INFLUENCE OF ZINC ON IMTERMETALLIC PHASE SELECTION IN Al-Mg COMPOUND CASTINGS

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ABSTRACT

A series of experiments were conducted to assess the impact of zinc additions on the morphology and soundness of the interface of Al-Mg compound castings. It was found that high amounts of zinc (>15wt%) are necessary to affect the morphology and microstructure of the interface. At these zinc concentration levels, the formation of the zinc-rich phases τ_1 and ϕ were observed along with the Al-Mg intermetallic phases β and γ. The micro hardness of all phases across the interface was found to be similar, ~200 Hv. This even hardness gradient is thought to avoid mechanical failure in the interface under load. In samples containing large concentrations of zinc (>15wt%), the formation of bubble shaped voids as well as the complete transformation of the aluminium alloy was observed. While the exact mechanism causing the voids has not been identified it thought to be connected to the Kirkendall effect.

KEYWORDS

Compound casting, Al-Mg joining, Interface formation, Phase selection

INTRODUCTION

Conventional single material components are increasingly failing to meet the demands, in terms of cost and performance, of the transport industry. Compound castings have been identified as a promising alternative as they possess a number of benefits (Bührig-Polaczek, Röth, Baumeister, Nowack, & Sussmann, 2006). Compound casting is described as a process in which a metallic melt is cast around a solid metal shape. Preliminary research has concluded that for the stability of such a resultant hybrid structure it is imperative that both metals form a sound connection via form closure, force closure, or material bonding. A continuous material bond between the two metals is also highly desirable as the formation of a crevice between the metals could lead to galvanic corrosion, particular in a humid environment (Lao, 2013; Rübner, Günzl, Körner, & Singer, 2011). Even though Al-Mg compound castings could offer the biggest potential in terms of weight savings to date only a limited amount of research concerning such structures exists.

To date, researchers have successfully joined pure aluminium and magnesium using a variety of casting processes (Emami, Divandari, Hajjari, & Arabi, 2013; Hajjari et al., 2011; Papis, Loeffler, & Uggowitzer, 2009). The interface of Al-Mg compound castings has been consistently reported to consist of three distinct layers: the Al -rich intermetallic phase β (Al_3Mg_2), the Mg -rich intermetallic phase γ ($Al_{12}Mg_{17}$) and the Mg-rich intermetallic γ + magnesium eutectic phase δ. More recent research has linked the growth of the β and γ layer to different growth rates and thus mechanisms, thereby explaining the varying relative thicknesses of each layer throughout literature. Growth of the β-phase is attributed to lattice diffusion and follows a parabolic growth. By comparison, the γ-phase grows via lattice and grain boundary diffusion and follows a non-parabolic growth rate (Brennan, Bermudez, Kulkarni, & Sohn, 2012; Liu, Long, Ma, & Wu, 2015). Increasing reaction time and temperature growth of the β-phase is the major driving force of interfacial growth, whilst at lower reaction temperatures and shorter times the γ-phase is dominant. While there is no clear description of the mechanical properties of the β- and γ-phase in the literature, several studies indicate that the γ -phase displays higher ductility with a similar level of hardness than the β-phase. Push-out tests have revealed that an increase in interface thickness (thickness of the β-phase), lessens the pushout resistance of a compound casting (Emami et al., 2013; Hajjari et al., 2011). Theoretical calculations of the mechanical properties of the $Al_{12}Mg_{17}$-phase, using first principle calculation, have identified this phase as non-brittle (Wang, Yu, Tang, Peng, & Ding, 2008). Despite the importance of the interface on overall properties of an Al-Mg compound casting structure, relatively little is known on how to actively influence the interfacial reaction. The use of aluminium alloys containing Silicon results in the formation of Mg_2Si particles in the interface. Amount and distribution of said particles mostly depends on the Silicon content of the aluminium alloy. However these particles also lead to an embrittlement of the interface and as such limiting any possible actual application (Schneider, McKay, & Nadendla, 2017). Moreover, it is known from Fe- Mg compound castings that certain elements alter the interfacial reaction during compound casting (Pierre, Bosselet, Peronnet, Viala, & Bouix, 2001; Pierre, Peronnet, Bosselet, Viala, & Bouix, 2002; Pierre, Viala, Peronnet, Bosselet, & Bouix, 2003; Springer, Szczepaniak, & Raabe, 2015; Viala, Pierre, Bosselet, Peronnet, & Bouix, 1999).

Thus the aim of the present research is to investigate the influence of zinc on the interfacial reaction in compound castings. Zinc has been deemed most promising to promote interfacial bonding as it:
- is a common alloying element and completely miscible in the solid and liquid phase in both aluminium and magnesium
- forms strength increasing $MgZn_2$ particles
- possess a lower activation energy and higher diffusion coefficient than aluminium and magnesium and thus diffuses faster than both (Kammerer, Kulkarni, Warmack, & Sohn, 2014)
- is proven to promote interfacial bonding in pure metal Al-Mg compound castings when applied as a coating (Xu, Luo, Chen, & Sachdev, 2014).
- is known to influence interfacial formation. Zinc promotes the growth of AlFe intermetallic needles in Al-Fe compound castings (Springer, Szczepaniak et al., 2015).

Consequently the addition zinc may modify the growth of the β- and γ- intermetallic phases as well as form new, possibly non-brittle, phases of the interface, most notably the τ- and ϕ- phases. Thus the aim of this research is to investigate the influence of zinc on interfacial formation in Al-Mg compound castings.

EXPERIMENTAL METHODOLGY

To establish the influence of zinc of interfacial formation a series of experiments (SERIES A) were conducted. In which 9 wedge shaped aluminium specimens with varying amounts of zinc (6wt% (AlZn6), 15wt% (AlZn15) and 30wt% (AlZn30)) were cast. To produce the alloys commercially pure aluminium (99.97%) and zinc (99.83%) were used. Surface roughness of the wedges was set to grit40 using SiC paper before cleaning their surface thoroughly with acetone and rinsing with ethanol. Each wedge, weight ~150 g, was placed within a cylindrical mould with a diameter of 70 mm. The mould and AlZn wedge were preheated to 400°C before being overcast with 300 g of a commercially pure AZ31 Mg alloy. The AZ31 was molten under a covergas (SF6 and Nitrogen) and heated up to 660°C. AZ31 was chosen over pure magnesium due to safety and handling issues. The casting was removed from the mould after 5min and quenched with pressurised air (4 min/6 bar). In a second series of experiments referred to as SERIES B, the whole assembly, consisting of mould and an AlZn30 wedge, were placed in a furnace, preheated to 200 and 400°C before being overcast with the AZ31 alloy. The whole assembly was subsequently left in the furnace for 15, 30 and 60 min after casting and then quenched with pressurised air (4min/6bar). To assess the impact of the process of compound casting on interfacial formation a reference diffusion couple experiment was also conducted. Two discs (diameter 28 mm, thickness 15 mm) of AlZn30 and AZ31 were clamped together and heated to 430°C for 3 h. Prior to heat treatment, the disks were ground to grit 80, cleaned with acetone and rinsed with ethanol. Castings were cut, polished and characterised. Characterisation was conducted using Vickers Microhardness measurements (2.94N/0,3KgF force with 10 s dwell), optical microscopy, backscatter electron microscopy (20keV) with EDX and XRD.

RESULTS AND DISCUSSION

The most obvious difference between the samples with different zinc content was interface thickness. It was assumed that the lower the liquidus temperature, the thicker the resulting interface would be as more material is dissolved during the casting process. As such, it was expected that a zinc concentration of 30wt% would result in a thicker interface compared to samples containing 15wt% and 6wt% zinc. However, this was not observed. The maximum in interface thickness was ~8400 μm at 15wt%. 30wt% zinc resulted in a thickness of ~6400 μm and for 6wt% it was ~2300 μm. This indicates that solid state diffusion plays an equally important role in interface formation as dissolution and crystallisation. An overview of the phases found in the interface after each experiment is in Table 1.

Table 1. Overview of phases in the interface for each experiment and the corresponding parameters.

	Al-Alloy	Mg-Alloy	Time [min]	T [°C]	Phases present in the interface			
Series A	AlZn6	AZ31	5	400	AlZn	β+Zn	Mg+γ+Zn	AZ31
	AlZn15				AlZn	β+Zn	Mg+γ+Zn	AZ31
	AlZn30				AlZn	β+τ_1+Zn	Mg+γ+ϕ+Zn	AZ31
Series B	AlZn30	AZ31	15, 30, 60	200	AlZn	β+Zn	Mg+γ+Zn	AZ31
			15, 30, 60	400	Mg+γ+ϕ	No intermediate layers	Mg+γ+Zn	

Similar to the results obtained by Cao et al. (2013) the addition of 6wt% of zinc does not have any significant impact on the composition of the interface. The interface consists on the aluminium side of a layer of β along with a number of smaller areas made up of γ within. The magnesium side of the interface consist of γ and eutectic magnesium. Zinc is found to be roughly evenly dissolved in the β- and γ-intermetallic phases. As the atomic radius of zinc is similar to both aluminium and magnesium, zinc is thought to be randomly substituted in the crystal lattice of the β- and γ- intermetallic phases. These findings are not strictly according to the calculated AlZn6-AZ31 binary phase diagram. According to it, primary aluminium and the τ_1- phase precipitate from the melt on the aluminium rich side. This may indicate that either the thermodynamic data the phase diagram is based on is incomplete in the corner of the Al-Zn-Mg system or that the precipitation of the primary aluminium and the τ- phase is inhibited. This suggests that diffusion reaction kinetics play a more important role than dissolution and crystallisation for the interface formation of this alloy combination. As the solubility of zinc in the intermetallic phases β and γ is over 15wt% (Petrov et al., 2006) increasing the amount of added zinc to 15wt% doesn't result in any significant changes in the interface. The β- and γ-phase as well as eutectic magnesium are the main constituents of the interface. Zinc is found again to be evenly dispersed across the interface.

Increasing the amount of zinc to 30wt% resulted in the formation of a much more complex interface (Figure 1). The lighter areas, the τ_1 ($Mg_{32}(Zn,Al)_{48}$) phase, contains a relatively large amount of zinc. These areas are dotted with primary aluminium and the β- phase. Unlike previous experiments the β-phase was not the main constituent of the layer closest to the aluminium alloy. Approaching the magnesium side of the interface, the main constituent of the darker areas changes to magnesium. Adjacent to the primary magnesium, a layer was found consisting of eutectic magnesium and φ ($Mg_{21}(Zn,Al)_{17}$) within a matrix of γ ($Mg_{17}Al_{12}$). The φ- phase is displayed in Figure 3 in greater detail. Within the φ-phase, numerous smaller magnesium precipitations are present. This morphology of the φ-phase shows resemblance to results obtained after the heat treatment of an AlMgZn cast alloy (Berthold, 2013). In all inspected samples, the layer consisting of φ and γ was always significantly thinner than the layer of the β- or β & τ_1 phase. This validates the earlier observation of the growth-rates and mechanisms of each phase. The interface of the diffusion couple lacked the τ_1- phase. A thin layer with a chemical composition indicating the β phase was found adjacent to the AlZn30 alloy. The majority of the interface consists of magnesium, γ and φ phases, with a near identical microstructure to the one acquired via the casting process. This might indicate that the aluminium rich side originates from a dissolution and crystallisation process directly from the liquid phase while the magnesium rich phases result from solid state diffusion.
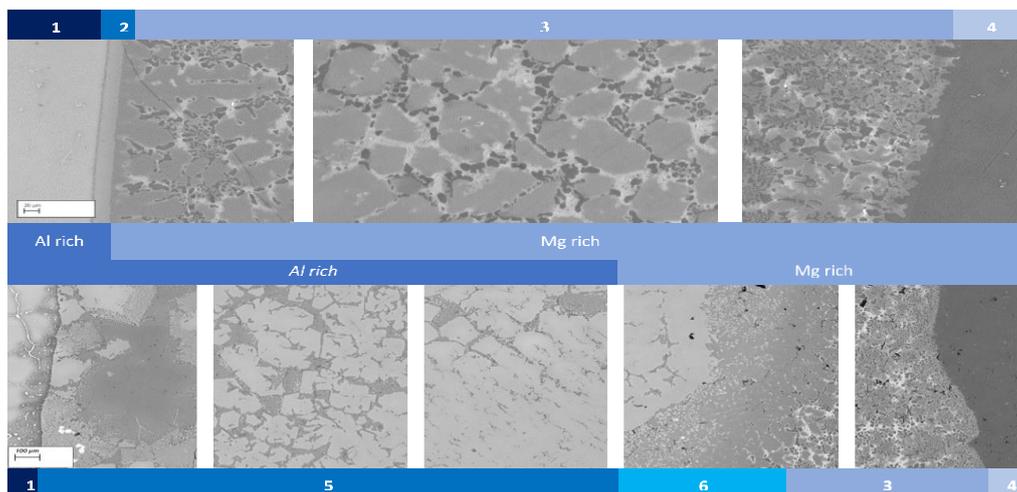

Figure 1. Top: Interface of an AlZn30-Az31 diffusion couple. Bottom: Interface of an AlZn30-Az31 compound casting. Composition of the interface is as follow*s*: (1) AlZn30, (2) β-phase, (3) 3: Mg+γ+φ-phases, (4), AZ31 (5) τ_1+β+Al,(6) Mg+γ

Results obtained from SERIES B differed greatly from those described from SERIES A. Subjecting the samples to a 400°C preheat temperature no distinct interface was present anymore in the samples regardless of holding time. Instead numerous regular shaped "voids" or "bubbles" were present in the AlZn30 wedge. The macro- and microstructure of these samples after a 30min holding time are displayed in Figure 2. The microstructure and chemical composition greatly changed in the AlZn30 wedge. These voids were enclosed by Mg, γ and ϕ. The outer areas of the sample were Mg and γ with zinc being dissolved in the magnesium and γ crystal. No traces of the aluminium rich β and τ_1- phases were found. It is known that several metastable phases exist in the Al-Mg-Zn system. As such it might be possible that a difference in the specific volume of the stable and metastable phases causes the observed voids during transformation of the microstructure. However, it is considered unlikely that differences in the specific volume would cause voids of the size (several mm) found in this study. Moreover no presence of a significant amount of metastable Al-Mg-Zn phases were found using XRD. Only other small amounts of the Mg- Zn phases (MgZn and Mg_2Zn_{11}) were detected. A more likely explanation for the presence of these voids is an imbalanced diffusion process known as the Kirkendall effect. These Kirkendall voids have been reported to be present in the interface of Al-Fe compound castings (Viala, Peronnet, Barbeau, Bosselet, & Bouix, 2002). Additionally, the samples preheated to 200°C didn't display these voids, indicating that the formation of these voids is temperature dependent. Again this is in conflict with the calculated phase diagram for 200°C, as seen in Figure 3, as the zinc rich phases should also form at this temperature. This indicates a strong correlation between phases formed and solid state diffusion.
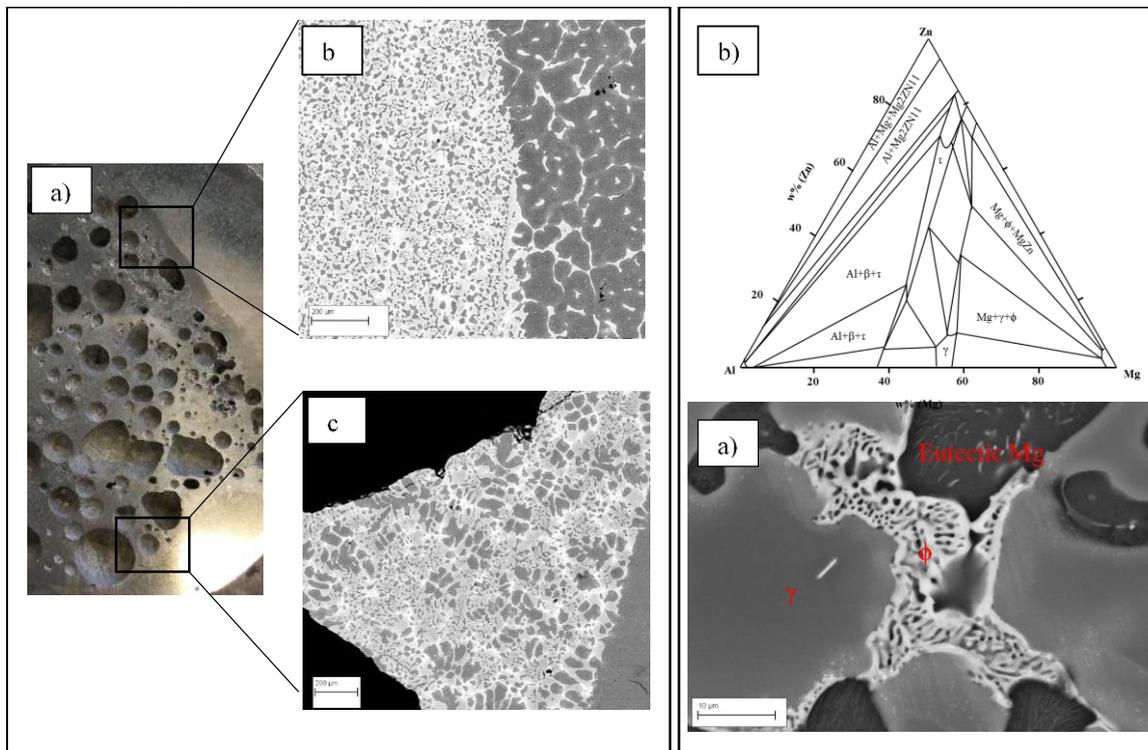

Figure 2. Right: a): Macrograph of the completely transformed AlZn30 alloy, b): SEM- micrograph of the Interface of the transformed AlZn30 alloy and the surrounding magnesium alloy, c): microstructure of the transformed AlZn30 alloy, consisting of magnesium, γ- and ϕ- phase.

Figure 3. b): ternary Al- Mg- Zn phase diagram at 200°C as calculated with Pandat. a): Micrograph of the φ-phase imbedded in a matrix consisting of eutectic magnesium and magnesium rich intermetallic phase γ.

The mechanical properties of the AlZn-AZ31 compound casting and diffusion couples were approximated using micro hardness. The hardness gradient of both samples can be seen in Figure 4. The figure shows that the hardness level of both samples are quite similar with no big distinction between the aluminium-rich and magnesium- rich intermetallic phases. This is deemed beneficial as a steep hardness gradient could facilitate mechanical failure during load. As expected, the interface itself is significantly harder than the AlZn and AZ31 base alloy due to its intermetallic nature. However, the magnesium- rich phases displayed increased ductility even at increased loads (10N) as no cracks were visible at the edges of the indents.
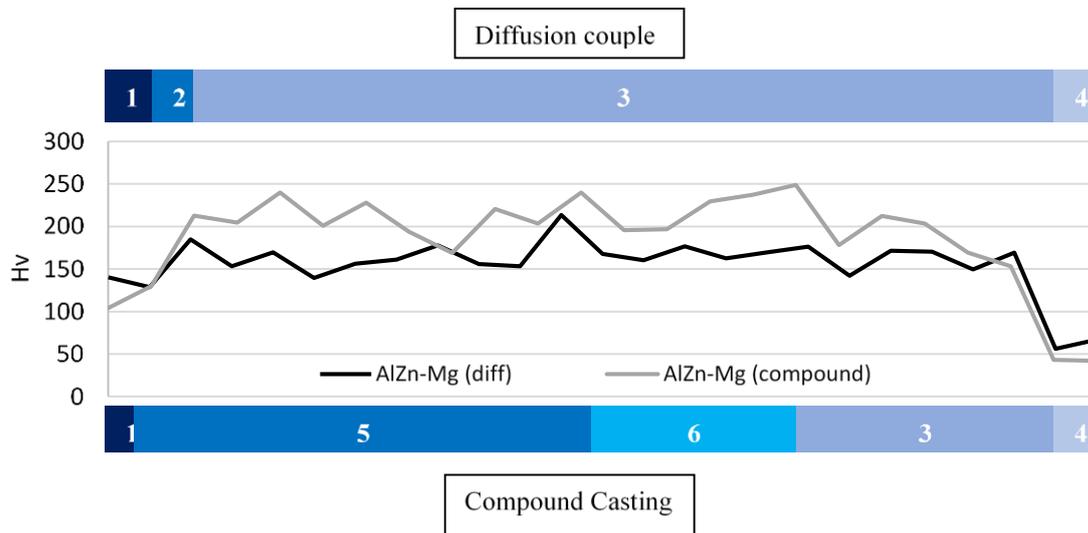

Figure 4. Micro hardness across the interface of an AlZn30-Az31 diffusion couple and compound casting. (1)AlZn30, (2) β-phase, (3) 3: Mg+γ+ϕ-phases, (4), AZ31 (5) τ_1+β+Al, (6) Mg+γ. The numbers indicate thickness and composition of the layer (as detailed in Figure1)

CONCLUSIONS

It has been shown that zinc modifies the growth and morphology of intermetallic phases in Al-Mg compound castings. Additionally to the Al-Mg intermetallic phases β and γ, the Al-Mg-Zn phases τ_1 and φ are formed in alloy combinations containing high amounts (~30wt%) of zinc. Moreover, the results indicate that the β- and τ_1 seem to directly precipitate from the liquid phase while the γ- and φ- phase are the result from a diffusion process. At elevated temperatures the formation of bubble shaped voids as well as the complete transformation of microstructure the AlZn alloy was observed. While the exact mechanism that caused this has not been identified, it is believed that solid state diffusion plays an important role in their formation, similar to the formation of Kirkendall voids, which have been observed in Fe-Al compound castings. Overall the addition of zinc results in a lower hardness but also shows signs of increased ductility over the Al-Mg intermetallic phases γ and β. The combination of φ, γ and magnesium appears to be significantly less brittle than the β-and τ_1 phases.

REFERENCES

Berthold, R. (2013). Crystal structure and phase stability of the phi phase in the al-mg-zn system (vol 32, pg 259, 2013). *Intermetallics, 36*, 138-138. 10.1016/j.intermet.2012.12.014

Brennan, S., Bermudez, K., Kulkarni, N. S., & Sohn, Y. (2012). Interdiffusion in the mg-al system and intrinsic diffusion in [beta]-Mg_2Al_3. *Metallurgical and Materials Transactions, 43*(11), 4043. 10.1007/s11661-012-1248-8

Bührig-Polaczek, A., Röth, T., Baumeister, E., Nowack, N., & Sussmann, T. (2006). Hybride leichtbaustrukturen in stahlblech-leichtmetall verbundguss. *Internationaler Expertenkreis Automobil-Leichtbau 15. Europäische Automobil-Leichtbaukonferenz,*

Cao, R., Wen, B. F., Chen, J. H., & Wang, P. (2013). Cold metal transfer joining of magnesium AZ31B-to-aluminum A6061-T6. *Materials Science and Engineering A, 560*, 256-266. 10.1016/j.msea.2012.09.065

Emami, S. M., Divandari, M., Hajjari, E., & Arabi, H. (2013). Comparison between conventional and lost foam compound casting of al/mg light metals. *International Journal of Cast Metals Research, 26*(1), 43-50. 10.1179/1743133612Y.0000000037

Hajjari, E., Divandari, M., Razavi, S. H., Emami, S. M., Homma, T., & Kamado, S. (2011). Dissimilar joining of al/mg light metals by compound casting process. *Journal of Materials Science, 46*(20), 6491-6499. 10.1007/s10853-011-5595-4

Kammerer, C., Kulkarni, N., Warmack, R., & Sohn, Y. (2014). Al and zn impurity diffusion in binary and ternary magnesium solid-solutions. Paper presented at the 407-411.

Lao,B.(2013).
Druckgegossene metallhybridstrukturen für den leichtbau- prozess, werkstoffe und gefüge der metallhybriden

Liu, W., Long, L., Ma, Y., & Wu, L. (2015). Microstructure evolution and mechanical properties of mg/al diffusion bonded joints. *Journal of Alloys and Compounds, 643*, 34-39. 10.1016/j.jallcom.2015.04.116

Papis, K. J. M., Loeffler, J. F., & Uggowitzer, P. J. (2009). Light metal compound casting. *Science in China, Series E: Technological Sciences, 52*(1), 46-51. 10.1007/s11431-008-0345-9

Petrov, D., Watson, A., . Grobner, J., Rogl, P., Tedenac, J. C., Bulanova, M., & Turkevich, V. (2006). Aluminium – magnesium – zinc. In G. Effenberg, & S. Ilyenko (Eds.), *Ternary alloy systems* (Vol 11A3 ed., pp. 191-209) Springer.

Pierre, D., Bosselet, F., Peronnet, M., Viala, J. C., & Bouix, J. (2001). Chemical reactivity of iron base substrates with liquid Mg–Zr alloys. *Acta Materialia, 49*(4), 653-662. 10.1016/S1359-6454(00)00346-3

Pierre, D., Peronnet, M., Bosselet, F., Viala, J. C., & Bouix, J. (2002). Chemical interaction between mild steel and liquid Mg–Si alloys. *Materials Science & Engineering B, 94*(2), 186-195. 10.1016/S0921-5107(02)00071-5

Pierre, D., Viala, J. C., Peronnet, M., Bosselet, F., & Bouix, J. (2003). Interface reactions between mild steel and liquid Mg–Mn alloys. *Materials Science & Engineering A, 349*(1), 256-264. 10.1016/S0921-5093(02)00793-1

Rübner, M., Günzl, M., Körner, C., & Singer, R. F. (2011). Aluminium–aluminium compound fabrication by high pressure die casting. *Materials Science & Engineering A, 528*(22), 7024-7029. 10.1016/j.msea.2011.05.076

Schneider, K., McKay, B., & Nadendla, H. B. (2017). Influence of alloying elements on intermetallic formation in al- mg compound castings. S*olidification Processing 2017,* 189.

Springer, H., Szczepaniak, A., & Raabe, D. (2015). On the role of zinc on the formation and growth of intermetallic phases during interdiffusion between steel and aluminium alloys. *Acta Materialia, 96*, 203-211. 10.1016/j.actamat.2015.06.028

Viala, J. C., Peronnet, M., Barbeau, F., Bosselet, F., & Bouix, J. (2002). Interface chemistry in aluminium alloy castings reinforced with iron base inserts. *Composites Part A, 33*(10), 1417-1420. 10.1016/S1359-835X(02)00158-6

Viala, J. C., Pierre, D., Bosselet, F., Peronnet, M., & Bouix, J. (1999). Chemical interaction processes at the interface between mild steel and liquid magnesium of technical grade. *Scripta Materialia, 40*(10), 1185-1190. http://dx.doi.org/10.1016/S1359-6462(99)00028-7

Wang, N., Yu, W., Tang, B., Peng, L., & Ding, W. (2008). Structural and mechanical properties of Mg17Al12 and Mg24Y5 from first-principles calculations. *Journal of Physics D: Applied Physics, 41*(19), 195408. 10.1088/0022-3727/41/19/195408

Xu, G., Luo, A., Chen, Y., & Sachdev, A. (2014). Interfacial phenomena in magnesium/aluminum bi-metallic castings. *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 595*, 154-158. 10.1016/j.msea.2013.11.093