9], the Mg–Al–Sr alloy (AJ52) and the Noranda alloy Mg–6Al–2Sr–Ca (AJ62X) [10–12], the Mg–Sr–Ca alloy (AJX500) [5], the General Motors alloy Mg–Al–Ca–Sr (AX52J, AXJ530, AXJ531) [13,14], the Mg–9Al–1Ca–Sr alloy (MRI153A) and the Mg–8Al–1Ca–Sr alloy (MRI153M) [15,16], the Mg–6.5Al–2Ca–1Sn–Sr alloy (MRI230D) [17–19], the Nissan alloy Mg–Al–Ca–RE [20], the Honda alloy Mg–5Al–2Ca–2RE (ACM522) [21], the Mg–0.5Zn–6Al–1Ca–3RE alloy (ZACE05613) and the Mg–0.5Zn–4Al–1Ca–1RE alloy (ZACE05411) [22], the Mg–4Al–RE (La, Ce) alloys (AE42, AE44) [23–25], the Mg–Al–Ba–Ca alloy [26], etc. The Mg–4Al–4RE (AE44) alloy is a major achievement among the Mg–Al based die-cast alloys with good combination of die castability, mechanical properties at elevated temperatures, and good corrosion resistance [25,27]. However, the general working temperature of these Mg–Al based die-cast alloys is at a level of approximately 150 °C, due to the forming of the Al-rich phases that are unstable when temperatures are close to or higher than 175 °C [5,28,29], and the high temperature creep resistance of the Mg–Al based die-cast alloys are also not perfect [30].

In addition to the Mg–Al based die-cast alloys, Al-free die-cast Mg alloys were developed for applications at elevated temperatures [30–34]. The Al-free die-cast Mg–2.5RE–0.35Zn alloy (MEZ) was developed with good creep resistance, but the ductility and strength of the alloy were low [31]. The Al-free die-cast Mg–RE–Zr–Zn alloys were well investigated with medium as-cast strength [32,33]. The Al-free die-cast Mg–4wt.%RE (La,Ce,Nd) alloy named HP2+ delivers higher mechanical performance especially creep resistance at elevated temperatures, which is a significant achievement for potential applications at 150–200 °C [30,34]. However, 4wt.% RE is near the maximum of Al-free die-cast Mg–RE alloys, and further addition of RE for higher working temperatures and elevated mechanical performance will make the Al-free die-cast Mg–RE alloys too brittle, with hot-tearing or die-soldering occurring during die-casting [34]. Therefore, it is still hard for the existing Al-free die-cast Mg alloys to work at elevated temperatures of above 200 °C.

In this work, different from the existing die-cast Mg alloys using Al-rich or Al-free in development, a new design for elevated die-cast Mg alloys was adopted, in which an appropriate addition of Al as a minor element was applied, and a new Mg–RE–Al die-cast Mg alloy was developed for applications at higher elevated temperatures of 200–300 °C.

2. Experimental

2.1. Melt preparation & HPDC

The designed die-cast Mg alloys, with the compositions of 2.0-3.5wt.% (La+Ce), 2.0-3.5wt.% (Nd+Gd), 0.5-1.5wt.% Al, 0.3-0.5wt.% Mn, 0.3-0.5wt.% Zn, and balanced Mg [35], were melted in a steel crucible using an electric resistance furnace, under the covering of protection gas. After melting, the melt was stirred and held at 720 °C for 30 minutes before HPDC. HPDC was conducted on a 4500 kN cold chamber machine. During HPDC, the HPDC die was heated by the mineral oil to a temperature of 225 °C, and the shot sleeve was heated by compressed hot water to a temperature of 180 °C. The pour temperature was controlled at 715 °C, and the intensification pressure was set at 320 bar.

2.2. Material tests

Tensile tests of the die-cast round bars with a gauge dimension of $\phi 6.35 \text{ mm} \times 50 \text{ mm}$ were performed on an Instron 5500 Universal Electromechanical Testing Systems equipped with Bluehill software and a 50 kN load cell, at room temperature and elevated temperatures of 150 °C, 250 °C and 300°C. The ramp rate for room temperature tensile tests was controlled at 1 mm/min, while the straining rate for high temperature tensile tests was maintained at 0.0002/s. Young's modulus of die-cast alloy was tested on a RFDA HT1600 machine from room temperature up to 300 °C. Rectangular shaped samples with dimensions of 40mm (*L*) x 12mm (*W*) x 2mm (*D*) were used for modulus testing. Modulus was tested during both heating and cooling cycles, in which both the heating rate and the cooling rate were set at 3 °C/min, while the modulus data was collected every minute. Thermal conductivity was measured on a laser flash machine from room temperature up to 300 °C.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the scanning electron microscope (SEM) microstructure of the die-cast Mg–RE–Al alloy in as-cast state. The Mg matrix phase was observed having two different grain sizes, i.e., the primary α_1 –Mg phase with a size of $\sim 20\text{--}50 \mu\text{m}$ and the secondary α_2 –Mg phase with a size of $\sim 2\text{--}10 \mu\text{m}$. The α_1 –Mg phase nucleated in the shot sleeve with lower cooling rate, so it was larger in size than the α_2 –Mg phase that nucleated in the die cavity with higher cooling rate [36–39].

Network of the other phases was found at the grain boundaries of Mg matrix phase, and the main body of the network at the grain boundaries was determined as the $Mg_{12}RE$ phase.

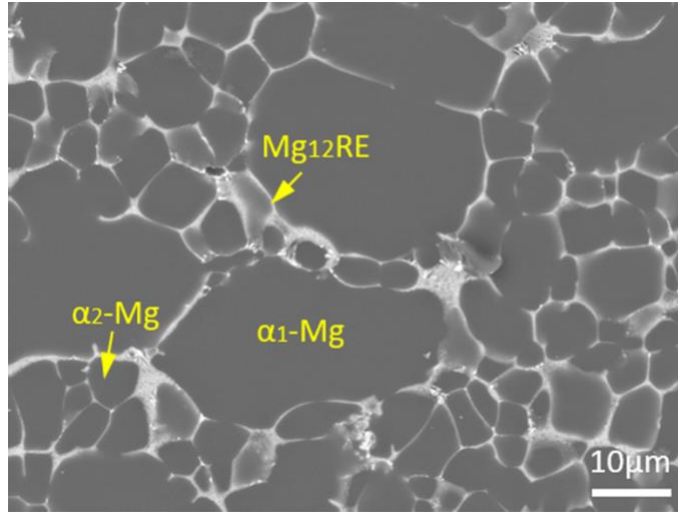


Fig. 1. Microstructure of the die-cast Mg-RE-Al alloy in as-cast state.

3.2. Ambient & elevated tensile properties

Fig. 2 displays the statistical mean tensile properties of the die-cast Mg-RE-Al alloy at room temperature and elevated temperatures of 150 °C, 250 °C and 300 °C. The statistical mean yield strength (YS) of the alloy at room temperature are 170 ± 2.8 MPa, and it is 32 % higher than that of the benchmark AE44 die-cast Mg alloy [4,34].

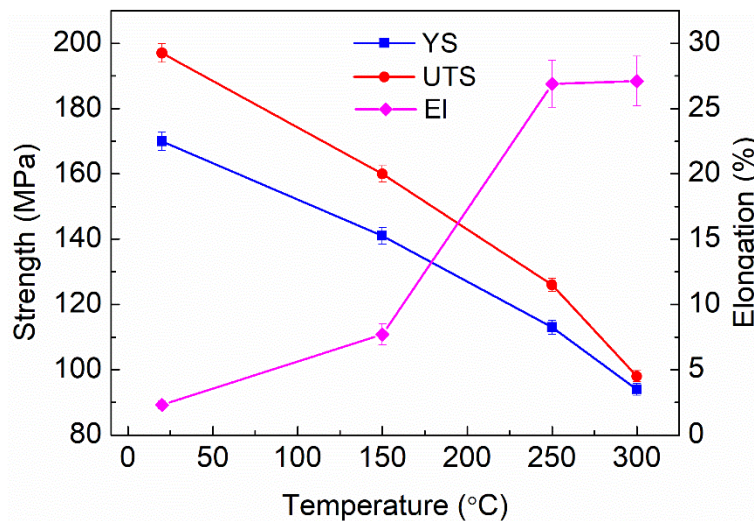


Fig. 2. Statistical mean tensile properties of the die-cast Mg-RE-Al alloy at room temperature and elevated temperatures of 150 °C, 250 °C and 300 °C.

The YS and ultimate tensile strength (UTS) of the alloy decrease gradually with the increase of temperature. The YS of the alloy at 150 °C, 250 °C and 300 °C are 141 ± 2.5 MPa, 113 ± 2.1 MPa and 94 ± 1.8 MPa, respectively, which are 30.5 %, 37.8 % and 42.4 % higher than that of the AE44 alloy, separately [4]. With the increase of the temperature from room temperature to 300 °C, the UTS of the alloy decrease from 197 ± 2.8 MPa to 98 ± 1.7 MPa. The die-cast Mg–RE–Al alloy also shows much better elevated creep resistance than the existing die-cast Mg alloys, and the creep properties will be disclosed elsewhere.

3.3. Ambient & elevated modulus

High temperature stiffness is important but seldom was reported for die-cast Mg alloys especially at elevated temperatures of above 200 °C. Fig. 3 shows the evolution of the Young's modulus of the die-cast Mg–RE–Al alloy versus temperature. The measured Young's modulus during heating and cooling test cycles fit well with each other. The room temperature Young's modulus of the alloy is 43.7 GPa, and it is in the normal range of 40–50 GPa ambient Young's modulus that is generally expected for cast Mg alloys [40,41]. The Young's modulus of the alloy decreases nearly linearly with the increase of temperature, and the Young's modulus of the alloy at elevated temperatures of 150 °C, 200 °C, 250 °C and 300 °C are 41.2 GPa, 40.2 GPa, 39.2 GPa and 38.2 GPa, respectively. With the increase of temperature from room temperature to 300 °C, the Young's modulus decreases only by 12.6 %, which demonstrates the good Young's modulus holding capability of the alloy at elevated temperatures.

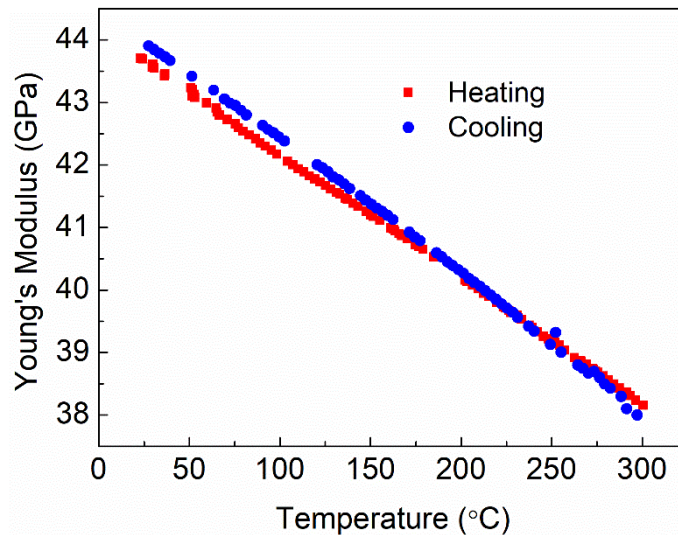


Fig. 3. Evolution of the Young's modulus of the die-cast Mg–RE–Al alloy versus temperature during heating and cooling test cycles.

3.4. Ambient & elevated thermal conductivity

Thermal conductivity is a key point that was usually neglected during the development of Mg alloys for elevated applications, and mechanical properties normally conflict with thermal conductivity at elevated temperatures. The engineering widely AZ91 die-cast Mg alloy for elevated applications up to 120 °C has a low room temperature thermal conductivity of 51 W/m·K [42], and the benchmark AE44 die-cast Mg alloy for elevated applications up to 175 °C only has an ambient thermal conductivity of 85 W/m·K [42]. Fig. 4 presents the thermal conductivity of the die-cast Mg–RE–Al alloy at room temperature and elevated temperatures. The Mg–RE–Al alloy has a good room temperature thermal conductivity of 105 W/m·K, which is 105.9 % higher than that of the AZ91 alloy, and it is still 23.5 % higher than that of the AE44 alloy. The room temperature thermal conductivity of the alloy is also comparable to the commercially widely used A380 die-cast Al alloy that has an ambient thermal conductivity of 110 W/m·K [42]. The thermal conductivity of the die-cast Mg–RE–Al alloy increases with increasing temperature, and the thermal conductivity of the alloy increases to 124 W/m·K at 300 °C.

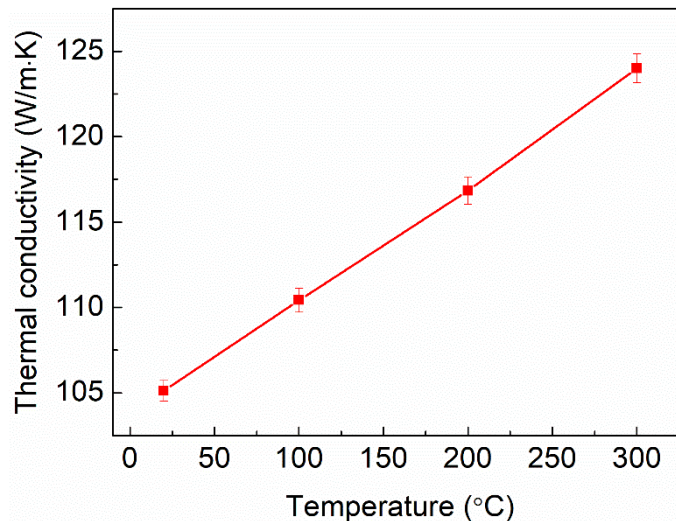


Fig. 4. Thermal conductivity of the die-cast Mg–RE–Al alloy at room temperature and elevated temperatures of up to 300 °C.

4. Conclusions

(1) The developed Mg–RE based die-cast Mg alloy has good strength at ambient and elevated temperatures. The ambient yield strength of the alloy is 170 MPa, and the alloy can achieve a yield strength of over 90 MPa at the elevated temperature of 300 °C.

(2) The developed Mg–RE based die-cast Mg alloy can maintain the stiffness well at elevated temperatures. The ambient Young's modulus of the alloy is 43.7 GPa. With the increase of temperature from room temperature to the elevated temperature of 300 °C, the Young's modulus of the alloy decreases only by 12.6 %.

(3) The developed Mg–RE based die-cast Mg alloy has good thermal conductivity at ambient and elevated temperatures. The room temperature thermal conductivity of the alloy is 105 W/m·K. With the increase of temperature from room temperature to the elevated temperature of 300 °C, the thermal conductivity of the alloy increases to 124 W/m·K.

Acknowledgements

Husqvarna Group is greatly appreciated for the financial and technical support of the work. Jon Gadd from BCAST laboratory is acknowledged for the technical support of the high pressure die casting experiments.

References

- [1] A.A. Luo, Magnesium casting technology for structural applications, *J. Magnes. Alloys* 1 (2013) 2–22.
- [2] N. Hort, H. Dieringa, K.U. Kainer, Magnesium pistons in engines: Fiction or fact?, *Magnes. Technol.* (2018) 349–353.
- [3] X.X. Dong, E.A. Nyberg, S. Ji, A die-cast magnesium alloy for applications at elevated temperatures, *Magnes. Technol.* (2020) 31–36.
- [4] X.X. Dong, L.Y. Feng, S.H. Wang, E.A. Nyberg, S. Ji, A new die-cast magnesium alloy for applications at higher elevated temperatures of 200–300°C, *J. Magnes. Alloys* (2020) <https://doi.org/10.1016/j.jma.2020.09.012>.
- [5] M.O. Pekguleryuz, A.A. Kaya, Creep resistant magnesium alloys for powertrain applications, *Adv. Eng. Mater.* 5 (2003) 866–878.
- [6] H. Hu, A. Yu, N.Y. Li, J.E. Allison, Potential magnesium alloys for high temperature die cast automotive applications: A review, *Mater. Manuf. Process.* 18 (2003) 687–717.
- [7] J.E. Hillis, S.O. Shook, Composition and performance of an improved magnesium AS41 alloy, *SAE Technical Paper* (1989) 890205.

- [8] E. Evangelista, E. Gariboldi, O. Lohne, S. Spigarelli, High-temperature behaviour of as die-cast and heat treated Mg–Al–Si AS21X magnesium alloy, *Mater. Sci. Eng. A* 387–389 (2004) 41–45.
- [9] A.A. Luo, M.P. Balogh, B.R. Powell, Creep and microstructure of magnesium-aluminum-calcium based alloys, *Metall. Mater. Trans. A* 33A (2002) 567–574.
- [10] M.O. Pekguleryuz, E. Baril, Development of creep resistant Mg–Al–Sr alloys, *Magnes. Technol.* (2001) 119–125.
- [11] M. Lefebvre, M. Pekguleryuz, P. Labelle, Magnesium-based casting alloys having improved elevated temperature performance, US Patent (2002) 6342180.
- [12] E. Baril, P. Labelle, M. Pekguleryuz, Elevated temperature Mg–Al–Sr: Creep resistance, mechanical properties, and microstructure, *JOM* 55 (2003) 34–39.
- [13] B.R. Powell, V. Rezhets, A.A. Luo, J.J. Bommarito, B.L. Tiwari, Creep resistant magnesium alloy die casting, US Patent (2001) 6264763.
- [14] B.R. Powell, A.A. Luo, V. Rezhets, J.J. Bommarito, B.L. Tiwari, Development of creep-resistant magnesium alloys for powertrain applications: part 1 of 2, SAE Technical Paper (2001) 2001-01-0422.
- [15] B. Bronfin, E. Aghion, F. Von Buch, S. Schumann, M. Katsir, Die casting magnesium alloys for elevated temperature applications, *Magnes. Technol.* (2001) 127–130.
- [16] E. Aghion, N. Moscovitch, A. Arnon, Solidification characteristics of newly developed die cast magnesium alloy MRI153M, *Mater. Sci. Technol.* 23 (2007) 270–275.
- [17] E. Aghion, B. Bronfin, F. Von Buch, S. Schumann, H. Friedrich, Dead sea magnesium alloys newly developed for high temperature applications, *Magnes. Technol.* (2003) 177–182.
- [18] E. Aghion, B. Bronfin, F. Von Buch, S. Schumann, H. Friedrich, Newly developed magnesium alloys for powertrain applications, *JOM* 55 (2003) 30–33.
- [19] E. Aghion, N. Moscovitch, A. Arnon, Mechanical properties of die-cast magnesium alloy MRI 230D, *J. Mater. Eng. Perform.* 18 (2009) 912–916.
- [20] K. Samato, Y. Yamamoto, N. Sakate, S. Hirabara, Heat-resistant magnesium alloy member, European Patent (1997) EP0799901A1.
- [21] S. Koike, K. Washizu, S. Tanaka, T. Baba, K. Kikawa, Development of lightweight oil pans made of a heat-resistant magnesium alloy for hybrid engines, SAE Technical Paper (2000) 2000-01-1117.

- [22] I.A. Anyanwu, Y. Gokan, S. Nozawa, A. Suzuki, S. Kamado, Y. Kojima, S. Takeda, T. Ishida, Development of new die-castable Mg-Zn-Al-Ca-RE alloys for high temperature applications, *Mater. Trans.* 44 (2003) 562–570.
- [23] B.R. Powell, V. Rezhets, M.P. Balogh, R.A. Waldo, The relationship between microstructure and creep behavior in AE42 magnesium die castings, *Magnes. Technol.* (2001) 175–182.
- [24] M.S. Dargusch, K. Pettersen, P. Bakke, K. Nogita, A.L. Bowles, G.L. Dunlop, Microstructure and mechanical properties of high pressure die cast magnesium alloy AE42 with 1% strontium, *Int. J. Cast Metal Res.* 17 (2004) 170–173.
- [25] P. Bakke, H. Westengen, The role of rare earth elements in structure and property control of magnesium die casting alloys, *Magnes. Technol.* (2005) 291–296.
- [26] S. Gavras, S.M. Zhu, M.A. Easton, M.A. Gibson, H. Dieringa, Compressive creep behavior of high-pressure die-cast aluminum-containing magnesium alloys developed for elevated temperature applications, *Front. Mater.* 6 (2019) 262.
- [27] S.M. Zhu, J.F. Nie, M.A. Gibson, M.A. Easton, P. Bakke, Microstructure and creep behavior of high-pressure die-cast magnesium alloy AE44, *Metall. Mater. Trans. A* 43A (2012) 4137–4144.
- [28] B. Mordike, Development of highly creep resistant magnesium alloys, *J. Mater. Process. Technol.* 117 (2001) 391–394.
- [29] A. Kielbus, Microstructure of AE44 magnesium alloy before and after hot-chamber die casting, *J. Achiev. Mater. Manuf. Eng.* 20 (2007) 459–462.
- [30] S.M. Zhu, M.A. Easton, T.B. Abbott, J.F. Nie, M.S. Dargusch, N. Hort, M.A. Gibson, Evaluation of magnesium die-casting alloys for elevated temperature applications: Microstructure, tensile properties, and creep resistance, *Metall. Mater. Trans. A* 46 (2015) 3543–3554.
- [31] I.P. Moreno, T.K. Nandy, J.W. Jones, J.E. Allison, T.M. Pollock, Microstructure and creep behavior of a die cast magnesium-rare earth alloy, *Magnes. Technol.* (2002) 111–116.
- [32] G. Atiya, M. Bamberger, A. Katsman, Microstructure, phase evolution and precipitation strengthening of Mg-3.1Nd-0.45Zr-0.25Zn alloy, *Magnes. Technol.* (2011) 249–253.
- [33] G. Atiya, M. Bamberger, A. Katsman, Microstructure and phase composition in a die cast Mg–Nd alloy containing Zn and Zr, *Int. J. Mater. Res.* 103 (2012) 1277–1280.

- [34] M. Easton, M.A. Gibson, S.M. Zhu, T. Abbott, J.F. Nie, C.J. Bettles, G. Savage, Development of magnesium-rare earth die-casting alloys. *Magnes. Technol.* (2018) 329–336.
- [35] X.X. Dong, E.N. Nyberg, M. Almgren, S.X. Ji, Swedish Patent (2019) Application No. 1950219-4.
- [36] X.X. Dong, H. Youssef, Y.J. Zhang, H.L. Yang, S.H. Wang, S.X. Ji, High performance Al/TiB₂ composites fabricated by nanoparticle reinforcement and cutting-edge super vacuum assisted die casting process, *Compos. Part B-Eng.* 177 (2019) 107453.
- [37] X.X. Dong, H. Youssef, Y.J. Zhang, H.L. Yang, S.H. Wang, S.X. Ji, Advanced heat treated die-cast aluminium composites fabricated by TiB₂ nanoparticle implantation, *Mater. Des.* 186 (2020) 108372.
- [38] X.X. Dong, H. Youssef, X.Z. Zhu, Y.J. Zhang, S.H. Wang, S.X. Ji, High as-cast strength die-cast AlSi9Cu2Mg alloy prepared by nanoparticle strengthening with industrially acceptable ductility, *J. Alloys Compd.* 852 (2021) 156873.
- [39] L.H. Liu, T. Zhang, Z.Y. Liu, C.Y. Yu, X.X. Dong, L.J. He, K. Gao, X.G. Zhu, W.H. Li, C.Y. Wang, P.J. Li, L.C. Zhang, L.G. Li, Near-net forming complex shaped Zr-based bulk metallic glasses by high pressure die casting, *Materials* 11 (2018) 2338.
- [40] T. Sumitomo, C.H. Cáceres, M. Veidt, The elastic modulus of cast Mg–Al–Zn alloys, *J. Light Met.* 2 (2002) 49–56.
- [41] Y.L. Xu, L. Wang, M. Huang, F. Gensch, K.U. Kainer, N. Hort, The effect of solid solute and precipitate phase on Young's modulus of binary Mg–RE alloys, *Adv. Eng. Mater.* 20 (2018) 1800271.
- [42] <https://www.leadingedgeonly.com/innovation/view/high-conductivity-mg-alloy>.