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Methods of introducing alloying elements into liquid magnesium

Wprowadzanie dodatków stopowych do ciekłego magnezu

Abstract

In recent years, magnesium alloys have gained widespread popularity as construction materials. This is due to their low density, high strength properties, and advances in their production technology. Properties of magnesium alloys depend primarily on the type, quantity, and quality of elements present in their composition. It is therefore necessary to carry out research on the further optimisation of the production technology of these alloys.

This article presents the results of studies carried out in order to determine the type, form, and parameters of the process of introducing selected alloying elements to magnesium in a manner which enables the manufacture of alloys with predetermined chemical composition. As part of the work, elements such as Al, Zn, Mn, Zr, Si, Cu, Ca, as well as rare earth elements (RE) were introduced into the liquid magnesium. The alloying elements were introduced into the melt at different temperatures in either a metallic form or as master alloys. While conducting studies, respective solubility graphs were plotted for the alloying elements showing the time taken for each element to dissolve to the required form at a specific temperature and concentration. The studies resulted in the development of several techniques of introducing selected alloying elements, which enabled the manufacture of various types of alloys.

Keywords: magnesium, magnesium alloys, alloying elements, magnesium castings

Streszczenie

W ostatnich latach stopy magnezu cieszą się coraz większym zainteresowaniem jako materiały konstrukcyjne. Związane jest to z ich niską gęstością, dobrymi własnościami wytrzymałościowymi oraz postępem w technologii ich wytwarzania. Własności stopów magnezu zależą głównie od rodzaju, ilości i jakości pierwiastków wchodzących w ich skład. Konieczne zatem jest prowadzenie

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badań nad optymalizacją technologii otrzymywania stopów na osnowie magnezu.W artykule przedstawiono wyniki badań mających na celu określenie sposobu, postaci i parametrów wprowadzania wybranych dodatków stopowych do magnezu tak, aby możliwe było otrzymanie stopów o założonym składzie chemicznym. W ramach pracy do ciekłego magnezu wprowadzano pierwiastki stopowe, takie jak: Al, Zn, Mn, Zr, Si, Cu, Ca oraz pierwiastki ziem rzadkich (RE). Składniki stopowe wprowadzano do ciekłego magnezu w postaci metalicznej oraz zapraw w różnych temperaturach. Podczas realizacji badań wyznaczono wykresy rozpuszczalności dodatków stopowych przedstawiające czas potrzebny na rozpuszczenie pierwiastka w danej postaci, przy określonej temperaturze i koncentracji. Przeprowadzone badania umożliwiły opracowanie technologii wprowadzania wybranych dodatków stopowych, dzięki czemu możliwe jest wytwarzanie różnych gatunków stopów.

Słowa kluczowe: magnez, stopy magnezu, dodatki stopowe, odlewanie magnezu

1. Introduction

Owing to its density of 1.74 g/cm^3, magnesium is the lightest metal used for various types of construction. Magnesium is approximately 35% lighter than aluminium, 60% lighter than titanium, and up to 75% lighter than steel or iron (Fig. 1).

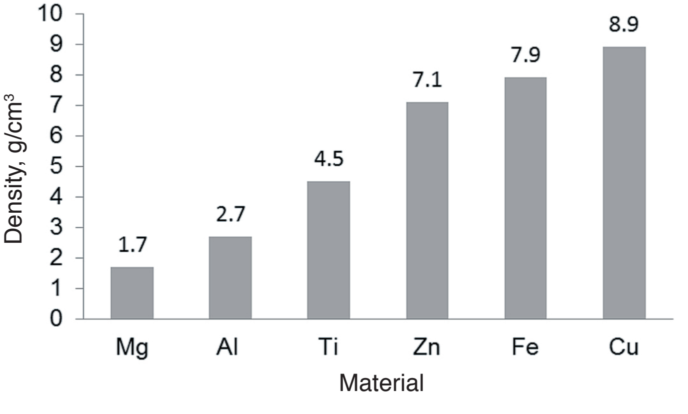

Fig. 1. Density of selected elements

Magnesium is characterised by a very high chemical activity, and a thin porous layer of magnesium oxide is formed on the surface when reacting with oxygen. Above 425°C, magnesium and its alloys have a tendency to oxidize, and at very high temperatures, they burn with a white flame when in contact with moist air. This presents serious difficulties in melting and casting. These factors require the use of preventive measures such as a protective gas atmosphere (e.g., dry air, N_2, Ar, SO_2, CO_2, SF_6, CF_3CH_2F), or various types of salts (KCl, MgF_2, CaF_2, MgO, $MgCl_2$) [1, 2].

Pure magnesium has low mechanical properties and, therefore, is produced in the form of alloys offering improved strength, corrosion resistance, and functional properties.

The melting point of pure magnesium is 650°C; however, for magnesium alloys containing various alloying elements in different concentrations, the temperature liquidus is comprised in the range of 560–700°C.

Magnesium alloys usually contain over 90% magnesium. Currently, the most commonly used magnesium alloys are those of aluminium, zinc, and manganese. The composition of magnesium alloys also includes other alloying elements that shape the properties, such as zirconium, calcium, copper, silicon, silver, tin, and lithium as well as rare earth elements (i.e., cerium, lanthanum, neodymium and praseodymium) (Tab. 1, Fig. 2) [1–3].

Table 1. The density and melting points of the selected alloying elements used in magnesium alloys [3–5]

Element	**ASTM designation system**	**Density, g/cm³**	**Melting temperature, °C**
Li	L	0.53	181
Ca	–	1.54	842
Mg	–	1.75	649
Si	S	2.33	1410
Al	A	2.70	660
Y	W	4.47	1522
La	E*	6.16	920
Pr	E*	6.48	931
Zr	K	6.52	1852
Ce	E*	6.77	798
Nd	E*	7.00	1010
Zn	Z	7.14	420
Mn	M	7.20	1244
Sn	T	7.28	232
Cu	C	8.92	1083
Ag	Q	10.5	961

* E – rare earths

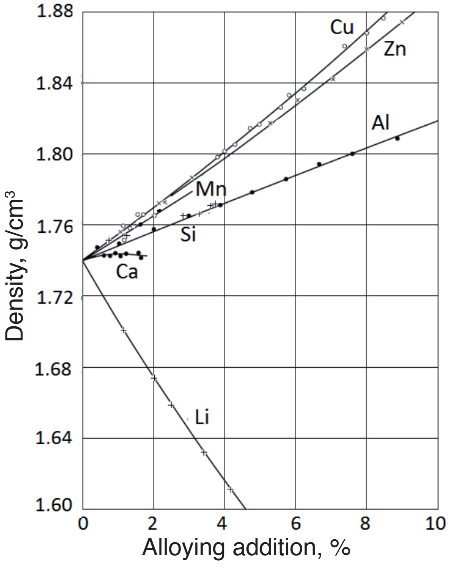

Fig. 2. Influence of alloying elements on the density of magnesium at room temperature [1]

Alloying elements present in magnesium alloys

Aluminium is the most commonly used alloying element; its content usually does not exceed 10%.

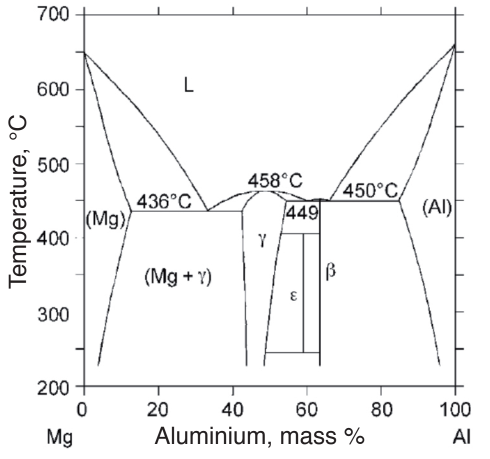

Fig. 3. Phase diagram of Mg-Al system [1]

Aluminium is one of the few metals that easily dissolve in magnesium, and its solubility limit at the eutectic temperature is approx. 12.7%, decreasing to 1% at room temperature (Fig. 3). This increases mechanical properties, corrosion resistance, and castability.

It also reduces casting contraction, but causes hot shortness. The highest strength is obtained at an aluminium concentration of approximately 5%. Alloys containing more than 6% Al are heat treatable. The presence of aluminium also abates the tendency of magnesium alloys to burning. Together with Al, other elements are also present, such as Mn, Zn, Si, and Li (AM, AZ, AS, LA alloys) [1, 3, 5, 6].

Zinc is the second most commonly used alloying element right after aluminium. The addition of zinc to magnesium alloys generally does not exceed 6%, and in the presence of Al and Mn raises strength and yield stress. Alloys containing approximately 5% Zn have the highest strength and ductility. Zinc also improves the corrosion properties of magnesium alloys. The undesirable phenomena related to the presence of zinc in higher concentrations are microporosity defects and hot shortness.

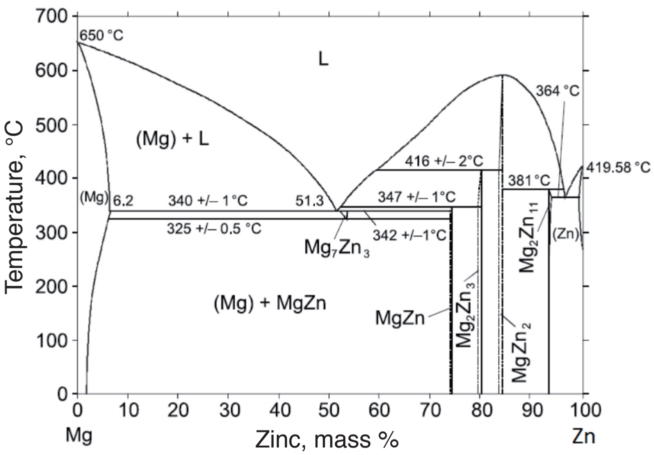

Fig. 4. Phase diagram of Mg-Zn system [1]

Zinc is readily soluble in magnesium, and its maximum solubility is 6.2% (Fig. 4). Magnesium-zinc alloys also contain elements such as zirconium, rare earth metals, and copper (ZK, ZH, ZM, ZC, ZE alloys) [2, 3, 5, 6].

Manganese is a component present in the majority of alloys; however, it is rarely used alone. Its content usually does not exceed 1.5%. In aluminium-containing alloys, manganese combines with the harmful contamination that is iron, and at the same time increases corrosion resistance. Manganese also improves yield strength and weldability slightly.

At a temperature of 652°C, manganese solubility amounts to about 2% (Fig. 5). It is used in alloys containing (among others) Al, Zn, Si, and Cu (AZ, AM, AS, ZC alloys) [1–3, 5].

Zirconium – its concentration does not exceed 1%; it refines the structure, thus improving the mechanical properties and machinability of the alloys. It can be used in alloys containing zinc, rare earth elements, thorium, yttrium, or combinations of these elements

(ZK, ZE, WE, EQ, K1A alloys). On the other hand, it can not be used in alloys containing aluminium or manganese, as it tends to form stable compounds with these elements. Zirconium also forms intermetallic phases with such elements as Fe, H, C, O, and N.

The solubility of zirconium in magnesium is 3.8%; but at 650°C, it only approaches 0.6% (Fig. 6) [1–3, 5, 6].

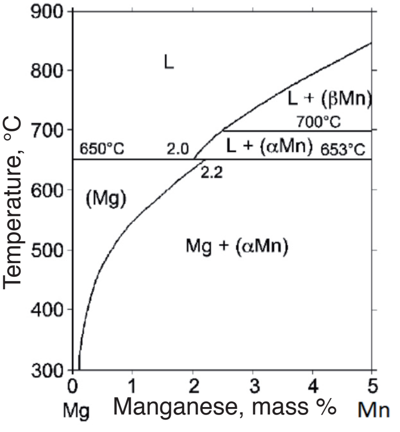

Fig. 5. Phase diagram of Mg-Mn system [1]

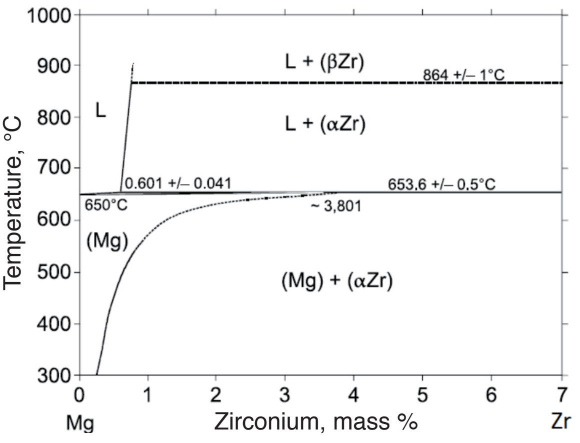

Fig. 6. Phase diagram of Mg-Zr system [1]

Addition of Silicon in magnesium alloys does not exceed 1.5%. It reduces corrosion resistance due to the presence of iron. It is added to improve castability as well as raise the mechanical properties and creep behaviour at elevated temperatures. This element is used (among others) with Al, Zn, and Mn (AS alloys) [1, 3, 5, 6].

Copper in magnesium produces intermetallic compounds of Mg_2Cu. Like with silicon, a concentration above 0.05% adversely affects the corrosion resistance of alloys, but it improves high temperature strength while reducing ductility. Copper is present (among others) with Zn and Mn [1, 3, 6].

Calcium in small amounts (up to 0.3%) is used to reduce magnesium oxidability and improve rollability. It has a positive impact on grain refinement, strength properties, and creep resistance. In a concentration above 1%, it significantly reduces strength properties [2, 4].

Rare earth metals (RE) like silicon and copper are beneficial for strength and creep resistance at elevated temperatures. They also raise corrosion resistance. Due to their high price, they are most frequently added in the form of "mischmetal" or "didymium." "Mischmetal" is a natural mixture of rare earth elements which contains approximately:

- 50% cerium,
- 25–35% lanthanum,
- 10–15% neodymium,
- 5–10% praseodymium.

"Didymium", in turn, is a mixture of approximately 85% neodymium and 15% praseodymium. These elements are used in alloys containing zinc and zirconium (ZE, WE, EQ alloys) [1–3, 6].

Yttrium is added with other rare earth metals to increase the strength of alloys at elevated temperatures (WE alloys) [6].

Lithium is used to reduce the density of magnesium alloys, as its specific gravity is 0.53 g/cm^3. Its addition results in a decrease of strength combined with increased ductility. Lithium has a highly-adverse effect on magnesium oxidation behaviour and burning during casting. Lithium alloys are of limited use due to their relatively-high price [2, 5].

Beryllium is a highly-carcinogenic element. As such, it may be added only in small amounts of 2–10 ppm to reduce the tendency of oxidation during melting and casting. Introduced in larger amounts, it may result in grain growth [6].

Silver improves the mechanical properties at elevated temperatures and is used in alloys containing zirconium and rare earth elements (EQ, QH alloys). Its use is limited due to its high price [1–3].

Thorium is one of the most effective elements to increase creep strength at elevated temperatures. However, due to its radioactivity, it has been decommissioned and replaced by other elements [2].

Tin increases yield strength and is used together with Al and Mn in magnesium alloys [3, 5].

Iron and nickel are extremely harmful contaminants in amounts above 0.005%, reducing corrosion resistance. In certain commercial alloys, the acceptable content of these elements may be 0.01–0.03% [1, 3, 5, 6].

The selection of appropriate alloying elements, as well as the selection of a method and parameters of their introduction into the melt influence both casting and mechanical properties (Fig. 7).

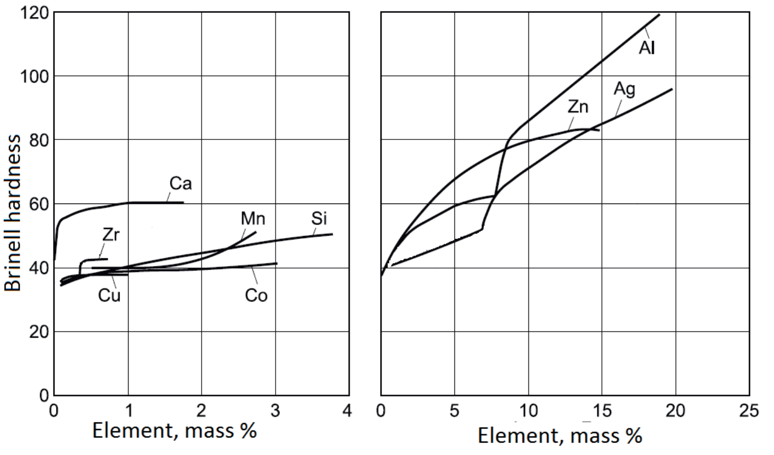

Fig. 7. Influence of alloying elements on hardness [1]

Magnesium alloys can be divided into casting alloys and wrought alloys with a breakdown into several groups (Tab. 2). Alloys belonging to both groups are heat treatable. The casting magnesium alloys usually contain more alloying elements than wrought alloys. Magnesium alloys can also be divided into alloys with and without aluminium.

Table 2. Most casting and wrought alloys [1–3]

Group of alloys	Designation alloy	
	USA / ASTM	International / ISO
MgAlZn	AZ31	MgAl3Zn1
	AZ61	MgAl6Zn1
	AZ80	MgAl8Zn
	AZ91	MgAl9Zn1
MgAlMn	AM50	MgAl5Mn
	AM60	MgAl6Mn
MgZnZr	ZK51	MgZn5Zr
	ZK60	MgZn6Zr
	ZK61	MgZn6Zr
MgZnREZr	ZE41	MgZn4RE1Zr
	EZ33	MgRe3Zn2Zr
MgAlSi	AS21	MgAl2Si
	AS41	MgAl4Si
MgZnCu	ZC63	MgZn6Cu3Mn
MgYREZr	WE54	MgY5RE4Zr
MgREAgZr	EQ21	MgRE2Ag1Zr

The most popular and, at the same time, the "oldest" magnesium-based alloys are alloys included in the AZ family. They are characterised by low price, good casting and mechanical properties, and fairly good resistance to corrosion. The following alloys have found the widest range of application: AZ91, AZ61, and AZ31 (containing 9%, 6%, and 3% Al, respectively) and about 1% Zn. Another popular group of alloys form the AM alloys, which are expected to offer improved conductivity and resistance to cracking. In this group, the most-widely-used alloys are AM50 and AM60 (containing 5% and 6% Al, respectively) and the addition of Mn. The third group of alloys covers alloys containing Zr (ZK alloys), of which the most-commonly-used are ZK60 and ZK61. Their use is, however, limited due to their lack of weldability. So far, they have gained popularity as alloys for plastic working. Another group comprises alloys containing (among others) rare earth elements improving the mechanical properties at elevated temperatures (ZE, EZ, WE, EQ, and QE alloys). Further groups of alloys with high mechanical stability at elevated temperatures include alloys with silicon (AS alloys) and copper (ZC alloys). For some time, interest as biodegradable materials has aroused the use the ultra-light magnesium alloys with lithium and calcium [1–3, 5–7].

Magnesium alloys have the highest tensile strength-to-density ratio (Rm/ρ). They have good damping capacity and weldability. Their disadvantages include poor ductility and impact strength, low corrosion resistance, and high affinity for oxygen. Today, thanks to progress in technology and new manufacturing methods, magnesium alloys are widely used in various industries. It should also be noted that the scope of their application as a construction material continues to grow. The greatest interest in magnesium components can be seen in all applications where component weight is of crucial importance, such as (among others) the automotive and aerospace industries, electronics, energy, medical and military areas, and cosmonautics [2, 7, 8].

2. Research methodology

During the manufacture of magnesium alloys, alloying elements are introduced into liquid magnesium in various forms and at various temperatures. Depending on the alloy grade that we want to obtain, adjustments are made in the concentration of individual elements as well as the time required for their dissolution. Time also depends on the size of the lumps of the added elements and on melt stirring intensity. Alloying elements must be properly selected to ensure that the produced alloy meets the requirements of high purity.

Table 3 shows the maximum concentration of selected alloying elements in magnesium alloys and in which concentrations the elements were added.

Table 3. Maximum concentrations of selected alloying elements

Element	Al	Zn	Mn	Zr	Si	Cu	Ca	RE
Maximum concentration [wt. %]	10.0	6.0	1.5	1.0	1.5	3.0	6.0	5.0

Tests were carried out in a 10-kg-capacity resistance furnace for magnesium melting, using a protective atmosphere consisting of a mixture of Ar and SF_6. The batch of charge was composed of cut Mg99.8 ingots and alloying elements, which were always preheated before being introduced into the melt. The total of all alloying elements introduced to each melt was 6 kg. The values of temperature at which the alloying elements were introduced were chosen basing on literature data and on the knowledge and experience of the authors.

To best illustrate the results of our studies, solubility graphs of the alloying elements were plotted. To determine the time required for the dissolution of an element, samples of chemical composition were taken after the lapse of 5, 10, 15, 20, 25, 30, 45, 60, and 90 minutes from the introduction of the element. The melt was stirred before sampling for chemical analysis.

The content of Ca was determined by atomic absorption spectrometry (AAS), while the content of other elements was determined by optical emission spectrometry (OES). On each sample, four measurements were taken for the analysis of chemical composition. The obtained results were next used for the calculation of an arithmetic mean. The value of this mean was, in turn, used for plotting of the smoothed solubility curve of the examined alloying element. Each of the added elements was introduced into molten magnesium at the melt temperature of 680 and 730°C (±5°C) using alloying elements in metallic form and in the form of master alloys without the content of other alloying elements. Elements such as Al, Zn, Cu, and RE were introduced in metallic form, Ca and Zr were added as 30% master alloys, and Mn and Si were introduced in both metallic form and as master alloys.

3. Research results

3.1. Introducing Al

Aluminium has a melting point similar to magnesium and can be added to molten metallic magnesium. During tests, two melts were made in which the content of the added aluminium was 10%. Dried and pre-heated pieces of Al99.5 ingots were added to molten magnesium at a temperature of 680 and 730°C. Due to the large volume of the introduced addition, the temperature of the bath decreased, contributing to the prolongation of dissolution time of this element. Samples for chemical analysis were taken for the time of 1.5 h at specified intervals; based on the results obtained, the dissolution curves were plotted (Fig. 8).

Although aluminium is one of the elements readily melted in magnesium, at the temperature of 680°C at which the addition of aluminium was introduced, the entire amount melted in 40 minutes. At a melt temperature higher by approximately 50°C, the aluminium melted twice as fast.

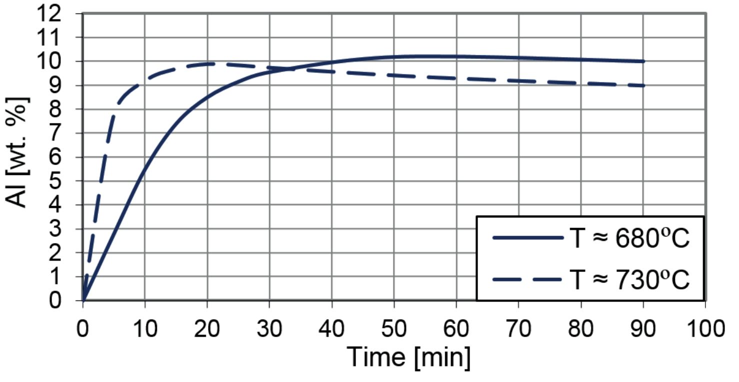

Fig. 8. Solubility curves of Al at temperatures of 680 and 730°C

3.2. Introducing Zn

Zinc has a low melting point, so it is introduced to the molten magnesium in metallic form. For both melts, the added batch was calculated at 6% Zn. After the addition of zinc in the form of a piece of metal, the melt temperature decreased. The graph below (Fig. 9) presents the curves of zinc dissolution in magnesium.

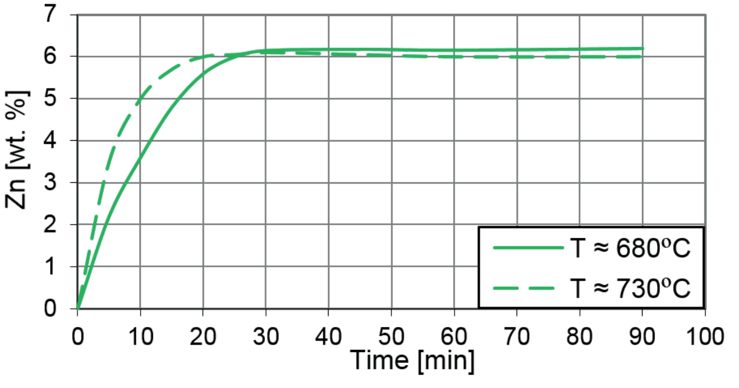

Fig. 9. Solubility curves of Zn at temperatures of 680 and 730°C

Depending on the temperature, after the lapse of 20 and 30 minutes after the introduction of zinc, the obtained concentration of the element was at a level of 6%.

3.3. Introducing Mn

Manganese has a very high melting point (1244°C), and its solubility in pure Mg is approximately 2% at the melting temperature, but it decreases when aluminium is added. Manganese can be introduced to the magnesium bath in a pure metallic form or as an $MnCl_2$ compound; to alloys of Mg-Al-Mn, it is introduced in the form of an Al-Mn (10–20% Mn) master alloy [1].

Manganese as pure electrolytic element is added in the form of small pieces or fine flakes. It should be introduced at elevated temperatures comprised in the range of 750–800°C, and the metal bath should be stirred vigorously [1].

The addition was calculated at 1.5% Mn in an alloy batch weighing 6 kgs. After melting the magnesium at a temperature of 760°C, manganese was added in the form of flakes approximately 0.5–1 cm in size. At a temperature of 750–765°C, samples were taken for chemical analysis.

Al-Mn master alloys are used for alloys containing Al and a small amount of Mn. The master alloy can be added to molten magnesium in the form of a solid or liquid, but such an addition is not always possible.

The batch was composed of Mg and the previously-prepared AlMn10 master alloy. After melting the magnesium at a temperature of 730°C, the master alloy was added. Samples were then taken for chemical analysis.

The last method that can be discussed is adding manganese in the form of an $MnCl_2$ compound. This most often occurs in the form of an $MnCl_2{\cdot}4H_2O$ compound. To add it to liquid magnesium, a dehydration treatment must be carried out. The rate of this operation depends on the temperature (which should be kept at a level above 200°C). The use of $MnCl_2$ is dictated by its ease of introduction, but this is not recommended due to the low efficiency and high rate of HCl emissions. Efficiency largely depends on the quality of the reagent. Additionally, anhydrous manganese chloride absorbs moisture from the air and must be stored in a suitable manner [1].

To enable the introduction of manganese in the form of an $MnCl_2{\cdot}4H_2O$ compound, dehydration was carried out. After drying the manganese chloride, it was wrapped with aluminium foil and added to magnesium (in the amount of 1.5% and at a temperature of 730°C. At a temperature in the range of 725–735°C, samples were taken for chemical analysis (Fig. 10).

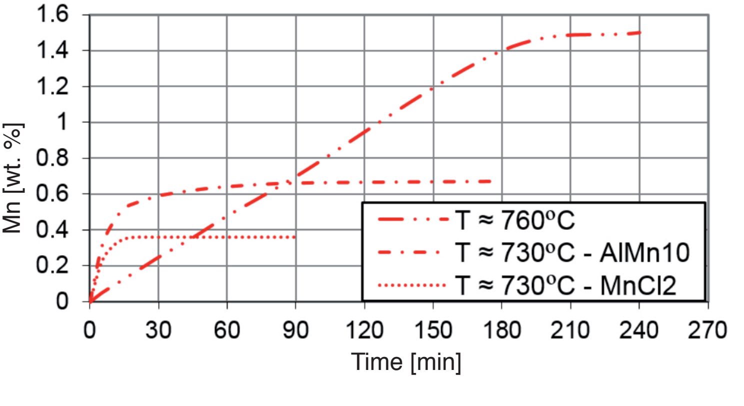

Fig. 10. Solubility curve of Mn introduced in various forms and temperatures

The highest content of manganese at a level of 1.5% was obtained when this element was introduced in the form of flakes at an elevated temperature (approximately 760°C) after holding for nearly 4 hours. Because of the limited solubility of Mn in magnesium in the presence of Al, for manganese added in the form of master alloy Al-Mn, 0.7% Mn has been achieved. The introduction of $MnCl_2$ at a temperature of 730°C enabled us to achieve the content of 0.37% Mn, which gave a low yield of approx. 25%.

3.4. Introducing Zr

Zirconium has a highly-stable oxide coating and a high melting point (1853°C); therefore, its introduction to a magnesium melt in metallic form is almost impossible. A technique of introducing Zr to magnesium was mastered by the Down Chemical Co. in the US and by Electron in England. The developed technique involves introducing an Mg-Zr master alloy produced by the zirconium chloride reduction with molten magnesium. At the moment, the most-commonly-used method worldwide is a Zirmax master alloy produced by Magnesium Elektron containing 33% Zr. The Mg-Zr master alloy is introduced to liquid metal at a temperature of 720–780°C, stirring the metal bath vigorously. To obtain the required degree of grain refinement in magnesium alloys, zirconium is added in an amount of 0.5–0.8%. In practice, however, the amount of zirconium added should be higher, since it acts as a strong agent to remove iron from magnesium and react with the steel crucible to form solid Fe-Zr compounds. After introducing the preset amount of Zr to the alloy, it is necessary to check the degree of grain refinement by casting a sample in the metal mould and breaking it. If the structure has undergone the required degree of refinement, the melt is ready for casting [1].

The batch was calculated at 3% Zr in 6 kgs of the alloy. Zirconium was added in the form of an Mg-Zr master alloy with 33% Zr at a temperature of 730°C. Samples for chemical analysis were taken after a vigorous stirring of the melt (Fig. 11).

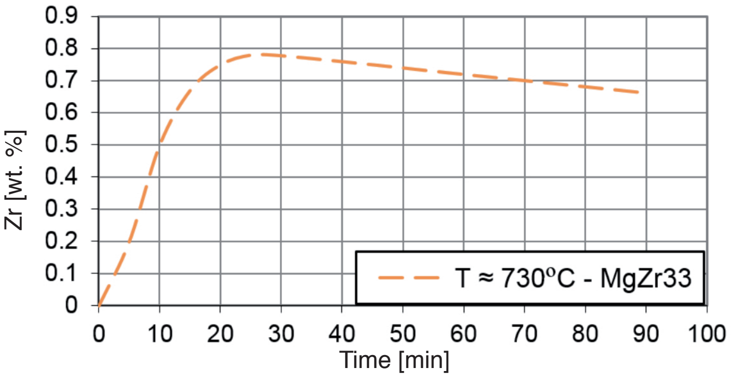

Fig. 11. Solubility curves of Zr at a temperature of 730°C

After a lapse of 25 minutes from the introduction of zirconium in an amount of 3% at a temperature of 730°C, the highest content of this element amounting to 0.78% was obtained. After saturating the melt with zirconium, its content in the solid solution slowly decreased due to reactions occurring between zirconium and iron, hydrogen, and other impurities.

3.5. Introducing Si

Due to its limited solubility and high melting temperature of 1410°C, silicon typically requires a higher temperature (700–750°C) and a longer time of holding. It can be introduced to Mg-Al-Si alloys as metallic silicon or as an Al-Si master alloy (Fig. 12).

Silicon was introducing in metallic form at temperatures of 680°C and 730°C, the batch was calculated at the content of 1.5% Si. Silicon was introduced in small lumps of 1–3 cm sizes.

Silicon was also introduced in the form of an AlSi30 master alloy. A previously-prepared Al-Si master alloy in the amount of 1.5% was introduced into liquid magnesium at a temperature of 730°C.

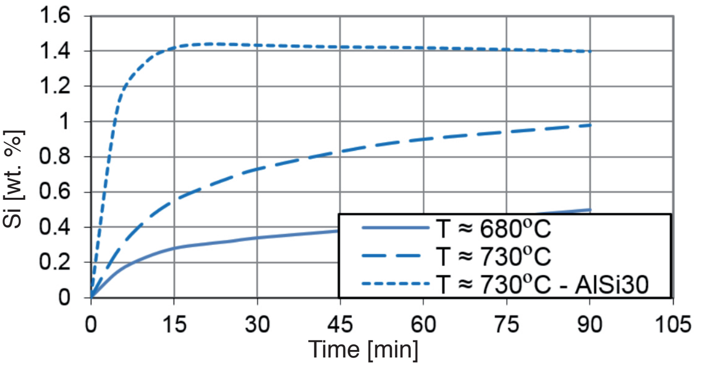

Fig. 12. Solubility curve of Si introduced in various forms and temperatures

Silicon introduced in metallic form did not dissolve completely at either of the two applied temperatures (680 and 730°C). After 90 minutes of holding at a temperature of 680°C, a content of 0.5% Si was obtained; while at a temperature of 730°C, the silicon content was 1% Si. On the other hand, in the case of an Al-Si master alloy introduced at a temperature of 730°C, the entire amount of silicon was melted as early as 15 minutes after its introduction into the melt.

3.6. Introducing Cu

Copper has a relatively-high melting point, and its concentration in a magnesium alloys does not exceed 3%. For both upper and lower temperatures, the batch was calculated at a content of 3% Cu (Fig. 13). Copper was introduced in the form of copper wire.

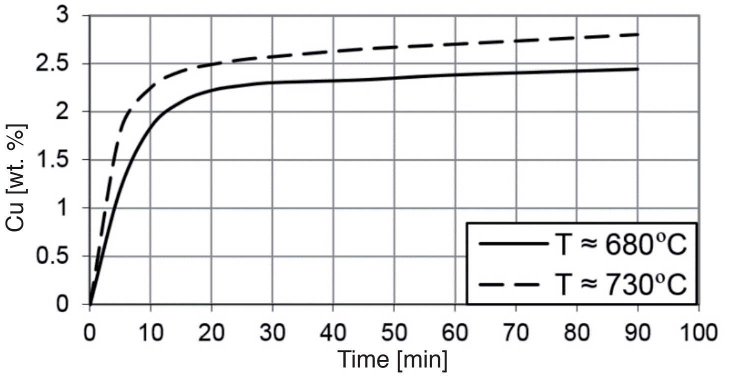

Fig. 13. Solubility curves of Cu at temperatures of 680 and 730°C

At both temperatures of 680°C and 730°C, copper to a certain level of concentration melted relatively rapidly. After 90 minutes of holding at a temperature of 680°C, the obtained content of copper was 2.45% Cu; while at a temperature of 730°C, the content of this element increased to 2.8% Cu.

3.7. Introducing Ca

Calcium can be introduced in the form of an Mg-Ca master alloy (15%, 20%, and 30%) in a temperature range of 670–720°C. Calcium is usually introduced into the melt shortly before casting, since it starts burning out if held for a longer time in the melt. Therefore, after each remelting of an Mg-Ca alloy, it is necessary to make up for the lost amount of the alloy.

Owing to the presence of other alloying elements included in their composition, magnesium-based alloys oxidise more slowly than pure magnesium. Even a small amount of calcium added to the alloy reduces the tendency of magnesium to oxidation. The following shows the effect of calcium on the surface of the cast samples (Fig. 14).

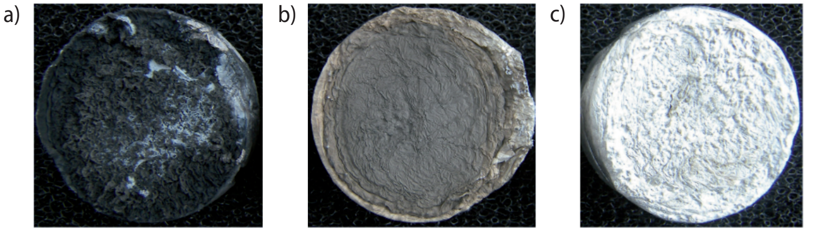

Fig. 14. The cast samples with varying Mg content of calcium: a) Mg without Ca; b) Mg with 0,06% Ca; c) Mg with 0,16% Ca

For both melts, the batch was calculated at a content of 6% Ca (Fig. 15). Calcium was added in the form of an Mg-Ca master alloy with calcium content equal to 28%.

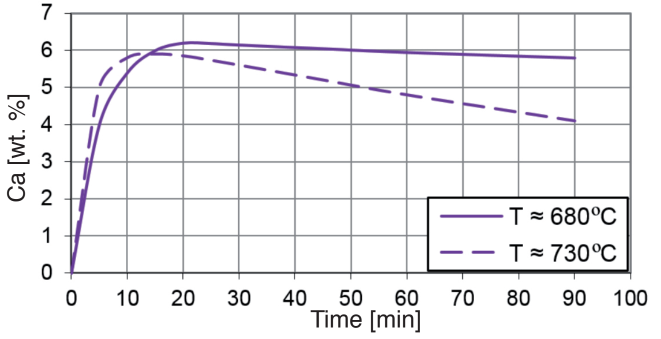

Fig. 15. Solubility curves of Ca at temperatures of 680 and 730°C

Calcium in the form of an Mg-Ca master alloy rapidly melted in the liquid magnesium; and as soon as 10–20 minutes after its introduction into the melt, the concentration achieved was at a level of 6%. At higher temperatures, the concentration of Ca decreases much faster.

3.8. Introducing RE

Rare earth elements (RE) include elements such as Ce, La, Pr, and Nd. They can be added in the form of the so-called "mischmetal" or "didymium." Their melting temperatures are in the range of 600–900°C. The addition of rare earth elements can lead to excessive oxidation of the alloy; therefore, particular care should be taken during melting and casting. These additives must be kept in a sealed container due to their easy oxidation in a humid atmosphere [1].

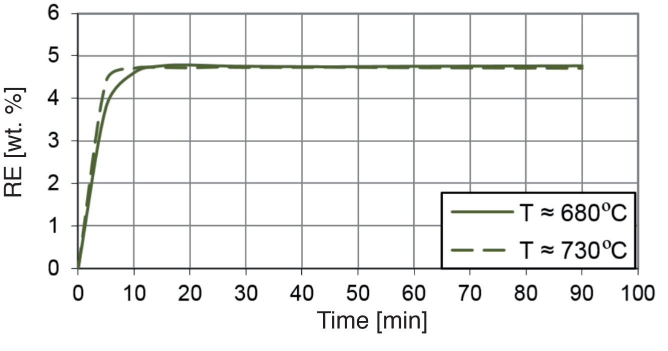

Fig. 16. Solubility curves of RE at temperatures of 680 and 730°C

Rare earth elements were introduced at temperatures of 680 and 730°C in the form of mischmetal in an amount of 5%. As claimed in the conformity certificate, the mischmetal used held 97% of rare earth elements, this including 50% Ce, 25% La, 13% Pr, and 9% Nd. The mischmetal was introduced in the form of small (2–3 cm) lumps wrapped in aluminium foil. After a vigorous stirring of the melt, samples for chemical analysis were taken (Fig. 16).

For both the lower and higher temperatures, the concentration of the examined elements was at a level of approx. 4.75% in a relatively short time after the introduction of mischmetal.

3.9. Summary

The tables below show the introduced and obtained concentrations of various alloying elements. Table 4 shows the elements that were introduced in metallic form at two different temperatures. Table 5 shows the results obtained for zirconium, which was introduced at one temperature only. The next two tables show the results obtained for Mn (Tab. 6) and Si (Tab. 7), which were introduced in various forms and at different temperatures.

Table 4. Comparison Al, Zn, Ca, Cu i RE

Element	Entered value [wt. %]	Result value [wt. %]	
		Temperature of 680°C	Temperature of 730°C
Al	10	10.2	10
Zn	6	6.2	6.1
Ca	6	6.2	5.9
Cu	3	2.4	2.8
RE	5	4.8	4.7

Table 5. Comparison Zr

Element	Entered value [wt. %]	Result value [wt. %]
		Temperature of 730°C
Zr	3.0	0.79

Table 6. Comparison Mn

Element	Entered value [wt. %]	Result value [wt. %]		
		Temperature of 760°C	Temperature of 730°C, $MnCl_2$	Temperature of 730°C, Al-Mn
Mn	1.5	1.4	0.36	0.67

Table 7. Comparison Si

Element	Entering [wt. %]	Obtained [wt. %]		
		Temperature 680°C	Temperature 730°C	Temperature 730°C, Al-Si
Si	1.5	0.5	1	1.4

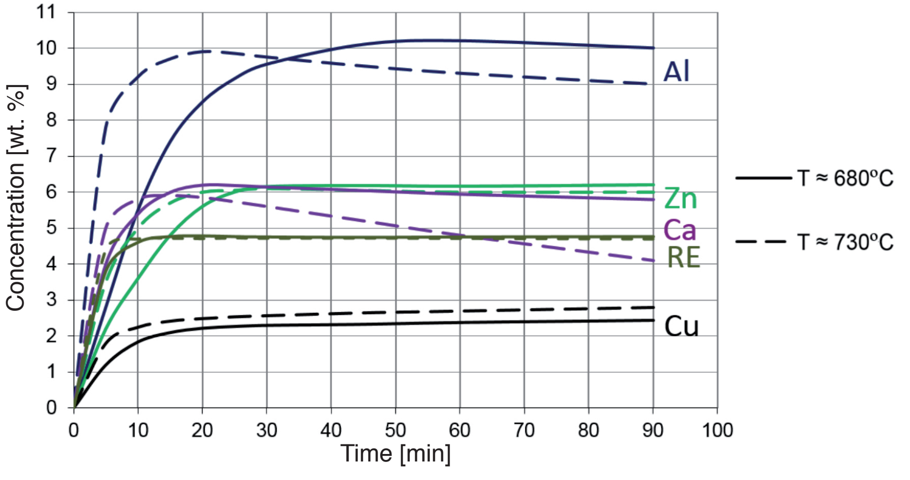

Fig. 17. Selection of the solubility curves of selected alloying elements introduced in metallic form at two temperatures

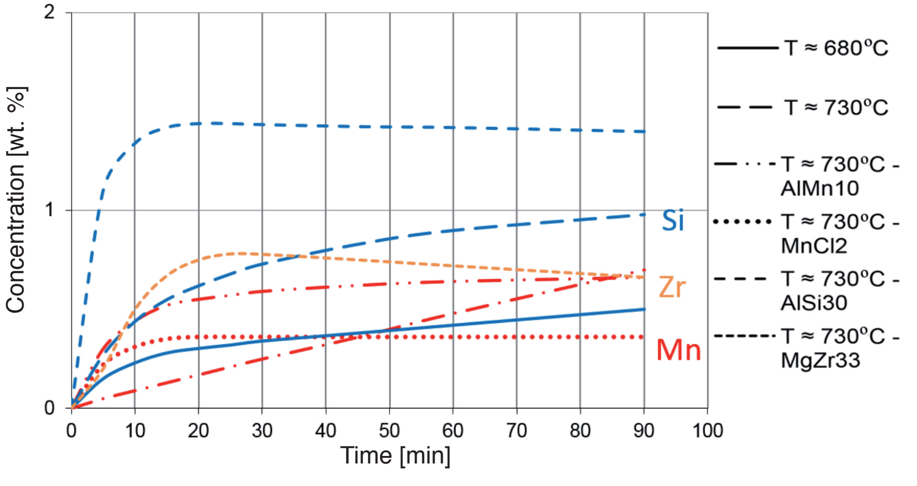

Fig. 18. Summary of solubility curves of selected alloying elements introduced in various forms and temperatures

The following graphs show the solubility curves of added alloying elements at temperatures of 680, 730, and 760°C, using additives in the form of metallic (Fig. 17) and master alloys (Fig. 18).

4. Conclusions

When alloying elements with high concentrations of aluminium or zinc were introduced into the metal bath, a considerable drop in temperature was observed, resulting in a longer dissolution time. For this reason, different values of melt temperature were reported when samples were taken for chemical analysis.

Elements such as aluminium, zinc, and copper can be added in metallic form directly to liquid magnesium at a temperature comprised in the range of 670–750°C. These elements are relatively easy to melt in the liquid magnesium. The rate of dissolution depends, however, on the concentration of the element, on the form in which it has been introduced, and on metal temperature.

Due to their high melting points and limited solubility in magnesium, elements such as Si and Mn should be introduced at a temperature higher than the above-mentioned values when added in metallic form. This considerably complicates the process of alloying with their participation.

Manganese can be introduced as Mn flakes, manganese chloride, or an Al-Mn master alloy. The highest concentration was obtained when introducing it in the form of flakes, but this method takes longer and requires higher temperatures of 750–800°C. The use of $MnCl_2$ does not require an increase of temperature. Its introduction is easy and fast, but it is inefficient and harmful to human health. The last method of introducing manganese is to add it in the form of an Al-Mn master alloy, but this method is applicable only to alloys containing aluminium.

Silicon can be introduced in metallic form or as Al-Si master alloy to Mg-Al-Si alloys. The quickest way of introducing this element into the melt is by adding it in the form of an AlSi30 master alloy.

In the production of alloys with the addition of zirconium, it is recommended to be aware of the high affinity of this element for iron, hydrogen, and other impurities. The Mg-Zr master alloy should be introduced in excess at an elevated temperature of 720°C minimum. An important aspect is also the control of its content when conducting the melt.

The temperature and time required to dissolve rare earth metals will depend on the form, chemical composition, and concentration of the various elements. For the introduced mischmetal, the assumed content was obtained in a relatively-short time and at a relatively-low temperature.

Calcium in the form of an Mg-Ca master alloy should be introduced at a low temperature and shortly before casting due to its quick introduction and burning out. Its content should also be made up during melting.

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