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Chapter 5

Corrosion of Materials in Liquid Magnesium Alloys and Its Prevention

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Additional information is available at the end of the chapter

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1. Introduction

Magnesium alloys with their unique physical and chemical properties are important candidates for many modern engineering applications. Their density, being the lowest of all structural metals, makes them the primary choice in global attempts aimed at reducing the weight of transportation vehicles. However, magnesium also creates challenges at certain stages of raw alloy melting, fabrication of net-shape components and their service. The first one is caused byvery high affinity of magnesium to oxygen, which requires protective atmospheres increasing manufacturing cost and heavily contributing to greenhouse gas emissions [1] [2] [3]. While magnesium exhibits high affinity to oxygen, at temperatures corresponding to semisolid or liquid states it is also highly corrosive towards materials it contacts [4] [5] [6]. This imposes challenges to the selection of materials used to contain, transfer or process molten magnesium during manufacturing operations.

Understanding the reactivity of liquid magnesium with engineering materials to eliminate or at least reduce the progress of corrosion is paramount not only during fabrication processes but also in other unique applications. They include joining of dissimilar materials where magnesium is one part of the joint couple and involves similar liquid/solid interface phenomena [7] [8]. Another example is the liquid battery cell, having two liquid metal electrodes, e.g. magnesium and antimony, separated by a molten salt electrolyte, that self-segregate into three layers based upon density and immiscibility. Such an assembly faces also corrosion issues [9]. During joining by exploring so-called compound casting [10], where two Mg alloys, one in the solid state and another one in the liquid state, are brought together, an interface formation by solid-liquid reaction is the essence of the phenomena leading to a metallurgical bond. Thus, at present, there are still challenges to be addressed to understand the mechanism of corrosion

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attack, compatibility of materials in respect to liquid magnesium and designing protection methods.

The aim of this chapter is to review fundamental aspects of corrosion in liquid magnesium alloys, assess degradation of selected metallic and ceramic materials in this environment and define methods of corrosion prevention.

2. Liquid metal corrosion

Liquid metal corrosion is understood as a physical or physico-chemical process that follows the formation pattern of metallic alloys. In contrast to corrosion of metals in aqueous solutions, no transfer of electrons is involved. The essential part of the process is dissolution accompanied by formation of a liquid alloy with mixed composition and chemical reactions resulting in creation of intermetallic compounds. Liquid metals are a group of coolants with increasing importance for high-temperature processes and power engineering. Due to great heat-transfer properties, liquid metals are used in the nuclear industry as heat transfer media [11]. Therefore, the majority of operating experience with liquid metal systems has been accumulated within the nuclear industry. The favorable thermo-physical properties of liquid metals allow for high rates of heat removal in comparison to other coolants, e.g., water/steam. Although nuclear reactor engineering with light liquid metal/alloy sodium and sodium-potassium and heavy liquid metal/alloy liquid lead and lead bismuth differ substantially from a liquid magnesium environment, general aspects of corrosion are similar. Common issues show also other applications such as liquid metal spallation targets in elementary particle sources, galvanizing of steel by hot dipping in a molten metal bath of Zn [12], as well as glass production or electronics cooling. Using liquid metals may enable alternative technologies like direct thermal-electric conversion or use of solarhigh temperature heat in chemical processes [13].

2.1. Factors affecting progress of corrosion

Three major steps that control the corrosion progress include (i) transport in solid state; (ii) reactions at the solid/liquid interface dominated by dissolution of the solid alloy and its transport into liquid magnesium and (iii) transport of species within the liquid state (Fig. 1). In a hypothetical static system, corrosion would continue until reaching the solubility limit. In the case of an engineering environment, alloying elements and impurities react with atmosphere forming oxides and nitrides that make the process more complex. In particular, the temperature gradient and the concentration gradient make the system dynamic, leading to mass transfer.

According to early research [14], the corrosive attacks are classified as: (i) simple dissolution, (ii) alloying between liquid metal and solid metal, (iii) intergranular penetration, (iv) impurity reactions, (v) temperature gradient mass transfer, (vi) concentration-gradient mass transfer or dissimilar-metal mass transfer. As variables controlling liquid metal corrosion, such factors as temperature, its gradient or cyclic fluctuation, surface area to volume ratio, metal purity, flow velocity and some characteristics of material being in contact with liquid metal, are named.

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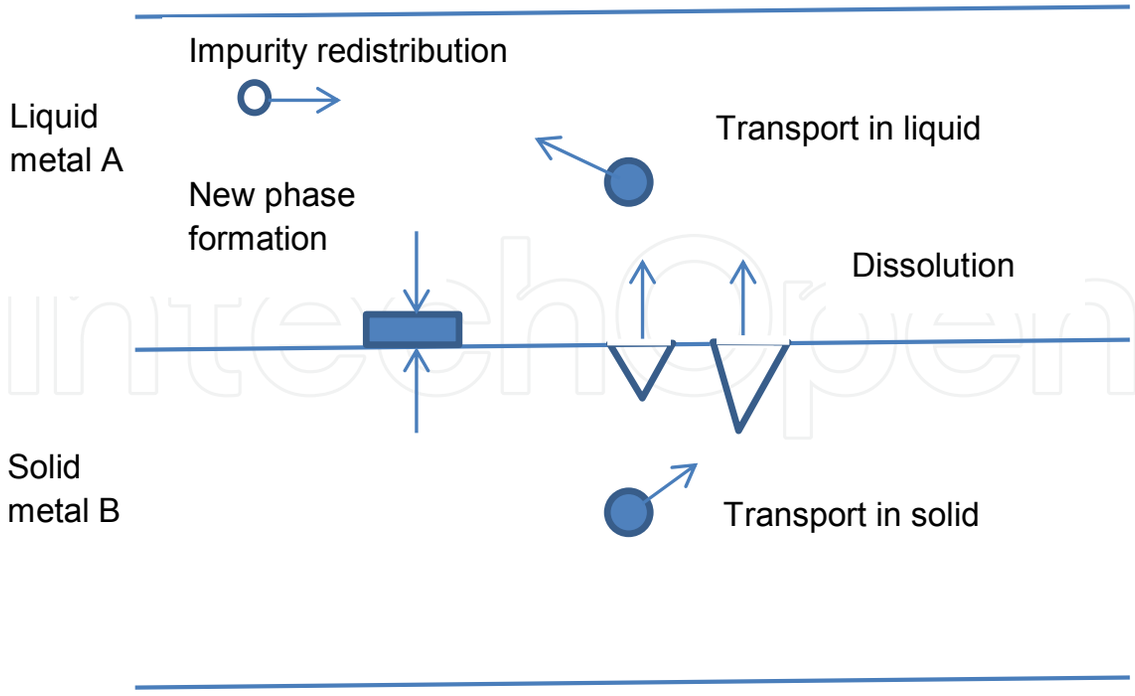


Figure 1. Schematics emphasizing phenomena involved during corrosion in liquid metals.

For certain liquid metals, the progress of corrosion may be reduced by adding to the liquid alloy either metallic or non-metallic corrosion inhibitors. It is believed that inhibitors decrease the corrosion rate by forming a protective film, separating the metallic surface from corrosive media. For example, metallic inhibitors added to liquid Pb and Pb-Bi caused the formation on a steel surface of a protective layer of nitrides or carbides by the chemical reaction between inhibitors and carbon and nitrogen in steel [11]. In particular, for carbon steels and low-alloy steels, additions of Zr and Ti were confirmed to be effective. At the same time, the effectiveness of Zr and Ti for stainless steel, being in contact with liquid Pb and Pb-Bi alloys, was very low.

An essential factor in corrosion progress is the corrosion front morphology. The ideally uniform corrosion front is possible in theory when the diffusion rate in the solid is fast enough to balance the mass transfer rate in the liquid. In practice, due to the fact that diffusion in solid is the slowest step, there is a development of the front morphology. In single-phase materials, the grain orientation, grain boundaries and impurities will contribute to different rates of corrosion progress over the surface. In multi-phase materials, phase chemistry and their crystallography impose additional complexity. A particular case is the preferred penetration of liquid metal along grain boundaries of the adjacent solid material, causing its embrittlement.

2.2. Models of liquid metal corrosion

At early stages of corrosion, the dissolution reaction is considered to be the fastest step, with mass transport in the liquid seen as the controlling step of the entire process. In contrast, at the steady state, either dissolution at the solid/liquid interface or mass transport in the bulk liquid is in control of the corrosion progress. It was revealed during experiments between austenitic

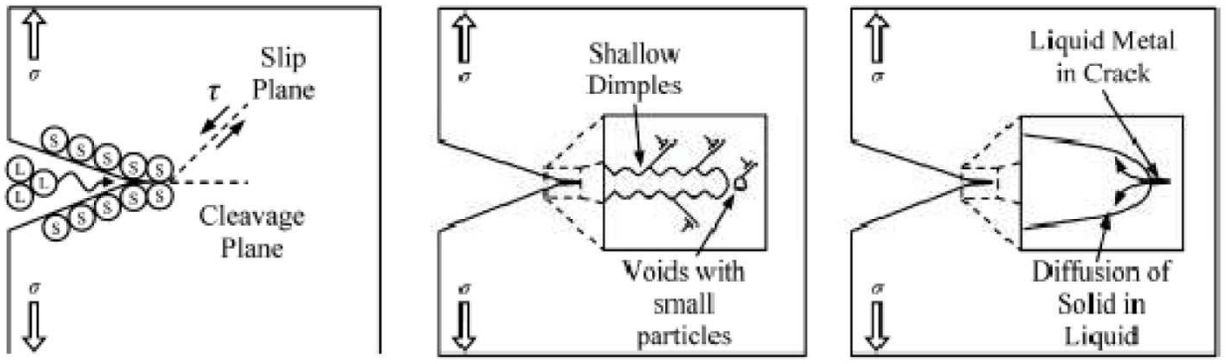


Figure 2. Existing failure mechanisms of corrosion in liquid metals: (a) decohesion model; (b) adsorption induced dislocation emission model; (c) dissolution condensation mechanism model [19].

stainless steel AISI 316L and liquid Ga, along with its alloys (Ga-14Sn-6Zn, Ga-8Sn-6Zn), the corrosion progress gravimetrically measured by metal losses, was significantly lower in Ga alloys than in pure Ga [15]. As an explanation, the lower diffusivity of species in pure liquid Ga than in Ga alloys was proposed.

For a nuclear reactor coolant system, a number of models were developed allowing the calculation of the corrosion rate and corrosion layer thickness [16]. They explore a mathematical analysis of the transport of various species in the solid phase, in flowing liquid phase and mass exchange at the interface between solid and liquid. The negative side of modelling so far is an exclusion of the pitting corrosion, stress corrosion cracking and liquid metal embrittlement due to a lack of theoretical and experimental data.

2.3. Liquid metal embrittlement

While being in contact with liquid metal under stress, certain metals experience a drastic reduction in ductility [17] [18]. It should be pointed out that the loss of ductility takes place in normally ductile metals. Often the phenomenon is seen as the crack propagation associated with a change of the fracture surface from ductile into brittle of an intergranular type. According to the conventional mechanism, the lower melting point liquid metal fills a crack in the solid metal, thereby weakening material at the crack tip and allowing it to propagate at much lower stress. Moreover, the traditional models considered the grain boundary segregation associated with formation of the interfacial phase. Existing failure mechanisms, including the decohesion model, adsorption induced dislocation emission model and dissolution condensation mechanism model are shown schematically in Fig. 2 [19]. There are many combinations of the matrix and embrittling solute [20], including steel embrittlement by liquid Cu, aluminum by Hg, or stainless steel by liquid Zn. The literature does not report that liquid magnesium is the embrittling solute but some alloying elements of magnesium alloys, e.g. Zn, are known as causing embrittlement.

There are also practical observations, which point out that: (i) liquid metal must be present and (ii) the area affected must be under stress [21]. According to Ref. [22] , the embrittlement will occur even when the liquid metal is removed from the solid metal surface before stressing.

As factors controlling the material susceptibility to liquid metal embrittlement, the low mutual solubility between the liquid and solid metals and an absence of intermetallic compound formation between the solid-liquid couple are frequently quoted. As revealed by a number of advanced analytical techniques of surface investigation, the micro-mechanism of liquid metal corrosion is more complex. For example, in the case of nickel infused with bismuth atoms a bilayer interfacial phase was detected by aberration-corrected scanning transmission electron microscopy [23]. This observation showed that adsorption can induce a coupled grain boundary structural and chemical phase transition leading to embrittlement. Experiments with several reactive couples including liquid Ga into Al, Hg into Ag and Ag into Cu showed that the size of the brittle fracture surface area is proportional to logarithm of the exposure time. There is also evidence [22] of the existence of an incubation period, being inversely proportional to the penetration speed of the liquid metal into solid metal. During a study of the 9%Cr martensitic steel in stagnant liquid environments of Pb, Pb-Bi or Sn the steel embrittlement can be explained by a reduction of the surface energy of the bare metal induced by some adsorption of the liquid metal [24]. This fact allowed understanding some experimental observations including (i) instantaneous effect of embrittlement with no requirements of solid-state diffusion; (ii) reduction of embrittlement with increasing temperature; increased propagation of surface crack into bulk alloy caused by cyclic loading.

2.4. Ceramic materials in contact with liquid metals

In contrast to metallic materials, ceramics show generally higher resistance to corrosive attack at high temperatures [25]. Due to degradation of mechanical properties of metallic materials, at a certain temperature range, ceramics represent the only choice for many advanced engineering designs. This applies also to an environment of liquid metals.

In the case of ceramics being in contact with molten metals, the destructive process involves a reduction-based removal of non-metallic elements from the solid, undermining their structural integrity [26] [27]. It is also claimed that ceramics when in contact with liquid low-melting metals experience the strength reduction. According to experiments with A-995 alumina exposed to liquid Sb, Pb, Ca, Bi and 50Bi-30Pb-20Sn*alloy (* all alloy compositions are in weight % unless indicated otherwise), a considerable reduction in strength by alumina was experienced [28]. In all cases, alumina ceramic was wetted by liquid metal, which adhered to their surface after solidification.

3. Corrosive nature of liquid magnesium and its alloys

In engineering practice, to generate the sufficient strength and other mechanical properties, magnesium is alloyed with other metals such as Al, Zn, Mn, Si, Cd, Ag, Zr, Ca, Sr, Be or rare earths. Moreover, magnesium alloys contain difficult to remove impurities, mainly Fe, Ni or Cu. Both the alloying elements and impurities change the corrosivity of liquid Mg in regards to materials they contact.

3.1. Corrosivity of pure magnesium

A selection of materials to sustain liquid magnesium, in terms of resistance to its corrosive attack and mechanical properties degradation due to high temperatures is a key task for engineering applications. It is generally known that iron is inert to molten magnesium. According to the Mg-Fe equilibrium phase diagram, below 1000 °C, Mg does not dissolve in Fe. In a Mg-Fe system, some solubility of Mg is possible only at high pressures and high temperatures. As reported in Ref. [29], the maximum solid solubility of Mg in Ni is 0.00043 at. % and the eutectic composition is at 0.008 at. % Fe.

In contrast to Fe, liquid magnesium reacts with nickel. According to Ref. [30], the solid solubility of Mg in Ni is less than 0.2. at. % Mg at 500 °C. In a Mg-Ni system there is one peritectic and two eutectic reactions [31]. There are two intermetallic compounds with Mg_2Ni melting at 760 °C and $MgNi_2$ melting at 1147 °C [32]. As pointed out in [33], the $MgNi_2$ phase extends from 66.2 to 67.3 at. % Ni.

During analysis of the liquid Mg-solid Ni reaction couple it was noticed that the compounds which are at the Mg/Ni interface, rich in the lower melting point elements, are the first phases formed in metal/metal binary reactions, i. e., Mg_2Ni [34]. It is quite surprising to find that the minority elements, such as Cu or Ni impurities, are the dominant diffusing species. This fact differs from results obtained in many metal/metal systems where the major diffusion species are usually the majority elements in the initially formed compounds. During an experiment with a diffusion couple of 99.999% purity liquid Mg at a temperature of 660 – 680 °C and solid Ni plate the intermetallic phase of Mg_2Ni grew at the interface and the Ni layer dissolved by diffusion throughout the intermetallic phase into liquid Mg [35]. Although according to the equilibrium phase diagram both phases Mg_2Ni and $MgNi_2$ could form, only the former one was detected.

3.2. Effect of major alloying elements

The number of elements that can be added during alloying is rather low due to their limited solubility in magnesium and a competition from phases formed between additions themselves. Of all alloying elements, aluminum is the most often used and its content, reaching up to 11%, is the largest of all metals explored for that purpose. Under equilibrium conditions the solubility of Al in α-Mg is 12.7% at 437 °C but in as-cast alloys a solid solution below 437 °C is enriched only with 2 – 3% of Al [36]. In general, Al is not distributed uniformly and in addition to macro-segregation, also micro-segregation occurs and is related to formation of precipitates and grain boundary enrichment.

The role of aluminum in liquid metal corrosion is substantial due to its large concentration in many Mg alloys and extremely high corrosivity [37]. An example showing Al reactivity when Mg-10%Al alloys contacts carbon steel is shown in Fig. 3. Molten aluminum dissolves practically all conventional alloys including, Fe, Ni, Cr and Co based grades. Although some alloys, such as Ni-Cr-Fe are used with molten Al, their lifespan is rather short. There is some potential ofTi alloys where protection against molten Al is believed to be provided by Ti oxides forming on Ti surface, thus separating both metals. The literature emphasizes also a strong influence

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of small amounts of Al present in Mg alloys. For example, less than 0.002 wt. % of Al or Si in liquid Mg at 723 °C reacts with Fe from steel creating α-Fe (Al, Si) solid solution [38]. By combining carbon from steel, impurities present in Mg form a compound of Fe_2 (Al,Mg)C. It has been concluded that the above phases were formed not only by solid-state diffusion in steel but also by dissolution-precipitation processes and migration of Fe in liquid magnesium. During a contact of molten magnesium alloys with H13 steel Al content was found to be the controlling factor in the type of phases formed [39]. For Al contents below 6%, FeAl/ (Fe, Mn)Al was the major phase formed with traces of $FeAl_2$ and Fe_2Al_5. For higher Al contents, the Fe_2Al_5 phase dominated and for Al exceeding 12%, the $Fe_{14}Al_{86}$ was the dominant one.

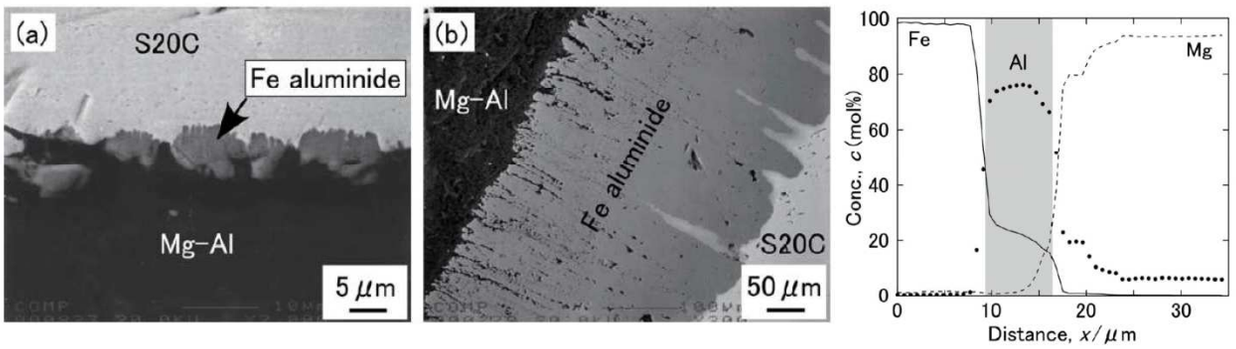


Figure 3. Microstructure of the interface between Mg-10% Al alloy and S20C carbon steel after short term (a) and long term (b) exposures. The concentration profile across interface (a) is shown in (c) [82]

A common ingredient of magnesium alloys is also zinc with a maximum solubility of 8.4%. Additions of zinc are used often in a combination with aluminum to improve the alloy strength at room temperatures or with zirconium and rare earths to generate precipitates that are stable at increased temperatures. From the shape of the αMg-β boundary at the equilibrium phase diagram of Mg-Al-Zn [40], it is seen that the addition of Zn allows more β precipitates to form at a fixed Al content of 8%. The β compound has a part of Al atoms substituted by Zn. Since for Mg-9Al-1Zn alloy at temperatures below 437°C it has the form of Mg_{17} $(Al,Zn)_{12}$, likely $Mg_{17}Al_{11.5}Zn_{0.5}$, the Zn content is expected to be higher [41].

Zinc, which melts at 419°C is a commonly used low melting metal with vast data and broad application experience. Both molten zinc and its alloys are used for hot-dip galvanizing of steel. There is solid evidence that they may cause liquid metal embrittlement of steel at temperatures as low as 400 °C. For example, liquid metal embrittlement can be induced into austenitic stainless steels by molten Zn during its welding with galvanized carbon steel [42]. It is known that refractory metals like Mo, W and their alloys withstand the corrosive attack by molten Zn up to 500 °C. During an experiment with testing Mo, Mo-30%W, W, DIN 1.4841 steel and graphite in a molten Zn environment at 500, 600, 650 and 700 °C for 168 h, differences in corrosion behavior were recorded [43]. While steel was dissolved, Mo was only partly attacked at 500 and 650 °C. At the same time, Mo-30%W, pure W and graphite showed satisfactory corrosion resistance.

3.3. Effect of minor elements and impurities

As emphasized already in section 3.2, the chemical compatibility of molten magnesium towards other materials may be altered by the presence of small amounts of other elements. They are not only limited to difficult-to-remove impurities but also to elements deliberately added in small quantities. Many magnesium alloys contain manganese; its major role is designed to bind harmful impurities of iron and heavy metals into harmless intermetallic compounds. In general, Mn has very limited solid solubility, reaching 2.2%, which in the presence of aluminum is further reduced to about 0.3% due to formation of MnAl, $MnAl_6$ and $MnAl_4$ compounds. Its maximum content in commercial magnesium alloys does not exceed 1.5 – 2 %. Based on free energy of oxide formations, Mn looks to be much less reactive than Mg or Al. According to observations in Ref. [44], in liquid Al alloys, a presence of Mn increased oxide layer thickness. Although oxide layer thickness increased with Mn content in Al alloy, oxide contained very small amounts of Mn. It was noticed during industrial practice that e.g. soldering is more likely to occur when die casting magnesium alloys such as AM60 with higher manganese content are used [39]. The die casting trials were also carried out to confirm the soldering development in high pressure die casting conditions [45]. The results showed that the formation of intermetallics started with the nucleation of the η-Fe_2Al_5phase. During the next stage, manganese substituted some of iron and this phase became $(Fe,Mn)_2Al_5$. Finally, a metastable phase $Mn_{23}Al_{77}$was formed at the outer layer of the surface exposed to liquid magnesium alloy.

During reaction of solid mild steel and liquid Mg-Mn alloys at 727 °C the chemical interaction was found to depend on the Mn content [46]. In all cases, the interface reactions led to formation of phases from the Fe-Mn phase diagram with the mechanism being dominated by solid state volume diffusion of Fe and Mn. The intergranular melt infiltration was added as the secondary phenomena. As shown in Fig. 4, for 0.6 – 0.7 at. %Mn, two sublayers were formed with chemistry of αFe (Mn) and γFe (Mn) [46]. For higher content of 1.3 at. %Mn, corresponding to the Mn saturated solution, the layer contained βMn (Fe).

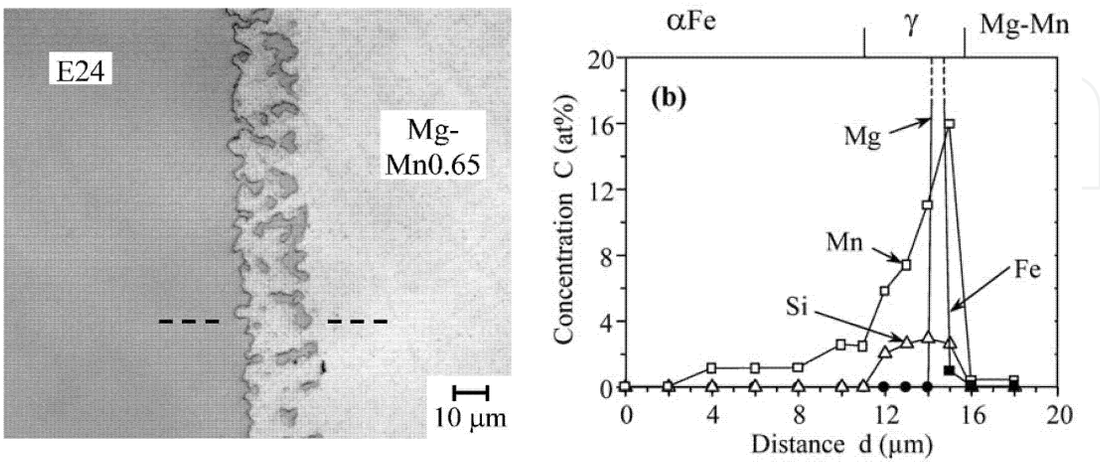


Figure 4. Interface between E24 mild steel and Mg-0.65 at% Mn liquid alloy after 65 h exposure at 727 °C (a) along with concentration profile across the interface (b) [46].

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The reactivity of liquid Mg-Si alloys containing up to 3.1 at. % Si with mild steel at temperature between 677 and 727 °C led to formation of a continuous layer at the solid/liquid interface [47]. For very low Si content of 0.025 at. % the layer consisted of αFe solid solution with less than 2 at. % Si. For higher Si contents from 0.045 at. % to 3.1 at. % the reaction layer consisted of α_1Fe_3Si ordered phase with Si content from 24.5 to 27 at. %. The reaction phase was formed by the solid-phase volume diffusion. Morphology of the solid/liquid interface and accompanying concentration profiles are shown in Fig. 5.

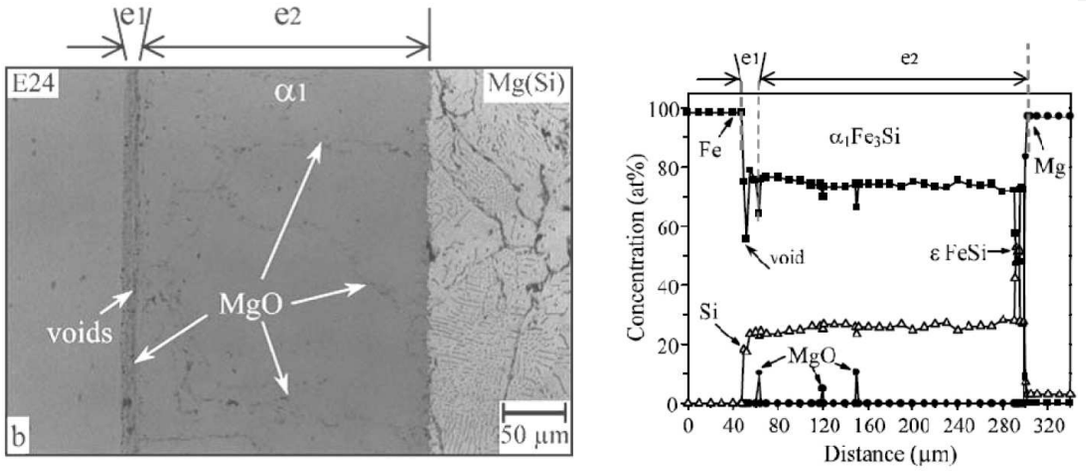


Figure 5. Interface between E24 mild steel and liquid Mg-3 at% Si after 250 min at 727 °C (a) and concentration profile showing location of Si in the reaction zone (b) [47].

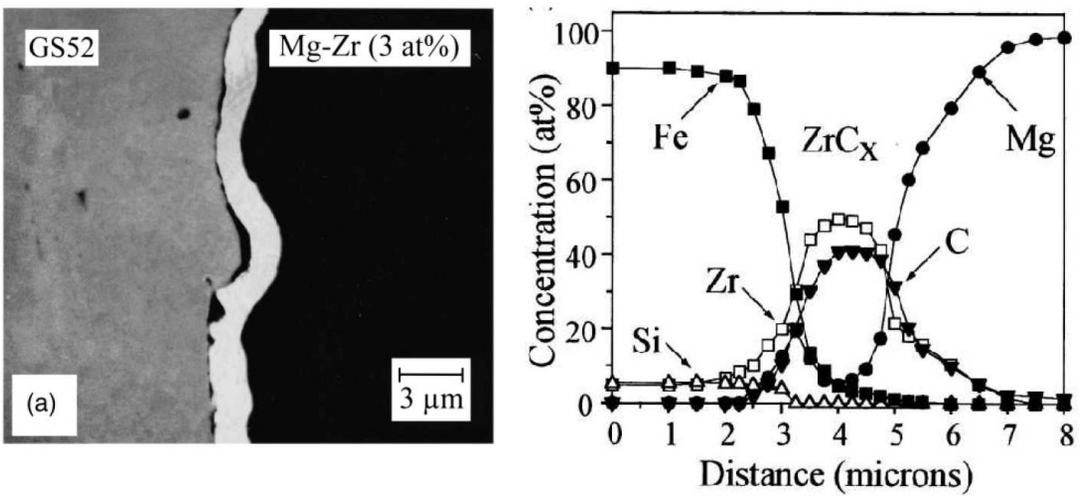


Figure 6. Interface between cast iron and Mg-3 at% Zr alloy after exposure of 65 h at 727 °C (a) and concentration profile showing Zr location in the reaction zone (b) [48].

The role of transition alloying elements in Mg alloys on their corrosivity in liquid state was also studied. It includes, for example the reaction between liquid Mg-Zr alloy at 727 °C and pure Fe, steel and cast iron [48]. Although iron is chemically compatible with liquid magnesium, it reacted with Mg-Zr alloys (Fig. 6). The primary reaction took place between Zr in liquid Mg-Zr alloys and iron, forming in the liquid the Fe-Zr compounds, mainly Fe_2Zr. The reaction mechanism is based on dissolution of the solid steel and crystallization within the Mg-Zr liquid alloy, enriched by the solute. The secondary reaction is between Zr and C from the steel substrate to form ZrC_x as a surface layer inhibiting corrosion progress.

4. Complex nature of material degradation by liquid magnesium in engineering applications

The materials in contact with liquid magnesium during manufacturing operations are subjected to multiple deteriorating effects which accompany the corrosive attack by molten metal. In addition to the corrosive attack of a purely chemical nature, there is an influence of accompanying heat and stress. Depending on processing details, the relative proportion of individual deteriorating factors and their contribution to overall damage experienced by materials are different.

4.1. Simultaneous effect of stress and corrosion

The components of magnesium processing equipment in direct contact with liquid metal are a subject of very demanding requirements in terms of materials used. In some cases, tight tolerances may not allow for substantial size change due to wear or corrosion during service. Similarly, high strength requirements may not allow for a reduction in mechanical properties over service time. The most common mechanisms of material degradation in liquid magnesium include [1]: (i) high temperature fatigue; (ii) thermal fatigue; (iii) corrosion fatigue, (iv) creep and stress rupture and/or (v) oxidation. The relative contribution of each mechanism depends on the specific application. An example of a combination of liquid metal, corrosion and fatigue (corrosion fatigue) is shown in Fig. 7. Under a cyclic load caused by melt pressure, corrosion sites act as stress risers, causing progressive crack propagation and premature failure.

4.2. Stress due to difference in thermal expansion

At relatively high service temperature, materials experience large dimensional changes due to thermal expansion. As may be deduced from Table 1, for components with a length of 2 m and service temperatures over 620 °C, an elongation may reach several millimeters. Such a difference should be considered during material selection. The key challenge occurs when two or more different materials are in direct contact at high temperatures. For example, when tool steel components are connected with each other by using Ni based alloy Inconel. As seen in Table 1, the coefficient of thermal expansion of the bolts is larger than that for the steel. To maintain a bolt preload, it is necessary to re-torque the bolts once the component reaches the

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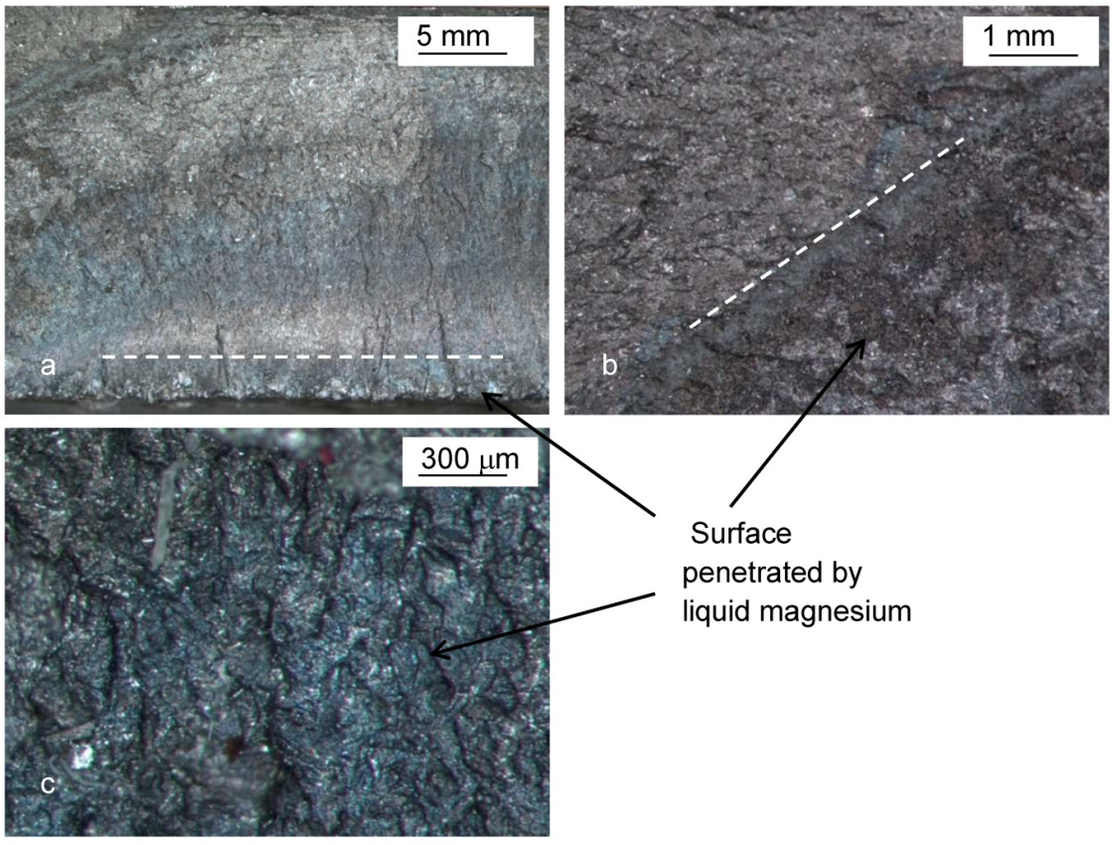


Figure 7. Fracture surface of tool steel after service in an environment of liquid magnesium alloy.

service temperature. Conversely, when the assembly is subsequently cooled to ambient temperature, bolts will shrink more than the steel component. Hence, without loosening of fasteners, this will cause large tensile stress to develop and fastener stretching that may eventually lead to premature failure. Similarly, materials of a die of a high pressure die casting machine or molten alloy distribution systems should exhibit similar thermal expansion or differences should be incorporated into design.

Alloy	100	200	300	400	500	600	700	900	1000 [°C]
AISI H13	11. 9	12. 4	12. 3	12. 7	13. 0	13. 3	13. 5		
DIN 1. 2888	9. 9	10. 4	10. 9	11. 3	11. 6	11. 8	11. 9		
Inconel 718	12. 8	13. 6	13. 9	14. 4	14. 8	15. 1			
Stellite 6	11. 3	12. 9	13. 6	13. 9	14. 2	14. 5	14. 7	15. 5	17. 5
Stellite 12	11. 5	12. 1	12. 6	12. 9	13. 3	13. 8	14. 3	15. 2	15. 6
Stellite 21	11. 0	11. 2	12. 0	12. 6	13. 1	13. 6	14. 3	15. 21	

Table 1. Example showing differences in coefficients of thermal expansion for selected alloys applicable in processing liquid magnesium (10^{-6} m/ (m K). Temperature range from 20 °C to the value indicated [86] [87]

4.3. Stress due to low thermal conductivity

Heat that is required for high temperature processing is not applied directly to magnesium. Instead, it is provided entirely from an external source and transferred through walls of a furnace crucible or the sleeve of a transfer pump. To achieve the fast rate of heat transfer, thermal conductivity of material used is of key importance. If a material has low thermal conductivity it not only requires a longer time to melt magnesium but creates a steep temperature gradient across the component wall thereby generating thermal stress. For thick walls the stress build-up may lead to thermal shock failure. It is seen in Table 2, that Ni-base and Co-base alloys with high strength at temperatures of liquid magnesium processing have rather low thermal conductivities. A particular case has a place when a material is in intermittent contact with liquid magnesium as with a nozzle, die/mold or elements of the melt transfer system. If a surface is subjected to frequent heating/cooling cycles, e.g. every 1-2 min, surface fatigue leads to crack formation. A top view of a steel surface damaged by intermittent contact with liquid magnesium is shown in Fig. 8. Surface microcracks, formed as a result of thermal fatigue, are cyclically filled with liquid alloy.

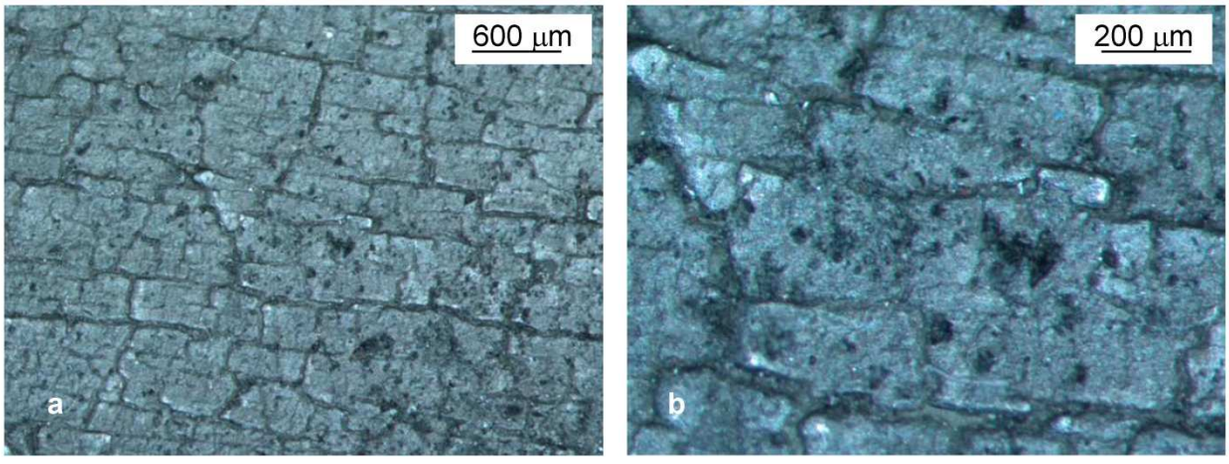


Figure 8. Top view showing surface of tool steel after intermittent exposures to liquid magnesium alloys.

Alloy	20	200	300	400	500	600	700	800	1000 [°C]
AISI H13	25. 5	27. 1		27. 7					
DIN 1. 2888	20. 5	24. 2		27. 5					
Inconel 718	11. 1	14. 1	16. 0	17. 7	18. 8	19. 9	22. 1	23. 7	
Stellite 6	14. 82								
Stellite 12	14. 6								
Stellite 21	14. 5								

Table 2. Example showing differences in coefficients of thermal conductivity for selected alloys applicable in processing liquid magnesium (W/m °C) [86] [87] [88]

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5. Material solutions in melting and casting equipment

The industrial equipment for magnesium processing, with components entirely or partly exposed to liquid metal, include crucibles of melting furnaces, elements of die casting and other machinery, parts of pumps and transfer systems. Although the primary requirement imposed on materials used includes the chemical resistance to molten magnesium, there are also other essential properties needed, depending on specific service conditions such as a sustainable level of strength and toughness, creep resistance as well as the resistance to oxidation in air at high temperatures. There are a number of commercial alloys applicable for this purpose that differ in chemical composition, as well as physical and mechanical properties. Examples of most common industrial solutions are listed in Table 3.

Resistance against liquid magnesium only		**Resistance against liquid magnesium accompanied by high temperature strength and wear resistance**	
Group of alloys	**Grade examples**	**Group of alloys**	**Grade examples**
Majority of tool steels	excluding (AISI A8, A9, A10)	Highly alloyed special steels	DIN 1. 2888, DIN 1. 2886
Low alloy steels	AISI 1330-4161 5115-6150	Chromium hot work steels	AISI H10-H19
Ferritic stainless steels	AISI 405, 430, 444	Tungsten hot work steels	AISI H21-H26
Martensitic stainless steels	AISI 403, 410, 440		
Special alloys	Nb-30Ti-30W		

Table 3. Metallic alloys applicable for components of magnesium processing equipment exposed to liquid magnesium alloys.

5.1. Crucibles and melting furnaces

The magnesium melting furnaces utilize as a heat source the electric resistance or gas heaters. Thus, an external surface of the crucible is additionally degraded by an exposure to the heat source. Because carbon steel scales on the outside of the melting crucible, being in contact with flame, other material combinations have been tried. The present furnace crucibles are manufactured of (i) ferritic stainless steel; (ii) bimetallic materials with an interior made of low carbon steel and an exterior of stainless steel; (iii) bimetallic design where an interior of low carbon steel is protected from the outside by nickel alloys, forming the oxidation resistant surface adjacent to the furnace heat source. An example of crucibles for handling liquid magnesium is shown in Fig. 9.

Magnesium crucibles for operation up to 850 ^{o}C could be manufactured of wrought or cast mild carbon steels with negligible nickel content. Welding is the dominant joining technique. In the case of using just carbon steel, a crucible lifetime is generally short, sometimes of the order of several days. An improved design of the single material crucible utilizes a ferritic stainless steel, such as AISI 444 [49] [50]. The steel is welded using a nickel-free and high



Figure 9. Commercial processes requiring equipment resistant to liquid magnesium: (a, b, c) crucibles for magnesium melting [83];

chromium stainless rod. As a result, the crucible lifetime is increased from six to ten times. Since ferritic stainless steels exhibit a tendency to brittle cracking, as a further improvement, bimetallic crucibles were introduced. During melting at 650°C, magnesium tends to leach the Ni out of Ni-containing alloys, a thick austenitic steel base such as AISI 316 is overlaid with a mild carbon steel liner such as AISI 1005 to protect it from a corrosive attack [51]. Another design suggests mild steel crucibles or a lining of 430 stainless grade. The nickel-chromium-iron alloy outside provides high temperature strength and oxidation resistance while the carbon steel inside is more compatible with the molten magnesium [52]. An example of reactivity of Mg with a crucible and a melt transfer pump is shown in Fig. 10.

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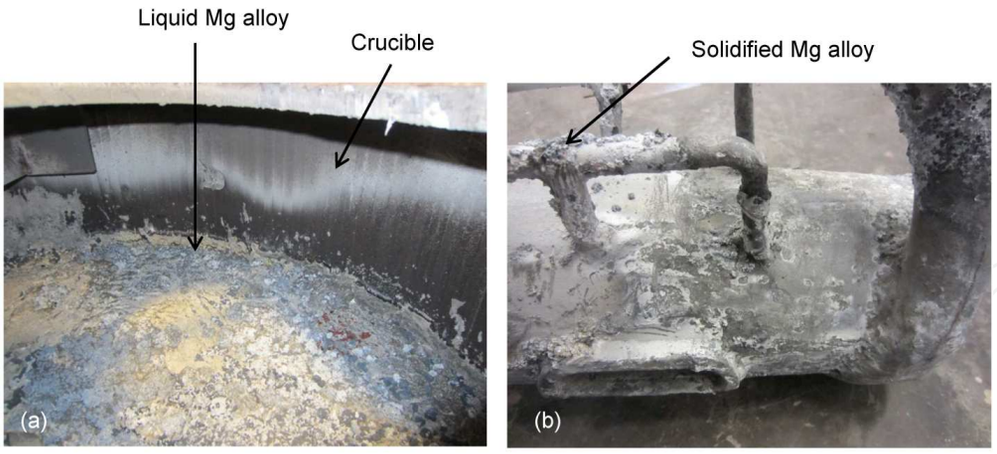


Figure 10. Magnesium reactivity with (a) crucible holding liquid magnesium alloy; (b) element of transfer system for liquid magnesium alloy with surface covered by solidified alloy.

5.2. Die casting machines

There are two techniques of die casting and corresponding machines for both processes with essentially different exposure conditions of their components to liquid magnesium. As a result, both applications require quite different material solutions.

During cold-chamber die casting, shown schematically in Fig. 11, the alloy melting is performed in a separate furnace. Then, a portion of molten material is transferred from the furnace crucible into the machine shot sleeve, where a hydraulically operated plunger pushes the metal into the die. The amount of liquid alloy transferred to the sleeve is larger than the part volume so the extra material is used to apply pressure during solidification in the die cavity, thus reducing the generated shrinkage. The typical injection pressure of a cold chamber system exceeds 70,000 kPa. Due to a need to transfer the molten metal from the furnace to the cold-chamber machine, the cycle time is reduced depending on the melt transfer solution.

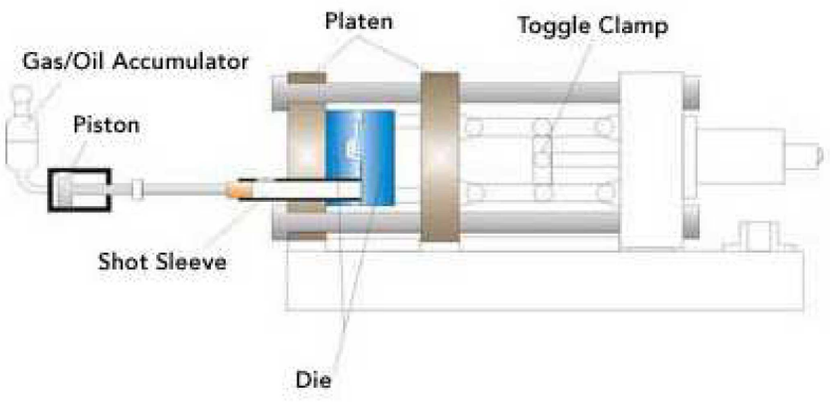


Figure 11. Schematics of cold chamber die casting machine with major components exposed to liquid magnesium alloys [84]

There are a number of components within the machine that are exposed to liquid magnesium, including shot sleeve, plunger, seal rings of the plunger, nozzle, sprue etc. An example of the shot sleeve is shown in Fig. 12a. The shot sleeve walls are in an intimate contact with liquid magnesium for only 1-2 seconds or 5% of the entire cycle duration so its average temperature is well below the melting point of magnesium alloy. However, the non-uniformity in temperature distribution as suggested in Fig 12b causes non-uniform deformation with a tendency to bending. As a result, a piston cannot slide smoothly inside the shot sleeve, causing friction and wear on both components. During flow into shot sleeve, the liquid alloy heats the inner wall surface reaching the highest temperature within the entire component. In extreme cases the sleeve deformation may lead to plunger seizing. A combination of high temperature, chemical attack, along with abrasion imposed by flowing alloy, contributes to the degradation observed. A similar wear location is also reported for shot sleeves used in die casting of Al alloys. A frequent location of the sleeve deterioration area is shown in Fig. 12c

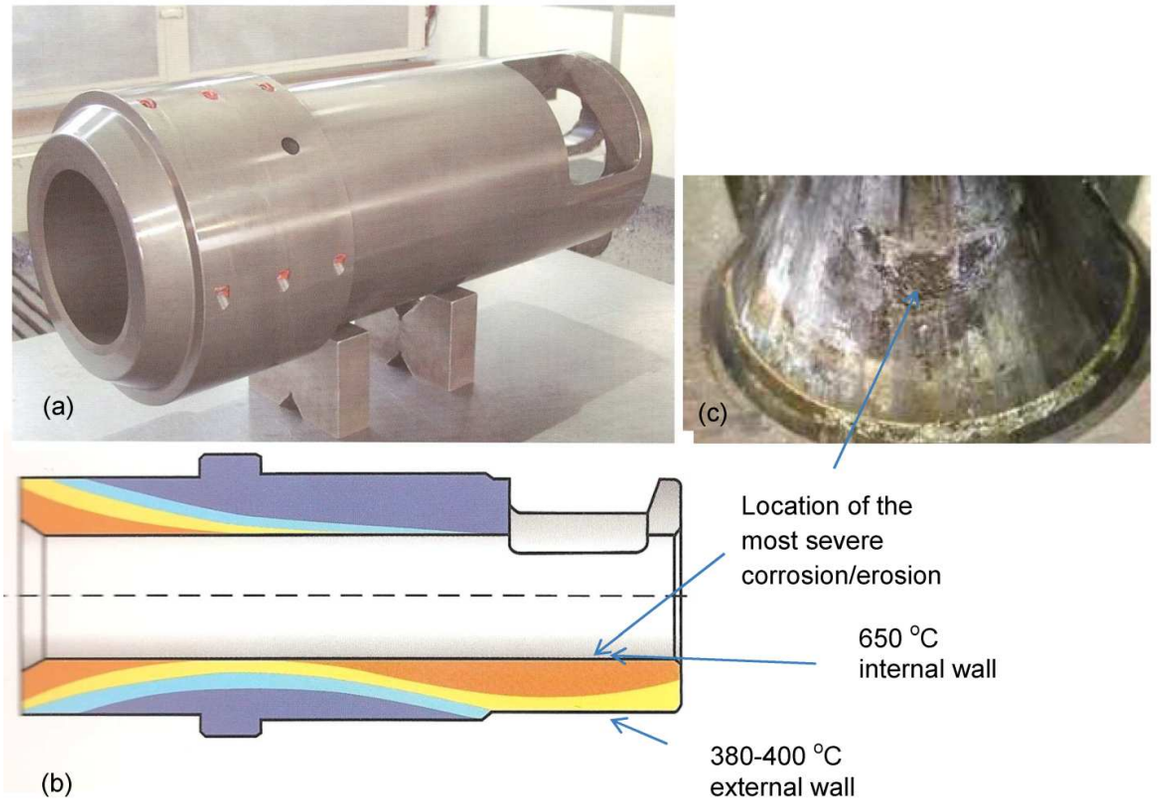


Figure 12. Design of a shot sleeve of a cold chamber die casting machine (a), schematics of temperature distribution (b) and surface deterioration due to a contact with liquid metal (c) [85].

To improve the temperature uniformity within the shot sleeve, thermoregulation is used, employing sleeve channels with circulating cooling/heating media (Fig. 13). The cooling channels help to take away the heat brought by molten alloy. As shown in Fig. 14, this solution substantially lowers the temperature difference between sleeve locations, reducing the extent of thermal fatigue. During selection of material for the shot sleeve there is a trade between

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durability and cost. As a result, the hot work tool steel of AISI H13 grade performs satisfactorily there.

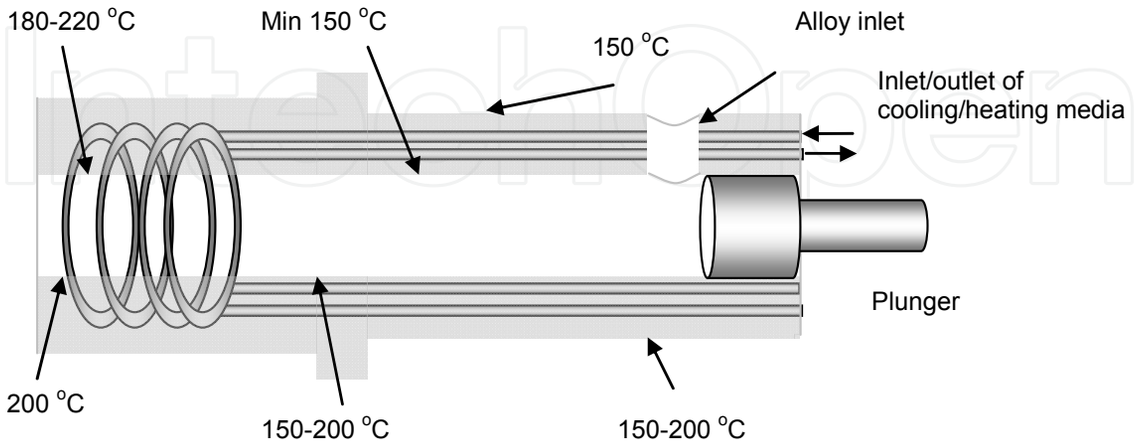


Figure 13. Schematics of thermoregulation within shot sleeve of cold chamber die casting machine [85].

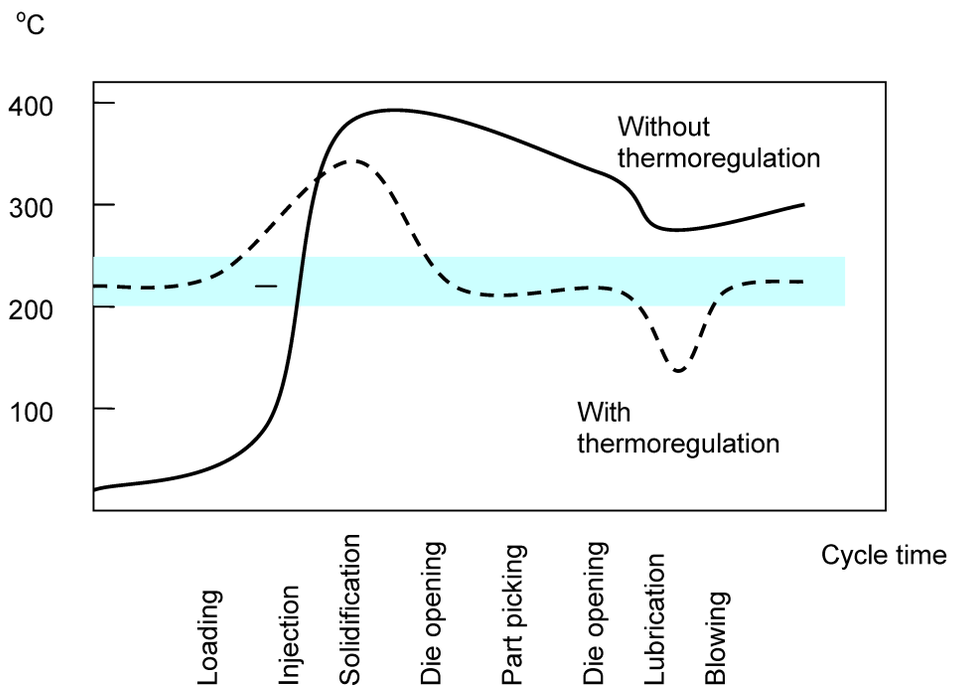


Figure 14. Temperature distribution profile within shot sleeve of cold chamber die casting machine with and without thermoregulation [85].

The hot chamber magnesium die-casting process uses a gooseneck and piston to inject molten magnesium into a die. As shown schematically in Fig. 15, the gooseneck is submerged into molten magnesium so through the side fill holes its cavity is filled with molten magnesium. The piston then forces the molten metal down from the top, delivering it through the gooseneck vertical delivery hole, nozzle and into the die without exposure to the environment. After the metal turns solid inside the die cavity, the die opens, the part is ejected and at the same time the piston retracts to its initial position above the fill holes. Then again, the die is closed, and the gooseneck is filled with molten metal and ready for the next injection cycle.

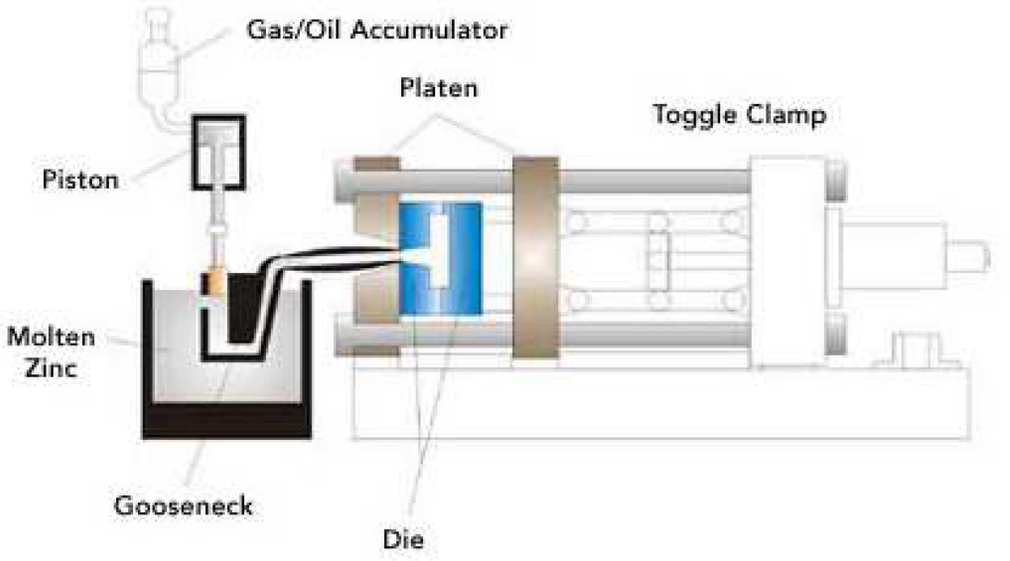


Figure 15. Schematics of hot chamber die casting machine with major components exposed to liquid magnesium alloys [84]

It is clear that more harsh conditions exist in the hot chamber machine. This is mainly because during all processing cycles, the hot chamber has a gooseneck completely submerged in molten magnesium. As a result, reduction in material strength caused by high temperature occurs, which has to be compensated by an increased size (Fig. 16). As such, the goosenecks are relatively robust. The massive component can be made of a casting using steel with high heat resistance, e.g. 1.2888 type. Due to issues with casting defects, it is frequently being replaced with wrought martensitic stainless steels, e.g. of AISI 420 type. Forging is an attractive alternative for the cast goosenecks. In the forging process, a solid billet can be shaped on open die presses, which consolidate the ingot center and eliminate porosity. It delivers a finished product that is more reliable and lasts longer [53]. Although the chemistry of AISI 420 steel provides lower resistance to tempering than DIN 1.2888, its high integrity in a wrought state may contribute to overall better performance. Another component exposed to liquid magnesium is the machine nozzle (Fig. 17a). Liquid magnesium along with melt pressure and non-uniform temperature distribution (Fig. 17b) often contribute to premature nozzle failure as seen in Fig. 17c.

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Figure 16. Goosenecks of hot chamber die casting machine: (a) part before exposure to liquid magnesium; (b, c) goose-neck after service with extensive corrosive attack [85].

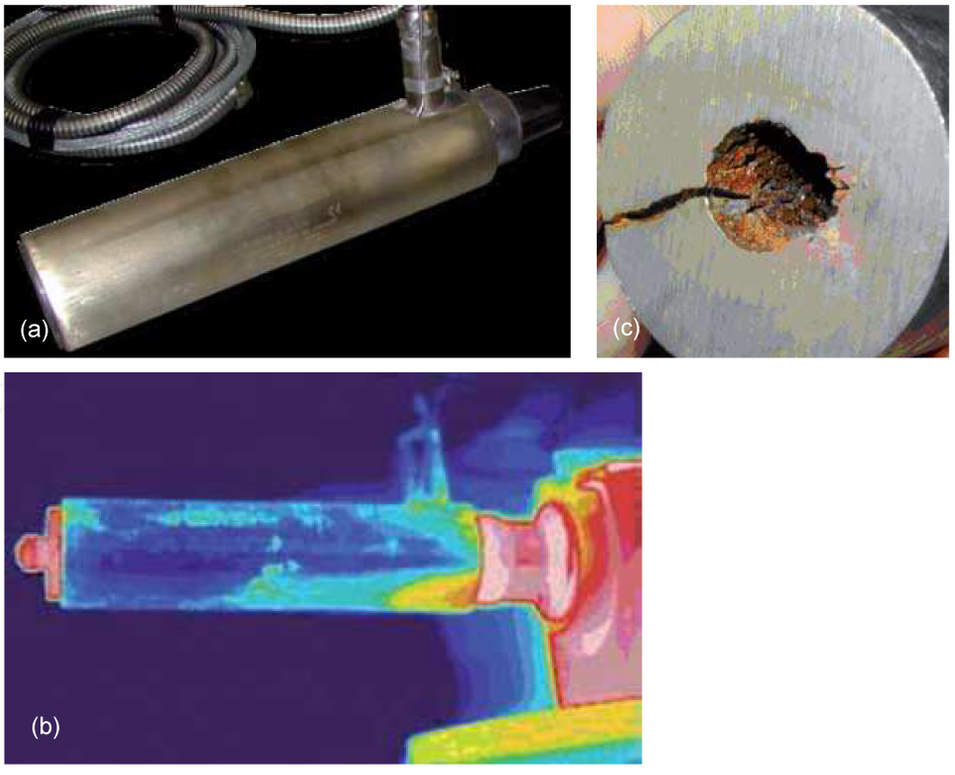


Figure 17. Nozzle of hot chamber die casting machine: (a) general view; (b) thermal profile showing temperature distribution; (c) section showing extensive corrosive attack and radial cracking [85].

5.3. Equipment of novel techniques of magnesium processing

In addition to high pressure die casting, there are a number of novel technologies at different advancement stages of commercialization, aimed at manufacturing net shape components from liquid or semisolid precursors [54] [55] [56] [57] [58] [59]. Of particular interest is equipment for semisolid processing of magnesium alloys and their composites. The key feature of machines for semisolid processing operating in thixo-mode, i. e., exploring only partial melting before injection, is reduced service temperature. Depending on the solid fraction targeted, the temperature reduction may be substantial. Instead of the overheated liquid used in die casting with a temperature of 670 °C, the process may require only 580 – 600 °C. This reduction may be of critical importance, affecting performance or even the applicability limit of some materials. At the same time, there is an essential difference in operating mode between die-casting and injection molding [1]. As opposed to short time intermittent contact, encountered between the shot sleeve of a cold chamber die casting machine and a molten metal, during injection molding the exposure of some machine components to molten alloy is permanent, reaching continuously in one interval up to thousands of hours. Moreover, while the shot sleeve of a die-casting machine has cooling channels, an injection molding barrel is extensively heated from outside. As a result, a substantial difference in service conditions renders the majority of solutions from melting and casting equipment not applicable to novel techniques of magnesium processing. Some materials with a sufficient combination of strength and corrosion resistance are still being researched [60].

6. Manufacturing techniques utilizing material combinations

The majority of materials maintaining strength at high temperatures are not chemically resistant to liquid magnesium. In fact, alloys with the best ability to maintain strength at high temperatures, easily react with molten magnesium. Therefore, separating thermal and corrosive factors increases the choices of material selection during the design of the magnesium processing equipment. The most typical techniques applicable to explore material combinations are characterized below.

6.1. Mechanical shielding

An interference-fit type connection may be used with components of specific shapes to cover the surface of an alloy which is prone to chemical attack by liquid magnesium while another alloy may be resistant against such attack. The technique applicable is called shrink-fitting and explores thermal expansion and contraction of metals to create a strong joint of a mechanical nature between two pieces, where one of each is inserted into the other. While in the past blow torches, hot plates and oil baths dominated as a heat source, the electric resistance and electromagnetic induction techniques are the commercially viable ones at present. Modern equipment allows uniform distribution of temperature with no danger of overheating by continuous monitoring the component temperature and adjusting its own heating power.

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The typical example involves shrink-fitting of two tubes where the larger one is preheated to expand its diameter. At the same time, the inner tube remains at room temperature or is additionally cooled using, e.g., dry ice (CO_2 at a temperature of –180 °C) to further reduce its diameter (Fig. 18). After an insertion of one tube into another and cooling to room temperature, both tubes are joined together. The interference value within the connection should be calculated to avoid exceeding the yield stress in both materials [61]. After excessive heating during service, simultaneous expansion of both tubes may eliminate interference and release preload. Thus, the high temperature applicability of such a connection depends on differences in coefficients of thermal expansion. The outer material cannot expand substantially more than the inner one. The connection is penetrable to air; so high temperature oxidation should be taken into account.

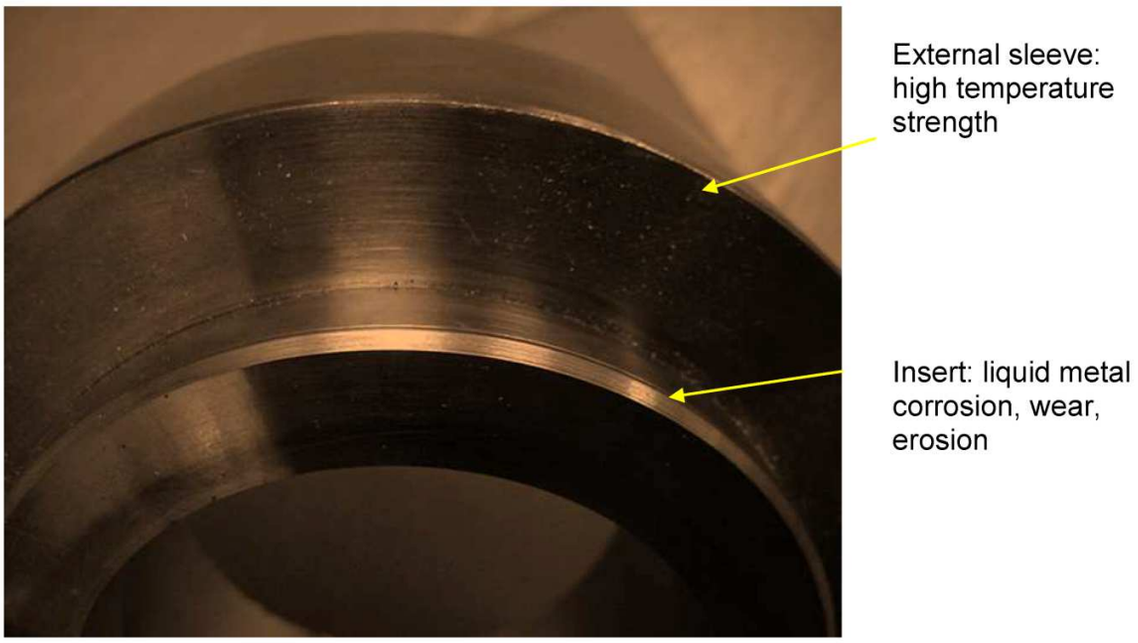


Figure 18. Concept showing tubes joined by a shrink fit method.

An application of shrink fitting is suggested for the manufacture of barrels for injection molding of magnesium [60]. In this design, an external shell with high temperature strength made of Inconel 718 superalloy is connected through shrink fitting with an internal liner made of Stellite 12 alloy. The latter one is corrosion resistant to liquid magnesium but it does not have sufficient ductility and tensile strength to withstand internal melt pressure.

6.2. Plasma transferred Arc (PTA) cladding

Cladding is a deposition of an alloy on the metallic substrate in order to modify the structure and physical characteristics of its surface required for certain applications. The most commonly used cladding techniques utilize the plasma transferred arc (PTA) and laser. PTA cladding is performed by melting of metallic, ceramic or cermets powder in a plasma arc before deposition.

Typical characteristics include high deposition rate and minimum penetration into the base (<5%). Layers up to 5 mm in a single pass can be formed with very low losses of the deposited powder. PTA gradually replaces older methods of conventional weld overlays with tungsten inert gas (TIG) or metal inert gas (MIG). The generally simple concept may become complex when applied to specific material combinations. Of particular importance for processing liquid magnesium is cladding alloys having high temperature strength with alloys resistant to wear and corrosive attack by molten magnesium.

6.3. Weld cladding of Ni-based with Co-based superalloys

Inconel 718 has good weldability and preferred techniques include gas tungsten arc, plasma arc and electron beam welding [62]. The process is performed on annealed material but the age-hardened alloys are also weldable. The post-welding treatment includes most often annealing and aging but in many instances aging is sufficient if material was welded in annealed condition. Preheating is not usually required, excluding warming up to prevent moisture condensation.

The typical defects during welding involving Inconel 718 alloy include:

i. solidification cracking, which occurs within a newly formed weld when the semisolid region experiences tensile stress and the high fraction of solid restricts the flow of liquid to fill interdenfritic regions;

ii. grain boundary liquation cracking or heat affected zone fissuring, which occurs within the heat affected zone as a result of local dissolution of grain boundary phases. Under rapid heating, the grain boundary phases area that is unable to dissolve fully into the surrounding matrix leads to formation of a low melting point eutectics and a melting of the grain boundary region;

iii. strain age cracking, which occurs during a post-weld heat treatment or high temperature service as a result of residual or applied stress. The microstructural image usually shows intergranular microcracks in either weld or heat affected zones due to precipitation and hardening of the alloy and transfer of stress on grain boundaries where hard precipitates may act as a crack nucleolus.

The Co-based alloys with high carbon content are difficult to weld. To prevent cracking, the alloy should be preheated and maintained at 540 °C minimum. The cooling rate should also be slower. While cladding Ni-base with Co-based alloys the requirements in regards of heat control are contradictory: fast cooling rate for Ni-based alloy to avoid hot cracking versus slow cooling rate for Co-based alloy to avoid cold cracks. As a possible solution it is suggested to use an underlayer. For this purpose a pure Ni or Inconel 82 layer with a thickness of 1-2 mm is recommended [63].

An application of PTA cladding for equipment used with liquid magnesium is specified in Ref. [64]. It was proposed that barrel head be manufactured of a Ni-based superalloy, such as Inconel 718, the melt channel clad with low C content, Co based compact (crack free) Stellite 21. The seal surfaces of the barrel head were clad with high C content Co based superalloy

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such as Stellite 12. The microstructure of Inconel 718 cladded with Stellite 21 is shown in Fig. 19. With Stellites in general, the primary face cubic centered cobalt dendrites are surrounded by a network of eutectic lamellae composed of cobalt and eutectic M_7C_3 carbides. The composition of M_7C_3 depends on alloy type and cooling conditions with a typical example of $Cr_{0.85}$ $Co_{0.14}$ $W_{0.01})_7C_3$ [65]. In addition to pure alloys it is also formed in a mixed zone, where chemistry of molten alloys combines.

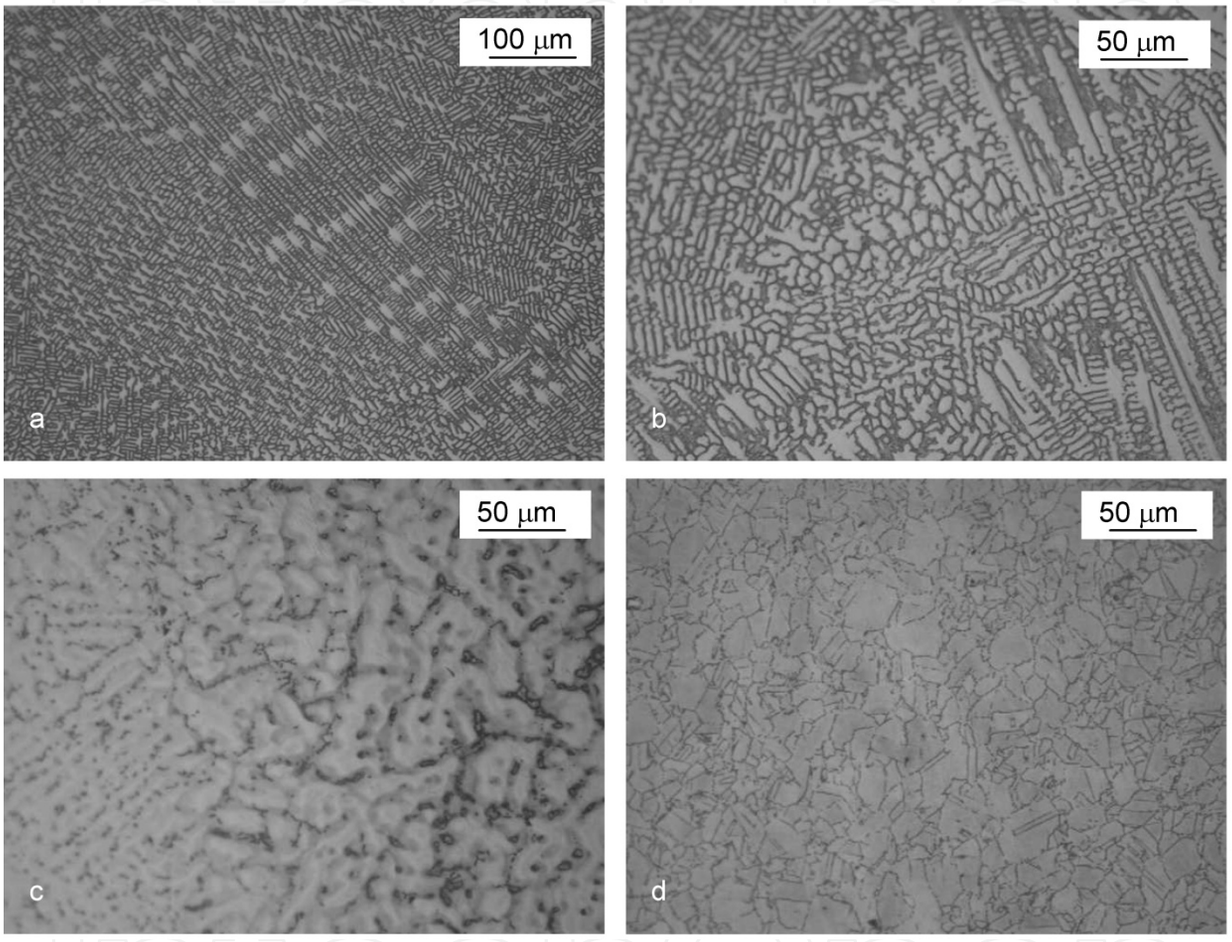


Figure 19. PTA cladding of Inconel 718 with Stellite 12 alloy: (a, b) microstructure of surface clad of Stellite 12; (c) transient zone between base and clad; (d) Inconel 718 in the substrate.

6.4. Laser cladding

Laser cladding represents the fusion of a different material to a substrate surface while ensuring the metallurgical bond with minimal melting of the substrate and chemistry dilution, as well as the small heat affected zone. It can be conducted in a single or two-stage process. In a single stage, called the blown powder cladding, the alloy powder, transported into the interaction zone between the laser beam and substrate, is subjected to heating. Melting starts at the substrate surface and powder particles form a pool. Selection of the laser energy allows to control the substrate melting. In the generally simpler, two stage cladding; the powder is

first pre-deposited on the substrate. To keep the powder on the surface, various binders are applied. Then, the powder is scanned by the laser beam while covered by an inert gas. Three distinct stages during melting of the powder are distinguished [66]:

i. first, the powder is rapidly melted by the laser before the melt gets in contact with the substrate;

ii. when the melt reaches the substrate surface, it solidifies due to a rapid flow of the heat into the substrate by conduction. There is no movement of the melt-liquid interface into the substrate;

iii. further applying the laser energy will move the former melt-solid interface deeper into the substrate.

Benefits of laser cladding include [67]: (i) very small heat-affected zone, which results in tiny deformation and stress; (ii) can be applied to virtually all metal materials; (iii) operation time is significantly shortened compared to arc welding; (iv) final product has high dimensional accuracy and integrity.

Laser cladding has application potentials in magnesium casting, e.g. in extending life time of dies/molds by increasing their wear resistance with hard surface layers to reduce erosion. By combining high wear with high tensile strength and high ductility, thermal or stress induced cracking during the casting process can be reduced. Since commonly used hot working tool steels have limited wear resistance, laser cladding is a very useful technique to improve their surface properties by multi-graded layers [68]. An application of laser cladding to deposit-Stellite 1 on AISI 4340 steel is described in Ref. [69]. Cobalt-based/carbide type alloys are well-known for their "hot hardness" and are extensively used for hardfacing of components made of conventional steels. The main challenge in deposition of Stellite 1 using laser cladding is crack sensitivity of this alloy during hardfacing process. To reduce the possibility of cracking, preheating of the substrate prior to the deposition process was tested to be effective. Investigation of die soldering during high pressure die casting led to a promising treatment with the laser clad Fe-W alloys [39]. An increased W content in the powder mix led to reduction in formation of intermetallic phases on die surface due to negligible possibility of a reaction between W and Al from Mg alloy during casting.

6.5. Centrifugal cast cladding

During centrifugal casting a liquid metal is poured into a rotating tube-like crucible and after solidification removed from it [70]. By replacing the crucible with the sleeve material, the process can be used for cladding of its inner surfaces. In addition, the liner material may be pre-applied as powder and subsequently melted while inside the sleeve [71]. The basic requirement is a safe difference between melting ranges of both alloys. The downside of this technique is that the cladded part has to be preheated to high temperatures causing coarsening of the microstructure and property reduction. An example of cladding the Inconel 718 with Stellite 12 is shown in Fig. 20. The metallurgical bonding formed assures strong connection. Due to severe overheat the grain growth occurred from an initial number 7 to number 00 according to the ASTM scale. Subsequent aging does not produce optimum phase morphol-

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ogy. On the other hand, a requirement to keep the temperature as low as possible causes incomplete melting of Stellite and individual powder particulates still remain within the liner.

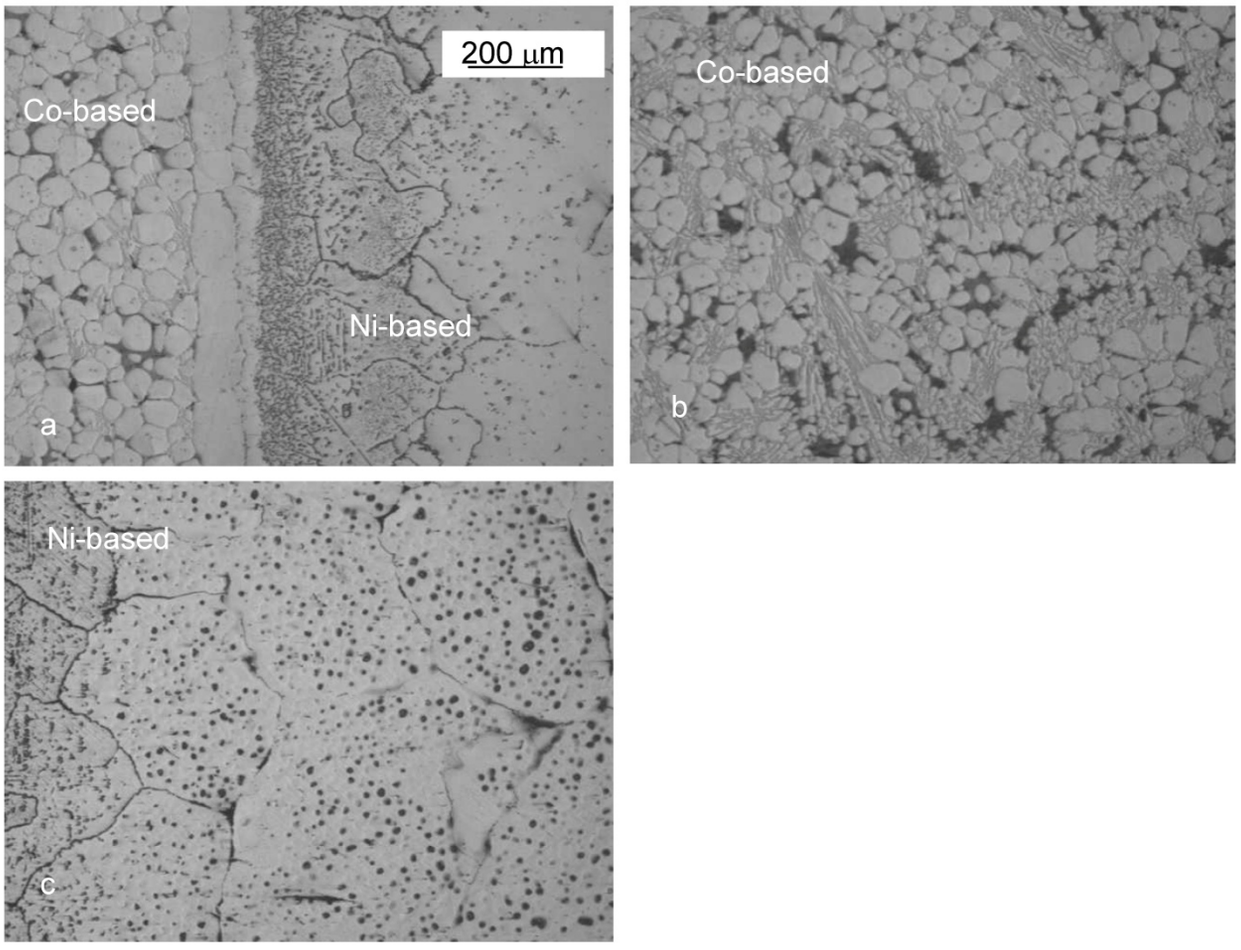


Figure 20. Microstructure of centrifugal inlay casting of Co-based alloy inside Ni-based shell: (a) interface region; (b) Co-based inner layer; (c) outer layer of Ni-based alloy.

6.6. HIP-cladding

Hot isostatic pressing (HIP) is a densification process for both encapsulated powders and pre-formed parts, e.g. castings. It was developed in 1955 at Battelle Laboratories, Columbus, Ohio to bond components of small Zircaloy-clad pin-type nuclear fuel elements while maintaining strict dimensional control. The technique involves the simultaneous application of a high pressure and elevated temperature. The isostatic nature of pressure is achieved due to its application through a gas, most frequently inert, and it should be distinguished from a conventional unidirectional pressing. The isostatic pressure in HIP-ing arises from molecules or atoms of gas colliding with the surface of the object [72]. Under conditions of heat and pressure the encapsulated powder or sintered components are densified to improve properties.

HIP-ing creates homogeneous material with a uniformly fine grain size and near 100% density. Internal voids are healed and a strong metallurgical bond is created within the entire volume. There also exists the Liquid HIP-ing, typically used for densification of castings, where to lower cost, molten salts and mechanically generated pressures are explored. HIP should also be distinguished from cold isostatic pressing (CIP) which is a compaction of powders enclosed in an elastometer mold. During manufacturing of near net shape components from a single alloy, a powder mixture of several elements is placed in a steel can container. Then air and moisture is removed from the powder by applying high temperature and vacuum. Finally, the container is sealed and HIPed. During application of HIP-ing for manufacturing of bimetallic structures, two different chemistry powders are placed into two separated chambers of the steel container. After HIP-ing is completed and external shape machined, the both alloys are separated by the interface layer, being the container wall. There is a metallurgical bond between the steel layer and alloys on its both sides. HIP ing is used to manufacture alloys such as Ni-based and Co-based superalloys [73], Nb-30Ti-20Wand also near-net shape components used for processing of molten magnesium. Besides, HIP-ing can be used for cladding selected surfaces of wrought substrates with another alloy [74]. In this process, a portion of the container is the wrought alloy. After HIP-ing, the thin steel container is machined out, leaving a bimetallic structure of wrought sleeve and powder cladding. In this technique, the HIP-ing behavior in the formation of an interfacial diffusion bonding among dissimilar materials is explored. A drawback of this type of cladding is a deteriorating effect of high temperatures required for HIP-ing on the structure of wrought alloy. In principle, the process may employ the same alloys as described above for weld cladding.

7. Surface modifications

The purpose of surface engineering is to enhance properties of superficial layers of materials by changing their chemistry and/or structure. There are two essentially different cases of surface protection, which depend on the substrate (base) material and its compatibility with molten magnesium. For materials resistant to chemical attack by molten magnesium, surface engineering aims at improving this resistance. In this case the coating failure does not lead to the catastrophic failure of the part. For materials not resistant to molten magnesium, surface engineering offers basic protection to the substrate. In this case, however, failure of the coating leads to catastrophic failure of the entire part.

7.1. Thermochemical diffusion treatments

Thermochemical diffusion is a surface treatment where the chemistry of superficial layers of materials is altered by introduction of some chemical elements from outside [75]. The atoms introduced combine with alloy elements, thus modifying existing phases and forming new ones. The major processes applicable to protection against liquid magnesium include nitriding, nitrocarburizing and boriding.

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7.1.1. Nitriding

Nitriding is a process of enriching the surface layer with nitrogen. In case of steel substrate a compound layer is developed on the surface constituted primarily of iron nitrides, Fe_4N called γ′ (gamma prime) or $Fe_{2-3}N$, called ε (epsilon). The structure of this compound zone is mainly determined by the underlying diffusion zone, which serves as a transition zone with declining hardness from the high hardness at the surface to that of the core of the material. There are several distinct approaches to nitriding [75]:

i. conventional gas nitriding, carried out in partially dissociated ammonia gas at 500-600 °C. The disadvantage is a lack of adequate control of the nitrogen concentration;

ii. gas nitriding where nitriding potential is continuously controlled taking into account varying compositions of the nitriding atmosphere during each stage of the cycle (Nitreg);

iii. ion nitriding where a plasma glow process ionizes nitrogen gas with heat causing the positive ions of nitrogen created to be drawn onto the surface of the component forming a uniform layer.

7.1.2. Ferritic nitrocarburizing

Nitrocarburizing is considered as a complementary process to nitriding and can be carried out in liquid, gaseous and plasma environments. During nitrocarburizing, the steel surface is enriched simultaneously with nitrogen and carbon. The process is carried out at 550 – 580 °C and depending on the composition of the base material and exposure time the penetration depth reaches from 200 μm to 1000 μm with a surface hardness from 700 to 850 HV. Assuming sufficiently high activities of carbon and nitrogen, the compound layer, formed at the surface, consists predominantly of ε and/or γ′ phases. Beneath it, there is a diffusion zone with N and C atoms dissolved interstitially in the ferrite lattice. While the compound layer brings a combination of resistance to wear and atmospheric corrosion, the diffusion zone improves the endurance limit [76].

It should be stated that steel nitriding is widely used for cold chamber die casting shot sleeves, die/mold surface, die pins, piston rings etc. Its effectiveness is limited, at least for some applications, first because chemistry of steels used for machinery of magnesium processing are not optimized for nitriding or nitrocarburizing. Moreover, high service temperature may diffuse away nitrogen from the surface layer, deteriorating its properties over time. An example of an H13 commercial piston ring from a cold chamber die casting machine is shown in Fig. 21. Although due to temperature experienced in service the initial case hardness, along with hardness of the base substrate are reduced, the overall ring performance after nitriding is substantially improved.

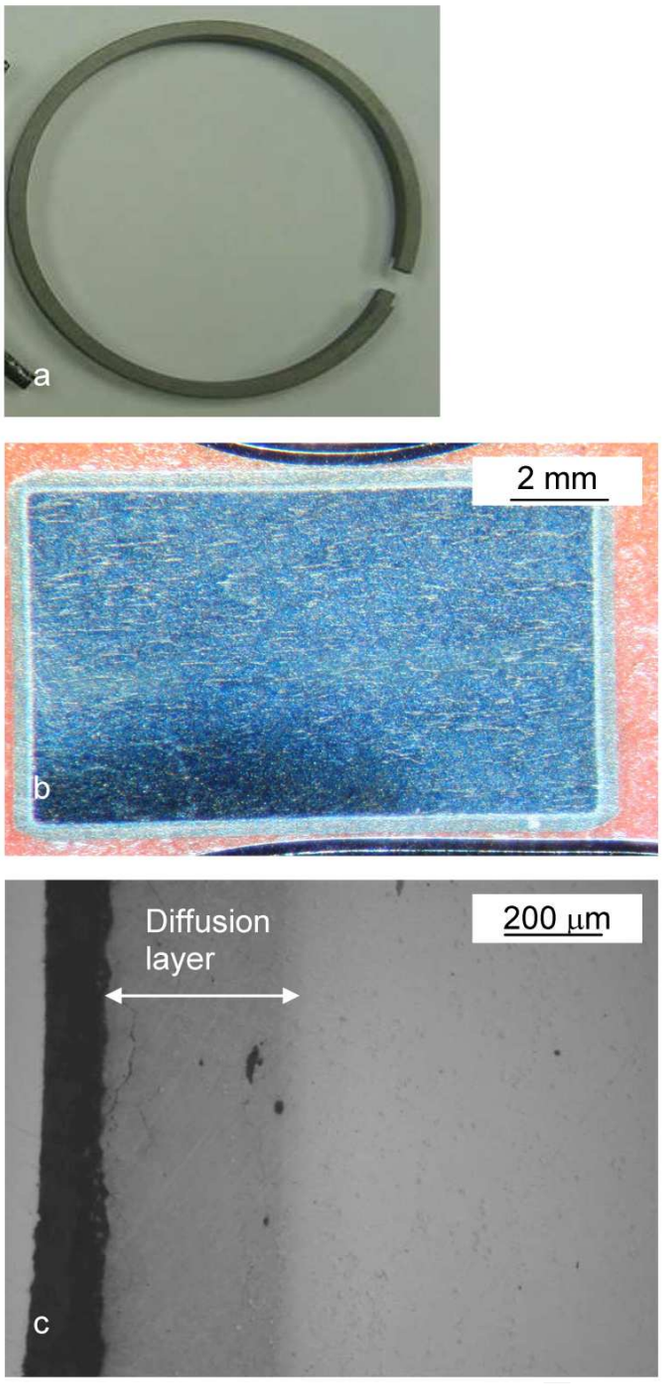


Figure 21. Nitrided layer on the H13 steel used for die cast piston ring: (a) piston ring; (b) macro cross section showing thick nitrided layer; (c) micro image showing the nitrogen penetration range.

7.1.3. Boriding (boronizing)

Boriding means an enrichment of the surface layer of the material with the elemental boron. Unlike nitriding, boriding is carried out at significantly higher temperatures, typically between 800 and 1000 °C [77]. Various implementation technologies include packing with solid

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mixtures of boron carbide and borax as the boron source, molten salt performed using anhydroux borax mixed with reducing agents, electrolytic carried out in an argon atmosphere using borax-based melts, plasma and vacuum boriding [78]. The surface hardness is in the range of 1500-2000 HV, which exceeds nitriding and nitrocarburizing. The technique may be applied to ferrous and nonferrous metals and alloys, e.g. Ti, Ni or Co. Depending on the substrate chemistry, the surface layer forms different compounds. For steel, Fe_2B is the major compound formed. For Ni the major compound is Ni_3B while boriding Co produced both Co_4B and Co_3B. The boriding treatment was explored to prevent soldering during Mg die casting.

7.1.4. Thermo-reactive diffusion (TRD)

The vanadium carbide thermo reactive diffusion creates a 5 – 10 μm thick surface layer with a hardness of 3200 – 3800 HV. The process is conducted in a packed or molten salt environment, where active vanadium enters the surface and combines with carbon atoms from steel to form vanadium carbides [79]. Vanadizing is performed at temperatures of 800 – 1000 °C. Thickness is well controllable by adjusting diffusion time and temperature for a given environment and steel chemistry. The layer has a very strong metallurgical-diffusion bond to the substrate, providing high peeling resistance. Thermo-reactive diffusion was originally developed to improve wear resistance. It has a thermal expansion mismatch with chromium hot work tool steel AISI H13. According to some data a minimum carbon content should be 0.3%. The process is effective in die casting operations and explored especially in Europe and Japan. The major parts treated include die casting cores and pins. According to [80], for Al casting, TRD coatings led to higher increase in tool life than nitriding. As a partial explanation is given that VC resists aluminum diffusion through the surface layer.

7.2. Coatings

According to general selection rules the coating should have high hardness and strength and moderate ductility. Its thermal conductivity, melting point and density should also be high while the coefficient of thermal expansion and coefficient of friction should be low [81]. Due to harsh environment of molten Mg, of a large number of coating techniques and coating chemistries, only several were found to provide improvement. Below is provided their brief characterization.

7.2.1. Physical vapor deposition (PVD)

PVD includes coating techniques where the transport of atoms or molecules to the coated surface is accomplished by a physical process. The technique of line-of-sight coating of complex geometries is difficult. The low deposition temperature of 100 – 500 °C minimally affects the substrate structure. Due to low temperature, however, it is difficult to achieve great adhesion. The coating chemistries applicable to Mg processing are given in Table 4 with indications of their thermal stability.

Name	Formula	Colour	Thermal Stability, °C	Hardness, HV	Typical thickness, µm	Characteristic features
Titanium nitride	TiN	Gold	600	2300	2-5	Used for moderate abrasions, ductile hard coat
Titanium carbonitride	TiCN	Grey-pink	410	3000	2-5	Shock resistance
Titanium aluminum nitride	TiAlN	Brown	800	3500	2-5	Extreme heat resistance
Zirconium nitride	ZrN	Yellow-gold	650	2600	2-5	Excellent lubricity
Chromium nitride	CrN	Silver	1750	695	2-10	Good wear resistance
Titanium diboride	TiB2	Silver	900	4000	1-2	High corrosion resistance, chemical stability at elevated temperatures
Titanium boron nitride	TiBN	Silver	800	3500	1-5	Heat-checking resistance, abrasive wear resistance

Table 4. Selection of PVD coatings applicable for components of magnesium processing equipment exposed to liquid magnesium alloys [89] [90] [91]

The general finding in regards to selected components of Mg processing equipment is that coatings provide substantial improvement against sticking of Mg to the surface and reduction of an overall degradation of a corrosive nature. This often allows the elimination of an acidizing step during cleaning and caused by this hydrogen ingress into the base. At the same time, however, 2-5 micron thick TiAlN coatings with mechanical bond to the substrate show severe limitations since they:

i. do not provide long lasting improvement in the extent of wear between metallic couples;

ii. do not provide a lasting chemical barrier with high integrity to separate the base material from liquid magnesium.

The barrier integrity is lost not only by the above named surface degradation mechanisms, but also by localized wear caused by hard particles which may enter the melt stream. During die casting of magnesium, tests of several PVD coatings [39], TiN on ground H13 steel were showing good performance. In contrast, PVD coating of CrN was dissolving with an intermetallics formed on its top, especially in Mg alloys with higher Al content.

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7.2.2. Chemical vapor deposition (CVD)

The CVD process uses chemical reactions to deposit coatings on the substrate. In general, the process is carried out at higher temperatures than PVD, up to 2200 °C which provides excellent adhesion. The temperature requirement reduces markedly a number of applicable substrates. Since the nature of CVD is non line-of-sight, it can be used to evenly coat complex geometries and internal surfaces. The typical chemistries deposited with CVD include CrC, TiN and VC. An applicability to liquid Mg of CVD coating itself is the same as discussed above for PVD method.

7.2.3. Thermal spray

During thermal spraying, the wire or powder materials are melted into droplets, and then propelled onto the selected substrate. Upon impact, they form platelets that bond to the surface, creating a dense coating with no alteration to the substrate structure. The technique allows the deposition of pure metals, alloys, intermetallics, carbides and ceramics. There are several techniques applicable for deposition spray coatings:

i. combustion flame spray, achieved by burning a mixture of oxygen and fuel gas in a torch having a flame-accelerating nozzle. Powder is injected into the nozzle by the carrier gas, where it melts and is projected to the surface;

ii. electric arc spray, achieved by energizing two wires of the coating material at different electrical potentials. Molten particles are generated by arcing the wire tips which are then atomized and accelerated towards the substrate by a compressed gas;

iii. hypervelocity oxygen fuel spray (HVOF) is achieved by burning a pressurized mixture of the fuel gas and oxygen. Powder is fed into the stream of hot gases and discharged through a flow expansion zone;

iv. plasma spray, achieved by exploring the heat transfer for electric arc to a plasma-forming gas. In the spray device the gas flow contains an axial stick cathode while the nozzle forms the anode. Heated to high temperatures gas ionizes to plasma. Powder, injected into the exit melts and is accelerated by hot gases towards the surface. Special cooling techniques keep the surface temperature low.

An example of thermal spray coating is shown in Fig. 22a. The top end represents a 0.13 mm thick ceramic coating of YSZ (yttria stabilized zirconia) which exhibits very low thermal conductivity and provides thermal insulation. The lower cylindrical portion is covered with a 0.2 mm thick metallic coating of NiCr6Al providing oxidation resistance up to 980 °C. In some cases the ceramic coatings are too brittle to withstand mechanical stress. To minimize their brittle nature the ceramic coatings may be used in a combination with metallic support. An example of the solution is given in Fig. 22b. The metallic grid provides support and reduces surface contact while the ceramic coating, filling gaps between them, reduces the heat transfer.

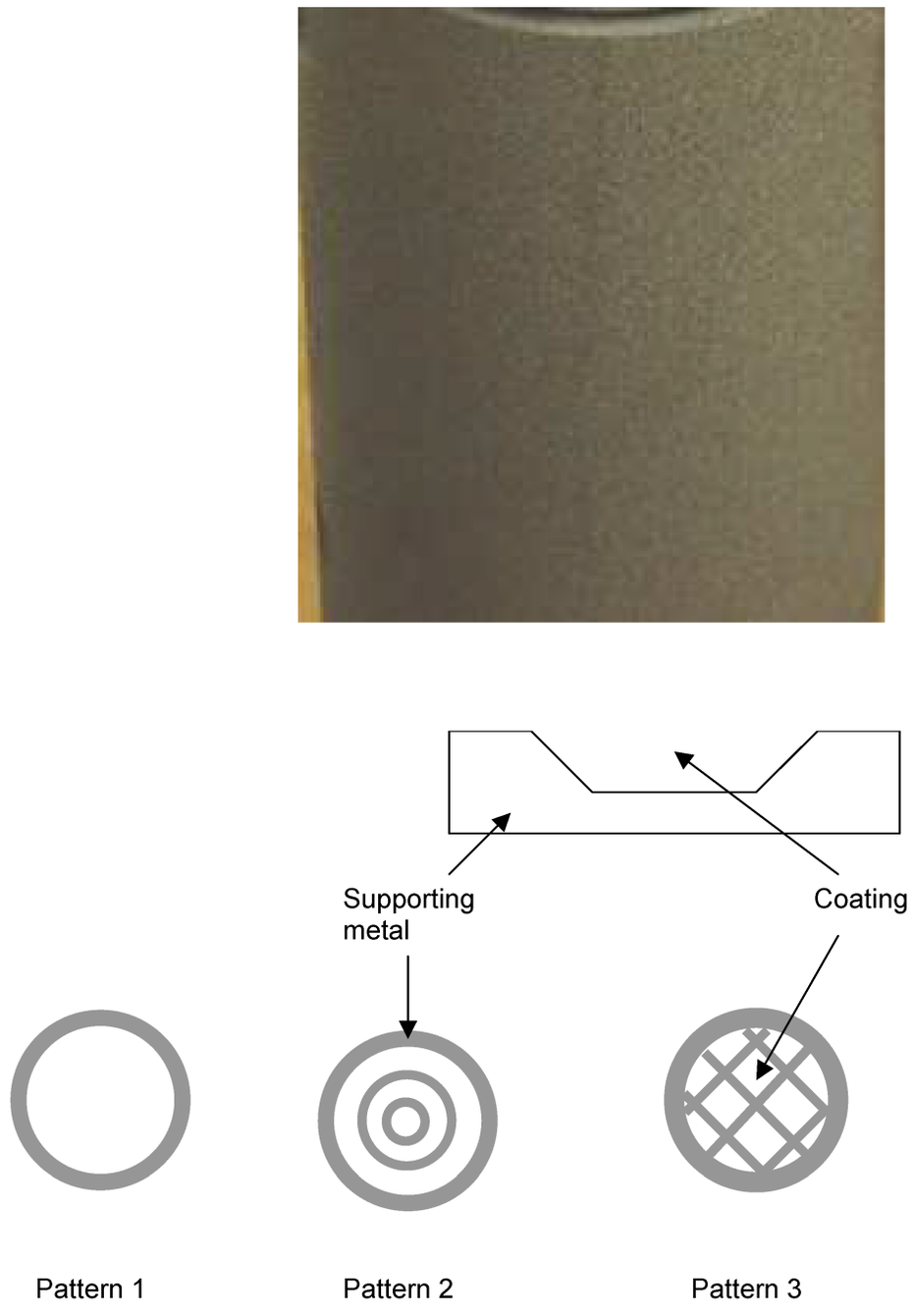


Figure 22. Ceramic coating of YSZ (yttria stabilized zirconia) deposited by thermal spray (a) macro view of the coating; (b) concept of the surface grooving pattern to support the brittle ceramic coating during impact.

7.3. Hybrids of surface treatments

Due to harsh service conditions of Mg processing, in some cases a single surface treatment may not be sufficient. It is claimed that single coating cannot eliminate completely the deteriorating effect of liquid magnesium alloys. Thus, in order to maximize the substrate protection, two or more surface modification techniques are combined. The multilayer hybrids

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combine advantages of individual layers. A concept, explaining the mechanism of substrate protection by multilayer coatings is shown in Fig. 23.

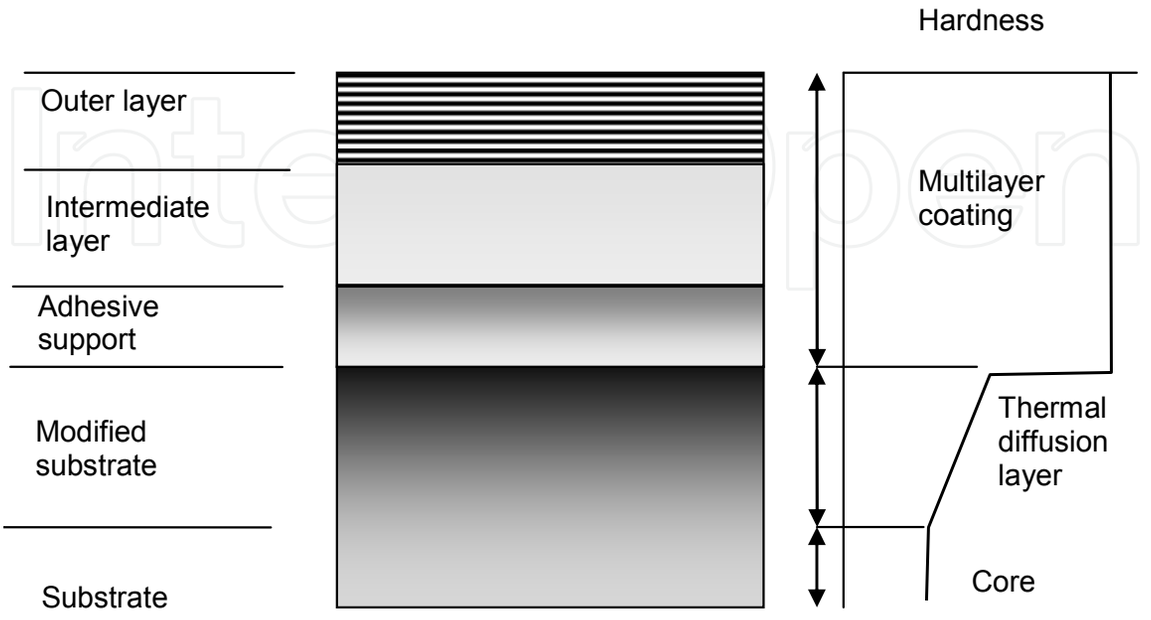


Figure 23. Concept of multilayer coatings deposited by PVD onto a steel surface enhanced by thermochemical diffusion

7.3.1. A combination of thermal diffusion layers with coating

The performance of coatings, especially those thin ones, depends on the properties of the substrate. It is clear that a hard coating will not last on soft substrate since it will crack and spall. In order to improve coating performance, substrates are subjected to special treatments. The most common is thermochemical diffusion treatment e.g. nitriding. Then, a coating is deposited on the top of the diffusion layer. An additional benefit is that in case of local failure of the coating, a diffusion layer may still protect the substrate. While this combination generally provides improvement, for some cases the substrate effect is negative. According to [39], TiN and CrN PVD coatings deposited on nitrided H13 steel showed poor adhesion and during Mg die casting process peeled off from the substrate. The poor performance was attributed to the decomposition of Fe-N nitride layer at increased temperatures due to diffusion of nitrogen.

7.3.2. Multilayer coatings

The progress in deposition technology allows the automatic control of the process so multilayer coatings may be formed. In practice, individual sub-layers will differ in terms of chemistry and structure. The properties of such a conglomerate exceed the properties of individual sub-layers. This method represents new type of surface treatment. In addition to coating conglomerates, multi-layer coating can be combined with diffusion treatment of the substrate. During trials with die casting of magnesium [39], the best performance was reached with multilayer

PVD TiN/CrN coatings which completely suppressed formation of intermetallics. In contrast, duplex TiN/CrN coatings did not show an improvement over single layer of TiN. When deposited on nitrided steel surface, decomposition of the Fe-N white layer due to internal diffusion reduced the coating performance.

8. Summary

The high temperature and corrosive attack of molten magnesium alloys impose a challenge on the selection of materials applicable for the hardware used for their processing. This challenge is magnified in the case of novel processing techniques where performance of materials used in conventional equipment of magnesium casting and handling is not satisfactory. Although modern metallurgy provides solutions to present requirements, the research continues to develop alloys capable of increasing the processing temperatures and extending the service life time of processing equipment.

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