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Metallurgy

Recycling of beryllium, manganese, and zirconium from secondary alloys by magnesium distillation in vacuum

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ABSTRACT

One of the methods for processing secondary magnesium raw materials containing rare refractory metals can be a distillation with the extraction of magnesium into condensate and the accumulation of rare metals in the distillation residue. The residue can be used as a master alloy for special alloys. To justify the possibility of this process, we calculated the boundaries of the vapor-liquid equilibrium fields for the regions of liquid solutions existence in the Mg – Be, Mg – Mn, and Mg – Zr systems at atmospheric pressure (101.33 kPa) and in vacuum (1.33 kPa). The value of the vacuum is due to the fact that a further increase in rarefaction will lead to the magnesium crystallization from the melt, and it will complicate the technology.We established that in the distillation process of magnesium removal from Mg – Be and Mg – Zr alloys, the vapor phase will be represented by more than 99.95 of magnesium. The presence of 0.45 mass.% Mn is possible in the Mg – Mn system at 1000 °C in thevapor phase – condensate . However, results of preliminary tests of the evaporation intensity established that the process conducted at 850-900 °C provides an acceptable evaporation rate of the volatile component (Mg) for technological conditions.Thus, we confirmed the possibility of the proposed method to process secondary light alloys containing beryllium, manganese, and zirconium, which can be involved in the main process intended to produce special alloys in the form of a master alloy with magnesium.

Keywords: magnesium, beryllium, manganese, zirconium, phase diagram, vapor-liquid equilibrium.

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Introduction

Magnesium alloys are used in a variety of industries due to their low specific gravity, high mechanical properties, high casting qualities, biological compatibility with the human body, and the possibility of recycling [[1], [2], and [3]]. A large number of new alloys are being developed now. New alloys have increased strength, ductility, heat resistance, corrosion resistance, variable crystal size in the matrix, and other properties. These magnesium materials include additives of manganese [[4], [5], [6], [7], [8], and [9]], zirconium [[10], [11], [12], [13], [14], [15], [16], [17], and [18]] and beryllium [[19], [20], [21], [22], [23], [24], and [25]].

The expansion of the scope of magnesium and its alloy application entails an increase in the amount of returnable magnesium scrap represented by details exhausted their service life and by waste generated during the processing of products and semi-finished products.

Currently, secondary magnesium scrap corresponding to the magnesium alloy is melted in crucible furnaces and then cast into ingots. Most of the scrap containing non-ferrous, ferrous, and rare metals is melted in a salt furnace and then added to liquid raw magnesium to make standard alloys. Some magnesium-based scrap is used to remove sulfur from cast iron. The issue of selling these alloys resulted in the search for other processing methods.

An alternative method to recycling magnesium scrap containing rare refractory metals may be the distillation of volatile components, in particular magnesium, from secondary raw materials with a concentration of alloying rare metals in the residue. In this case, the residue can be used as a magnesium-based alloy during alloying of special alloys. The high magnesium vapor pressure relative to that of Zr, Mn, and Be at moderate temperatures (700 – 900 °C) allows to magnesium release into the vapor phase and then into the condensate. The judgment about the possibility of separating molten systems into components or the lack thereof follows from state diagrams that include the vapor-liquid equilibrium boundaries. The construction of such phase diagrams is possible based on the thermodynamic functions of the solutions' formation and evaporation, in particular the vapor pressure values of the components that make up the system.

In this article, we present the state magnesium diagrams with beryllium, manganese, and zirconium supplemented by vapor-liquid equilibrium fields. Since magnesium is the basis of the alloys, we calculated the boundaries of the vapor-liquid equilibrium fields in the concentration regions of the existence of liquid solutions based on experimental data on the values of the saturated vapor pressure of the components determined by us. The results of experiments and calculations are presented below.

Experimental part

Preparation of magnesium alloys with beryllium, manganese and zirconium. In binary systems of magnesium with refractory metals - beryllium, manganese, and zirconium, the highest concentration field of liquid alloys existence is present in the system with beryllium. It is presumably up to 90 at. %Be. The existence of liquid solutions up to a concentration of 2-2.5 at. % was established in the magnesium-manganese system, and up to 0.2 at. % Zr in the magnesium–zirconium system. Therefore, we prepared magnesium-beryllium alloys containing from 20.17 to 76.31 at. % Be (Table 1), magnesium-manganese alloys containing from 0.45 to 2.31 at. %Mn (Table 2), and magnesium-zirconium alloys with zirconium content from 0.051 to 0.180 at. % (Table 3) for research.

Table 1 – Composition of magnesium – beryllium system alloys

Alloy No.	Wt. %		At. %	
	Mg	**Be**	**Mg**	**Be**
1	45.57	54.43	23.69	76.31
2	64.73	35.27	40.49	59.51
3	83.47	16.52	65.19	34.81
4	91.43	8.57	79.83	20.17

Table 2 – Composition of the magnesium-manganese system alloys

Alloy No.	Wt. %		At. %	
	Mg	**Mn**	**Mg**	**Mn**
1	99.80	0.20	99.55	0.45
2	99.51	0.49	98.89	1.11
3	98.96	1.04	97.69	2.31

Table 3 – Composition of the magnesium–zirconium system alloys

Alloy No.	Wt. %		At. %	
	Mg	**Zr**	**Mg**	**Zr**
1	99.986	0.014	99.949	0.051
2	99.971	0.029	99.880	0.110
3	99.952	0.048	99.820	0.180

To prepare the alloys, magnesium was used with a content of the main element of 99.99 wt. %, beryllium – 99.9%, manganese – 99.9%, zirconium – 99.6%. The alloys were synthesized using the ampoule method, which consists of the following. The initial components in the form of sawdust were loaded into quartz ampoules in quantities necessary for the alloy preparation of a given composition. The ampoules were washed several times with neutral gas (argon), evacuated, and sealed at a pressure of 1 Pa. The fusion of the components was carried out at a temperature of 800-850 °C for 12 hours, followed by quenching in water.

Determination of the liquid-vapor phase transition boundaries. The construction of the liquid-vapor phase transition boundaries of molten systems is complicated by the high boiling temperatures of solutions, the difficulty in determining the concentration of components in the vapor phase that is in equilibrium with the alloy, and the problem of instrumentation design for ebulliometric measurements.

In this work, the boundaries of the melt and vapor coexistence fields were calculated based on the partial pressure of the saturated vapor of the alloy components. Due to the absence of the boiling process of liquid metal solutions because of the high density of the metals that form them, the boiling point was determined to be equal to the temperature at which the sum of the partial vapor pressures of the system's components under Dalton's law is equal to atmospheric (0.1 MPa) or other pressures corresponding to the conditions of vacuum technologies.

The composition of the vapor phase (y_1, $y_2 = 1 - y_1$) above a solution of a certain composition (x_1, $x_2 = 1 - x_1$) at the boiling point was determined based on the Clapeyron-Mendeleev equation: $P_iV = n_iRT$, from which:

$$y_1(y_2)[mole\ fraction] = \frac{n_1(n_2)}{n_1+n_2} = \frac{p_1(p_2)}{p_1+p_2},$$

where: x_1 and $x_2$are the number of moles of the first and second metal in the alloy; n_1 and n_2 are number of moles of the first and second metal in the vapor phase; p_1 and p_2 are the partial pressures of saturated vapor of the first and second components.

Phase transformations of condensed phases at low pressures were not taken into account because the temperatures of phase transitions change by (5.0 – 5.6) × 10^{-3} °C (calculated by us) during the move from atmospheric pressure to vacuum according to the authors [26].

Determination of the saturated vapor pressure values of metals. It should be noted during the assessment of magnesium, beryllium, manganese, and zirconium vapor pressure [27] that magnesium vapor pressure is incomparably higher concerning Be, Mn, and Zr. That is, the boiling point method should be considered the most acceptable way to determine the vapor pressure in binary systems of magnesium with the indicated metals. This method is based on a sharp increase in the evaporation rate of the volatile component near the equalization of the saturated vapor pressure of the metal and a given inert gas pressure. The boiling point method and the device for its implementation are described in detail in our work [28].

In this work, we present the method for determining the values of partial pressures of components over the studied magnesium alloys using the example of the Mg – Be system.

First, we determined the partial pressure values for saturated magnesium vapor($\overline{p}_{Mg}$). In this case, we assumed that the vapor above the melt is represented entirely by magnesium. Then, we found the activity coefficient under the definition of thermodynamic functions by equation:

$$\gamma_{Mg} = \frac{\overline{p}_{Mg}}{p^o_{Mg} \times x_{Mg}},$$

where: p^o_{Mg} is the vapor pressure over elemental magnesium; x_{Mg} is the atomic fraction of magnesium in the alloy.

The beryllium activity coefficient (γ_{Be}) was calculated by numerical integration of the Gibbs-Duhem equation with the use of the auxiliary function proposed by Darken [29]. After transformation [30], this function relates lnγ_{Mg} and lnγ_{Be} in the form of an equation convenient for numerical integration:

$$\ln\gamma_{Be} = -\frac{\ln\gamma_{Mg} \times x_{Mg} \times x_{Be}}{Be} + \int_{x_{Mg}=0}^{x_{Mg}} \frac{\ln\gamma_{Mg}}{(1-x_{Mg})^2} dx_{Mg},$$

where x_{Be} is the atomic fraction of magnesium in the alloy which is equal to $x_{Be} = 1 - x_{Mg}$.

As a result of this calculation, we can find the partial vapor pressure of beryllium ($\overline{p}_{Be}$) as: $\overline{p}_{Be} = p^o_{Be} \times \gamma_{Be} \times x_{Be}$ or $\ln\overline{p}_{Be} = \ln p^o_{Be} + \ln\gamma_{Be} + \ln x_{Be}$. Here p^o_{Be} is the vapor pressure above elemental beryllium.

Results and Discussion

Determination of the vapor pressure values over the Mg – Be, Mg – Mn and Mg – Zr melts. The values of magnesium vapor pressure determined experimentally by the boiling point method ($\overline{p}_{Mg}$, experiment), as well as the vapor pressure values of magnesium ($\overline{p}_{Mg}$, calculation), beryllium ($\overline{p}_{Be}$), manganese ($\overline{p}_{Mn}$) and zirconium ($\overline{p}_{Zr}$), calculated by approximating experimental data, are given in Tables 4-6.

Table 4 – Partial vapor pressures of magnesium and beryllium over Mg – Be melts

Alloycomposition, at. fraction		Temperature К/°C	$\overline{p}_{Mg}$, experiment, kPa	$\overline{p}_{Mg}$, calculated, kPa	$\overline{p}_{Be}$, kPa
Mg	**Be**				
0.2369	0.7631	1123 850	1.07	1.04	2.61×10^{-7}
			1.07		
			0.93		
		1223 950	3.60	3.62	3.82×10^{-6}
			3.33		
			3.87		
0.4049	0.5951	1123 850	1.87	1.87	1.98×10^{-7}
			2.00		
			1.73		
		1223 950	6.93	6.93	2.83×10^{-6}
			7.20		
			6.67		
0.6519	0.3481	1073 800	1.73	1.69	2.08×10^{-8}
			1.60		
			1.73		
		1173 900	6.93	6.85	3.94×10^{-7}
			6.93		
			6.67		
0.7983	0.2017	1073 800	2.40	2.38	8.18×10^{-9}
			2.13		
			2.53		
		1173 900	9.33	9.15	1.80×10^{-7}
			9.20		
			8.93		
1.0	–	1023 750	1.73	1.72	–
			2.0		
			1.47		
		1273 1000	38.00	38.01	–
			37.20		
			38.80		

Table 5 – Partial vapor pressures of magnesium and manganese over Mg – Mn melts

Alloycomposition, at. fraction.		Temperature K/°C	$\overline{p}_{Mg}$, experiment, kPa	$\overline{p}_{Mg}$, calculated, kPa	$\overline{p}_{Mn}$, kPa
Mg	**Mn**				
1.0	–	1023 750	1.73	1.72	–
			2.0		
			1.47		
		1273 1000	38.00	38.01	–
			37.20		
			38.80		
0.9955	0.0045	1023 750	1.73	1.72	1.66×10^{-7}
			1.70		
			1.76		
		1123 850	6.91	6.98	1.37×10^{-6}
			6.97		
			7.04		
0.9889	0.0111	1023 750	1.70	1.71	3.08×10^{-7}
			1.75		
			1.71		
		1123 850	6.87	6.94	2.80×10^{-6}
			7.08		
			6.89		
0.9769	0.0231	1023 750	1.60	1.69	5.09×10^{-7}
			1.69		
			1.79		
		1123 850	6.67	6.87	5.01×10^{-6}
			6.87		
			7.06		

Table 6 – Partial vapor pressures of magnesium and zirconiumover Mg – Zr melts

Alloycomposition, at. fraction.		Temperature К/°C	$\overline{p}_{Mg}$, experiment, kPa	$\overline{p}_{Mg}$, calculated, kPa	$\overline{p}_{Zr}$, kPa
Mg	**Zr**				
1.0	–	1023 750	1.73	1.72	–
			2.0		
			1.47		
		1273 1000	38.00	38.01	–
			37.20		
			38.80		
0.9995	0.0005	1023 750	1.73	1.72	1.63×10^{-21}
			1.76		
			1.71		
		1123 850	6.95	7.00	2.93×10^{-19}
			6.97		
			7.01		
0.9988	0.0012	1023 750	1.73	1.72	3.15×10^{-21}
			1.75		
			1.71		
		1123 850	6.91	6.99	6.39×10^{-19}
			7.11		
			7.02		
0.9981	0.0018	1023 750	1.69	1.72	4.27×10^{-21}
			1.71		
			1.71		
		1123 850	6.71	6.99	9.18×10^{-19}
			6.82		
			6.96		

After mathematical processing, we obtained the following temperature-concentration dependencies, expressing the partial pressure values of the component studied systems:

- for the Mg – Be system:

$$\ln\overline{p}_{Mg}[Pa]=(-14746x_{Mg}^{3}+35273x_{Mg}^{2}-23214x_{Mg}-$$
$$-13395)\cdot T^{-1}+12.452x_{Mg}^{3}-29.745x_{Mg}^{2}+20.106x_{Mg}+$$
$$20.367+\ln x_{Mg}$$

$$\ln\overline{p}\ _{Be}[Pa]=(14746x_{Be}^{3}-31084x_{Be}^{2}+14836x_{Be}-$$
$$-35780+3094\ln x_{Be})\cdot T^{-1}-12.452x_{Be}^{3}+26.289x_{Be}^{2}-$$
$$-13.194\ \ _{Be}+24.574-1.028\ln x_{Be}$$

- for the Mg – Mn system:

$$\ln\overline{p}_{Mg}[Pa]=(-301x_{Mg}^{2}-669x_{Mg}-15153)\cdot T^{-1}+$$
$$+0.254x_{Mg}^{2}+0.413x_{Mg}+22.544+\ln x_{Mg}$$

$$\ln\overline{p}_{Mn}[Pa]=(-301x_{Mn}^{2}+1873x_{Mn}-31097-$$
$$-1271\ln x_{Mn})\cdot T^{-1}+0.254x_{Mn}^{2}-1.429x_{Mn}+$$
$$+25.363+1.921\mathrm{l}\ \ x_{Mn}$$

- for the Mg – Zr system:

$$\ln\overline{p}_{Mg}[Pa]=(-327x_{Mg}^{2}-973x_{Mg}-14823)\cdot T^{-1}+$$
$$+0.298x_{Mg}^{2}+0.745x_{Mg}+22.168+\ln x_{Mg}$$

$$\ln\overline{p}_{Zr}[Pa]=(-327x_{Zr}^{2}+2281x_{Zr}-71967-$$
$$-1627\ln x_{Zr})\cdot T^{-1}+0.298x_{Zr}-1.937x_{Zr}+$$
$$35.098+2.341\ln x_{Zr}$$

Construction and analysis of a phase diagram with a liquid-vapor phase transition. The boundaries of the liquid and vapor coexistence fields at atmospheric pressure (L+V) and in vacuum (L+V 1.33 kPa, shaded) were calculated based on the partial pressure values of the vapor components in the region of existence of liquid solutions of the Mg – Be, Mg – Mn and Mg – Zr systems. The choice of the vacuum value (1.33 kPa) is because a decrease in pressure less than the specified value can lead to the crystallization of magnesium from the melt, this will complicate the distillation process.

We plotted the fields on existing state diagrams of condensed phases [[31], and [32]], shown in Fig. 1-3. From the analysis of the boundary location on phase diagrams, it is possible to conclude next.

The vapor phase for magnesium systems with beryllium and zirconium will be represented by elemental magnesium when the evaporation process is performed up to the boiling point of magnesium at atmospheric pressure (1107 °C). Distillation of magnesium at 1000 °C will be accompanied by the occurrence of 0.2 at. (0.45 mass) % Mn at vapor for liquid Mg – Mn alloys. However, preliminary tests of the evaporation process intensity have established that the process conducted at 850-900 °C provides an acceptable evaporation rate of the volatile component (Mg) for technological conditions.

The evaporation process for magnesium from its alloys with beryllium will be accompanied by the accumulation of the Be compound in the residue. Thus, when magnesium evaporates from its alloy with beryllium (10.0 mass. % Be) at 900 °C in a vacuum, the average evaporation rate was 5,5×10^{-3} kg/(m^{2}×sec) with magnesium extraction into the condensate of 61.20% and accumulation of 22.26 mass. % Be. During the extraction of 96 % Mg into the vapor phase, the average evaporation rate amounted to 2.61×10^{-3} kg/(m^{2}×sec) with the accumulation of 64.76 mass.% Be in the distillation residue.

When magnesium evaporated from an alloy with manganese (4.0 mass. % Mn) under similar conditions, the average evaporation rate was 2.09 × 10^{-3} kg/(m^{2} × sec) with 94.12 % extracting into the condensate. 41.67 mass. % Mn being accumulated in the residue.

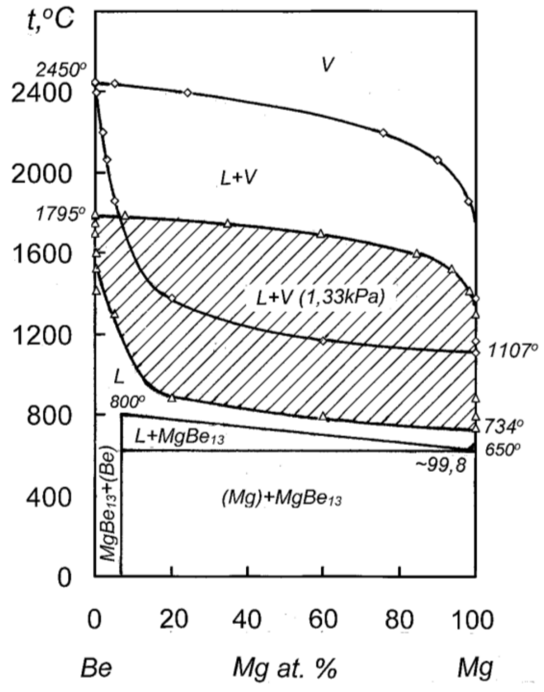

Figure 1– Mg–Be phase diagram

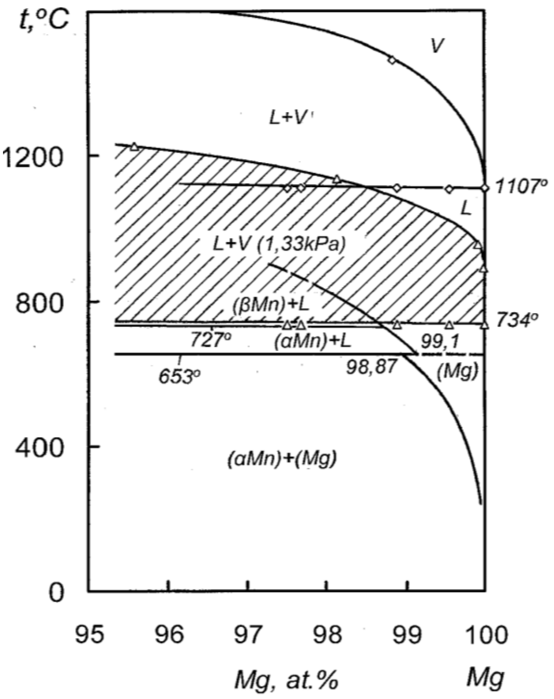

Figure 2 –Mg–Mn phase diagram

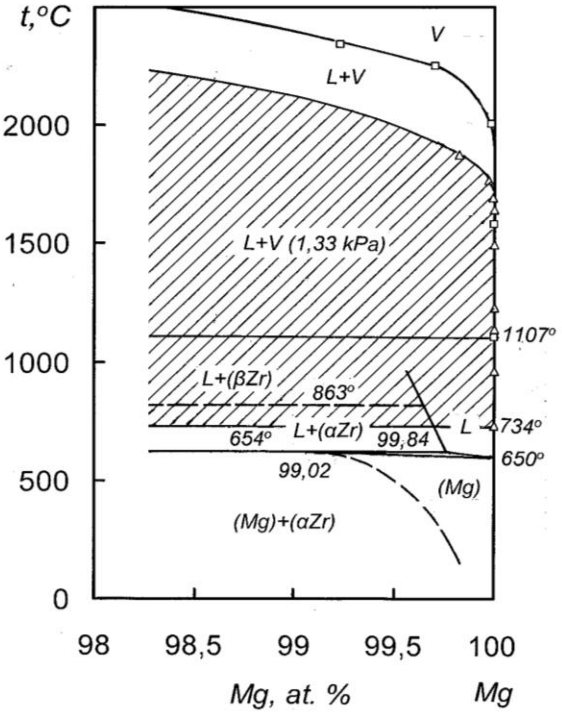

Figure 3 –Mg–Zr phase diagram

During the distillation of magnesium from its alloy with zirconium (1.85 mass. % Zr) within an hour at 900 °C, 92.56% Mg was extracted into the condensate with an accumulation of 20.11 wt. % Zr in the residue.

Thus, from secondary light alloys based on magnesium, the magnesium can be converted into condensate by distillation in a vacuum, which can be mixed with raw magnesium. The distillation residue with a significant content of beryllium, manganese and zirconium, with a combined or separate content of each, can be used as a master alloy in the production of special alloys. The latter ensures recycling – the return of rare refractory metals to the processes for manufacturing alloys with different physical properties.

Conclusions

During the analysis of methods for processing secondary magnesium raw materials containing rare refractory metals, the use of the latter, including as a deoxidizer in ferrous metallurgy, was established. An alternative method intended to process secondary raw materials may be a distillation process with the extraction of magnesium into the condensate and the accumulation of rare metals in the distillation residue, followed by the use of the residue as a master alloy for special alloys.

Based on complete state diagrams of the Mg – Be, Mg – Mn, and Mg – Zr systems, including the liquid–vapor phase transition, the boundaries of which are calculated based on experimentally determined values of the components' saturated vapor pressure, the possibility of the proposed method to process secondary light alloys containing beryllium, manganese, and zirconium have been confirmed. The residues containing beryllium, manganese, and zirconium can be involved in the main process to produce special alloys in the form of a master alloy with magnesium.

Technological experiments have shown the possibility of technical implementation of the process with an intensity of magnesium evaporation acceptable for industrial production.

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Conflict of interest. The corresponding author declares that there is no conflict of interest.

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ТҮЙІНДЕМЕ

Құрамында сирек қиын балқитын металдар бар қайталама магний шикізатын өңдеу әдістерінің бірі магнийді конденсатқа бөліп алу және дистилляция қалдығында сирек металдарды жинақтау арқылы айдау процесі болуы мүмкін. Алынған қалдықтар арнайы қорытпалар үшін лигатура ретінде қолданылады. Магний қорытпаларын айдау арқылы өңдеу мүмкіндігін негіздеу үшін атмосфералық қысымда (101,33 кПа) және вакуумда (1,33 кПа) Mg – Be, Mg – Mn және Mg – Zr жүйелеріндегі сұйық ерітінділердің болу аймақтары үшін бу-сұйықтық тепе-теңдік өрістерінің шекаралары есептелді. Соңғысының шамасы қысым астында одан әрі жоғарылайды, нәтижесінде балқымадан Mg кристалданады, бұл технологияны қиындатады. Mg – Be және Mg – Zr қорытпаларынан магнийді кетіру процесінде бу фазасында магний 99,95-ден жоғары болатыны анықталды. Mg – Mn жүйесінде 1000 °C температурада бу фазасында (конденсат) 0,45 масс.% Mn болуы мүмкін. Дегенмен, булану процесінің қарқындылығын алдын ала сынаулар процесті 850-900 °C температурада жүргізу технологиялық жағдайлар үшін ұшпа компоненттің (Mg) булануының қолайлы жылдамдығын қамтамасыз ететінін анықтады. Осылайша, зерттеулер магниймен негізгі қорытпа түріндегі арнайы қорытпаларды алудың негізгі процесіне соңғыларын тарта отырып, құрамында бериллий, марганец және цирконий бар екінші реттік жеңіл қорытпаларды өңдеудің ұсынылған әдісінің мүмкіндігін растады.

Түйін сөздер: магний, бериллий, марганец, цирконий, қалыпты диаграмма, булы-сұйықтық тепе-теңдігі.

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Рециклинг бериллия, марганца и циркония дистилляцией магния в вакууме из вторичных магниевых сплавов

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АННОТАЦИЯ

Одним из способов переработки вторичного магниевого сырья, содержащего редкие тугоплавкие металлы, может быть дистилляционный передел с извлечением магния в конденсат и накоплением редких металлов в остатке от дистилляции. Полученный остаток возможно использовать в качестве лигатуры для специальных сплавов. Для обоснования возможности переработки магниевых сплавов дистилляцией рассчитаны границы полей парожидкостного равновесия для областей существования жидких растворов в системах Mg – Be, Mg – Mn и Mg – Zr при атмосферном давлении (101,33 kPa) и в вакууме (1,33 kPa). Величина последнего обусловлена тем, что дальнейшее увеличение разрежения приведет к кристаллизации Mg из расплава, что затруднит технологию. Было установлено, что в дистилляционном процессе удаления магния из сплавов Mg – Be и Mg – Zr паровая фаза более, чем на 99,95 будет представлена магнием. В системе Mg – Mn при 1000 °C в паровой фазе (конденсате) возможно присутствие 0,45 mass.% Mn. Однако, предварительными испытаниями интенсивности процесса испарения было установлено, что ведение процесса при температурах 850-900 °C обеспечивает приемлемую для технологических условий скорость испарения летучего компонента (Mg). Таким образом, проведенными исследованиями подтверждена возможность предложенного способа переработки вторичных легких сплавов, содержащих бериллий, марганец и цирконий, с вовлечением последних в основной процесс получения специальных сплавов в виде лигатуры с магнием.

Ключевые слова: магний, бериллий, марганец, цирконий, диаграмма состояния, парожидкостное равновесие.

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