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Thermodynamic studies of the binary system of magnesium with the alloying metal – beryllium

Abstract: The results of studies to obtain thermodynamic constants of condensed and vapor phases of binary systems of magnesium with beryllium are presented in this paper, and liquid-vapor phase transitions at atmospheric pressure and in vacuum are also constructed. Mg - Be alloys of a given composition were prepared as a result of this work. The partial pressures of magnesium over binary alloys with beryllium were determined with the use of the boiling point method (isothermal variant). The partial vapor pressure of beryllium was found by numerical integration of the Gibbs-Duhem equation. The partial pressures of magnesium and beryllium are represented by temperature-concentration dependences. The boundaries of melt and vapor coexistence fields of magnesium-beryllium system at atmospheric pressure and in vacuum of 1.33 kPa are calculated and plotted on the state diagram. It is established that the separation of magnesium-beryllium system alloys does not involve technological difficulties.

Keywords: magnesium, beryllium, metal, alloy, diagram of state.

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Introduction

Magnesium is one of the common light structural metals, and it has low elasticity, strength and corrosion resistance. The specified parameters are significantly improved by alloying with the help of aluminum, zinc, beryllium, zirconium, titanium, etc. Magnesium and its alloys have found wide application in such areas as aerospace, automotive, computer, biomedical, energy due to high specific strength and stiffness, good biocompatibility, large hydrogen storage capacity (Chen, 2022; Song, 2022; Thangarasu, 2022; Wu, 2022; Yang, 2021; Zhou, 2022; Mohammadi Zerankeshi, 2022; Bobe, 2022; Dai, 2022; Sun, 2022; Zhu, 2022).

To date, the recycling method of light alloys, with a low content of refractory alloying elements based on magnesium, is poorly studied and is relevant due to the increase number of magnesium-containing products used. The number of used and failed devices, mechanisms and their components that need special recycling increases with the growth of their consumption (Mansurov, 2020). These materials are secondary raw materials for the extraction of valuable components, including magnesium, and are relevant worldwide (Barannik, 2010; Non-ferrous metals, 2023).

Well-known process flows intended to process magnesium scrap (Engh, 2021) include preliminary smelting in a crucible furnace to produce ingots with an average composition. The obtained ingots containing impurity elements of various metals are used in the process to prepare standard alloys as additives to raw liquid magnesium (Barannik, 2010).

To date, the processing method for light magnesium alloys containing refractory alloying elements has been poorly studied. Physical and chemical studies conducted for distillation processing of secondary magnesium raw materials containing rare refractory metals with the development of the recycling process for light alloys after remelting and obtaining new special alloys will provide new knowledge in this field.

Obtaining magnesium-beryllium alloy is difficult due to the fact that the vaporization temperature of magnesium is lower than the melting point of beryllium. Solid beryllium does not dissolve in magnesium at atmospheric pressure. It is known that beryllium immersed in boiling magnesium does not react with it. The magnesium boiling point can be raised to a temperature above the beryllium melting point, if magnesium is put in a hydrogen atmosphere, and a pressure of 100-120 atm is created. The matter of beryllium melting even under these conditions is placed in question. Deoxidation of beryllium compounds by molten magnesium is more promising. Accordingly, various methods were proposed to facilitate the release of oxide-free beryllium in a finely dispersed state under such conditions where melting can be accompanied by an exothermic reaction.

Thus, it is currently believed that beryllium cannot be widely used in magnesium alloys, with the exception of very small additives introduced to protect the alloy from burning out during the casting process and to reduce oxidation in the solid state.

Research Materials

Magnesium - beryllium field of existence of liquid alloys in the binary system is present presumably up to 90 at. % Be (Nayeb-Hashemi, 1987).

The alloys were obtained in sealed quartz ampoules preloaded with metals in the form of sawdust in a certain ratio, at a temperature of 800-850 °C for 12 hours, followed by quenching in water. Air was evacuated from the ampoules before sealing, so that the residual pressure was 1 Pa. Metals with the content of the main element, wt. %: Mg 99,99; Be 99,9 % were used. The compositions of the prepared alloys are specified in Table 1.

Table 1. Composition of magnesium - beryllium system alloys

Alloy number	Wt. %		atm. %	
	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

Research Methods

The composition of the obtained alloys of magnesium with beryllium was determined by chemical analysis method with the use of atomic emission spectrometer - Optima 8300 DV "Perkin Elmer".

The condensate obtained from the magnesium distillation from its alloys with beryllium was preliminarily studied to select the method to determine the vapor pressure of the alloy components.

The results showed that the vapor phase above the magnesium and beryllium melts is almost completely represented by magnesium. In this regard, the most acceptable way to determine the saturated vapor pressure of magnesium is the boiling point method (isothermal option). 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 experimental part was conducted with the help of a vertical thermogravimetric unit with a quartz reactor where the alloy suspension is located, with an electric furnace, a vacuum pump intended to create a vacuum in the reactor, a cathetometer to fix the mass loss. A chromel-alumel thermocouple (thermoelectric converter DTPK021-1,2/0,7) with a single-channel microprocessor meter-regulator TRM1 with an accuracy of ± 5 °C is used to control the temperature in the reaction area. Pressure is measured with an M110 aneroid barometer with an accuracy of ± 67 Pa (± 0.5 mm Hg) and a McLeod manometer with an accuracy of ± 10 Pa. The sample was weighed before and after the experiment with a PA214C analytical balance (Ohaus-Pioneer) with an accuracy of ± 0.1 mg.

The partial vapor pressure of beryllium was found by numerical integration of the Gibbs-Duhem equation.

Preliminary experiments showed that experiments must be performed at 800 °C and above to fix the boiling point reliably.

The method intended to calculate based on the partial pressures of the saturated vapor of the system components was taken as a basis to determine the liquid-vapor phase transition boundaries. The existing state diagram of the Mg - Be system was corrected by adding the melt - vapor phase transitions obtained by recalculation of the alloy compositions and the vapor phase composition.

Research Results

The magnesium vapor pressure values experimentally determined by the boiling point method, as well as the calculated values of magnesium and beryllium partial vapor pressures are specified in Table 2.

Table 2. Magnesium and beryllium partial vapor pressures over Mg-Be melts

Alloy composition, at. fraction.		Temperature, K/°C	\bar{p}_{Mg} , kPa		\bar{p}_{Be} , kPa
Mg	Be		experimental,	estimated,	
0.2369	0.7631	1123 850	1.07	1.042	$2.61 \cdot 10^{-7}$
			1.07		
			0.93		
0.4049	0.5951	1223 950	3.60	3.624	$3.82 \cdot 10^{-6}$
			3.33		
			3.87		
0.6519	0.3481	1073 800	1.87	1.688	$2.08 \cdot 10^{-8}$
			2.00		
			1.73		
0.7983	0.2017	1173 900	6.93	6.845	$3.94 \cdot 10^{-7}$
			7.20		
			6.67		
0.2369	0.7631	1073 800	2.40	2.379	$8.18 \cdot 10^{-9}$
			2.13		
			2.53		
0.4049	0.5951	1173 900	9.33	9.146	$1.80 \cdot 10^{-7}$
			9.20		
			8.93		

The partial values of the vapor pressure of magnesium and beryllium are represented by the following temperature-concentration dependencies:

$$\ln \bar{p}_{Mg} [Pa] = (-14,746x_{Mg}^3 + 35,273x_{Mg}^2 - 23,214x_{Mg} - 13,395) \cdot T^{-1} + 12.452x_{Mg}^3 - 29.745x_{Mg}^2 + 20.106x_{Mg} + 20.367 + \ln x_{Mg} , \quad (1)$$

$$\ln \bar{p}_{Be} [Pa] = (14,746x_{Be}^3 - 31,084x_{Be}^2 + 14,836x_{Be} - 35,780 + 3,094 \ln x_{Be}) \cdot T^{-1} - 12.452x_{Be}^3 + 26.289x_{Be}^2 - 13.194x_{Be} + 24.574 - 1.028 \ln x_{Be} . \quad (2)$$

The boundaries of the vapor-liquid equilibrium fields were calculated based on the partial values of vapor pressure. They were used to supplement the existing diagram. Figure 2.6.1 shows the state diagram of beryllium - magnesium with the boundaries of the vapor-liquid equilibrium fields at atmospheric pressure and in a vacuum of 1.33 kPa.

The boiling point was determined to be equal to the temperature at which the sum of the partial vapor pressures of the system components is equal to atmospheric (101.3 kPa) or other pressure corresponding to the conditions of vacuum technologies under Dalton’s law due to the absence of the boiling process for liquid chalcogenide solutions due to the high density of their constituent components.

The vapor phase composition is defined as the partial pressure fraction of the component in the total pressure above the alloy.

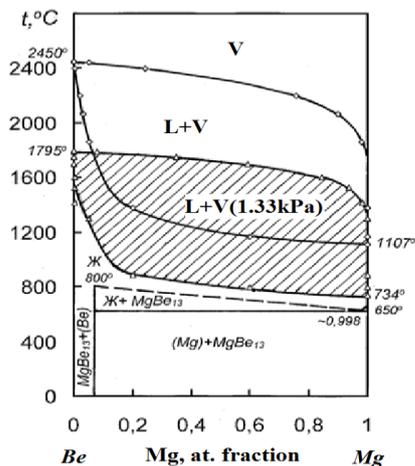


Figure 1. Phase diagram of magnesium - beryllium system

Conclusion

Insufficient information (or its absence) on the vapor-liquid equilibrium in the magnesium-beryllium system has been established based on the analysis of the study results in published works enabling us to judge about the possibility to separate melts into components. The magnesium partial pressure values over beryllium binary alloys were determined by the boiling point method (isothermal variant), and the partial pressure of beryllium was found by the method of numerical integration of the Gibbs-Duhem equation. The obtained values of partial pressures of the Mg-Be system components were presented in the form of temperature-concentration dependences. Then the boundaries of the liquid and vapor coexistence fields were calculated based on these dependences, and the existing state diagram was supplemented.

It can be seen during analyzes of the supplemented phase diagram that the coexistence fields of melt and vapor phases at atmospheric and low pressure (133 kPa) overlap each other. Considering the position of the boundaries of the coexistence fields of liquid and vapor at atmospheric pressure and in vacuum it can be seen that the separation of magnesium-beryllium system alloys does not involve technological difficulties. The vapor phase will be represented by magnesium.

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