

REFERENCES

1. Gorshunov N.M., Gudenko S.V. On possibility of isotope separation owing to nonequilibrium vibrational exchange in afterdischarge zone // Physicochemical processes at atom and molecule selection: Collected reports of the 8th All-Russian scientific conference. – Moscow: CRI atominform, 2003. – P. 133–136.
2. Tumanov Yu.N. Low-temperature plasma and high frequency electromagnetic fields in processes of obtaining materials for nuclear power engineering. – Moscow: Energoatomizdat, 1989. – 279 p.
3. Pushkarev A.I., Novoselov Yu.N., Remnev G.E. Chain processes in low-temperature plasma. – Novosibirsk: Nauka, 2006. – 226 p.
4. Vlasov V.A., Pushkarev A.I., Remnev G.E., Sosnovsky S.A., Ezhov V.V., Guzeeva T.I. Experimental investigation and mathematical modeling of fluoride compound reduction by pulse electron beam // Bulletin of the Tomsk Polytechnic University. – 2004. – V. 307. – № 5. – P. 89–93.
5. Remnev G.E., Furman E.G., Pushkarev A.I., Karpuzov S.B., Kondratiev N.A., Goncharov D.V. Pulse high-current accelerator with matching transformer // Pribory i Tekhnika Eksperimenta. – 2004. – № 3. – P. 130–134.
6. Trusov B.G. Software TERRA for computing plasmachemical processes // Materials of 3^d International symposium on theoretical and applied plasma chemistry. – Ples, 2002. – P. 217–218.

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MAGNESIUM ISOTOPES SELECTION AT RECRYSTALLIZATION OF $MgCl_2 \cdot 6H_2O$

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The change of Mg isotope composition at grain-refined zone of $MgCl_2 \cdot 6H_2O$ has been studied. It is shown that light isotope ^{24}Mg enrichment occurs on that crystal end to which grain-refined zone is moving. Isotopes ^{25}Mg , ^{26}Mg are concentrated in the initial crystallization zone. Segregation coefficient increases at influence of constant magnetic field or direct electric current on molten zone. The obtained data are compared with the data on magnesium isotope segregation by the other physicochemical methods.

Introduction

Floating-zone refining often called zone melting is applied for deep purification of substances and their obtaining in single crystal form. As floating-zone refining may be used for separating substances with very close properties and isotopes with low content may be considered with a certain approximation extent as a peculiar impurity to the main isotope then there is a possibility to change the ratio of stable isotopes in salts and metals under the influence of floating-zone refining [1].

Magnesium chloride ($MgCl_2 \cdot 6H_2O$) was chosen as the main object of investigation. Such choice is stipulated by three factors. Firstly, $MgCl_2 \cdot 6H_2O$ is melted at low temperature (116,7°C) that simplifies considerably instrumental process registration; secondly, $MgCl_2 \cdot 6H_2O$ in the experimental conditions is melted completely without the given phase; thirdly, magnesium has three isotopes ^{24}Mg , ^{25}Mg and ^{26}Mg in the ratio 78,60, 10,11 and 11,29 % [2] and in this case ^{24}Mg may be considered as the main isotope and isotopes ^{25}Mg and ^{26}Mg as impurity to the main isotope.

The aim of the work was to study magnesium isotope segregation in the process of floating-zone refining of $MgCl_2 \cdot 6H_2O$ and reveal of factors intensifying this process.

Technique of carrying out the experiments

Investigations were carried out at the samples of $MgCl_2 \cdot 6H_2O$ of «analytically pure» qualification with the length of 100 mm and diameter 3 mm. The samples

were prepared in the following way. Magnesium chloride crystalline hydrate $MgCl_2 \cdot 6H_2O$ was heated to its complete melting and glass tube was filled up with it; after that the tube was soldered from both ends.

Studying the influence of continuous current on change of isotope composition of $MgCl_2 \cdot 6H_2O$ in the process of floating-zone refining the ends of samples were connected by platinum electric contacts with constant current source TEC-42 (HTP 15.10). Voltage equal to 50 V causing continuous current with the strength of 1,3 A in electric circuit was supplied to electrodes. Electric current density amounted to 0,65 A/cm². Motion of melted zone along the sample was performed by sample traveling through stationary heaters.

The experiments were carried out at the device having five zones of heating and cooling. Nichrome wire was used as heating elements. The temperature of molten zone was supported in the range of 120±1 °C that promoted salt area melting by ingot height in 3...4 mm. Melt cooling was naturally-aerial. Temperature of cooling zone amounted to 20±2 °C.

Studying the influence of magnetic field on changing $MgCl_2 \cdot 6H_2O$ isotope composition in the process of floating-zone refining the permanent magnets with magnetic field intensity of 0,3 T were used. Magnetic field intensity was measured by Hall device.

After the experiment 10 mm of each end of glass tube was cut, samples of $MgCl_2 \cdot 6H_2O$ were taken off and analyzed. Preliminary researches showed that at float-

ting-zone refining on the boundaries of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ samples isotope composition changes only by magnesium therefore, magnesium isotope composition was determined in all experiment. The analysis was performed by the method of mass spectrometry at isotope mass spectrometer MX-1301T.

Results and their discussion

As a result of carried out experiments it was stated that isotopes ^{25}Mg and ^{26}Mg are concentrated in the initial crystallization zone and isotope ^{24}Mg travels with molten zone and concentrated in the final zone of crystallization. This observation may be explained by the fact that isotope ^{24}Mg possesses higher diffuse mobility and correspondingly it may move to a large degree than isotopes ^{25}Mg and ^{26}Mg .

Samples at different number of crystallization stages and different velocity of travel of molten zone were obtained experimentally. Change of ratio of isotopes $^{24}\text{Mg}/^{26}\text{Mg}$ (^{25}Mg) in the initial grain-refined zone in the samples with different number of stages is shown in Fig. 1.

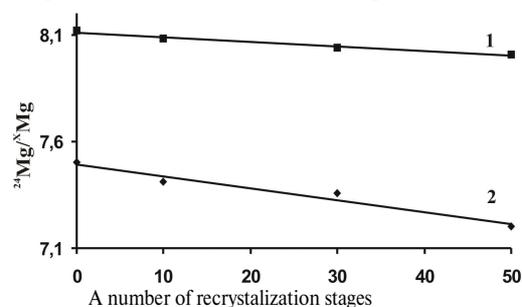


Fig. 1. Change of ratio of isotopes $^{24}\text{Mg}/^{26}\text{Mg}$ (^{25}Mg) in samples with different amount of stages of floating-zone refining in the initial zone: 1) $^{24}\text{Mg}/^{25}\text{Mg}$; 2) $^{24}\text{Mg}/^{26}\text{Mg}$

Change of isotope ^{24}Mg in the initial grain-refined zone at different traverse speed of molten zone is shown in Fig. 2. It follows from experimental data that increasing a number of recrystallization stages and decreasing ingot traverse speed the degree of magnesium isotope separation increases.

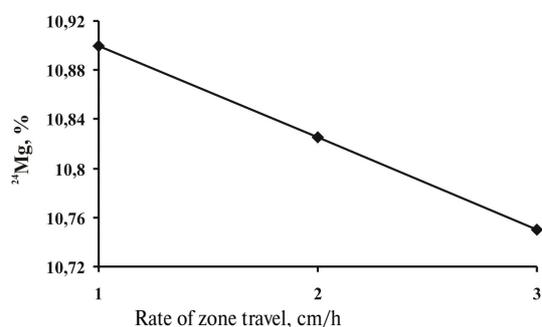


Fig. 2. Change of isotope ^{24}Mg content in the initial crystallization zone at different zone traverse speed after 30 stages of crystallization

Change of magnesium isotope composition by the length of ingot $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ after 30 stages of floating-zone refining with molten zone traverse speed of 3 cm/h is shown in Fig. 3. It is known [3] that in the case of zone

melting the impurities are concentrated on the area amounting about $\frac{1}{3}$ from ingot length at small quantities of recrystallization stages. In the given case both ^{24}Mg enriching and ^{26}Mg depletion are not located near sample $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ends and occupy areas with the extent about $\frac{2}{3}$ of its length. This indicates that isotopes and impurities behavior at floating-zone refining is different [3]. As the compound containing water in its composition is used as the object of investigation then such difference in behavior of isotopes and impurities may be connected with the fact that the process of ion salvation (hydration) which may restrain ion diffusion and impede isotope separation is overlapped on the process of magnesium isotope distribution at recrystallization.

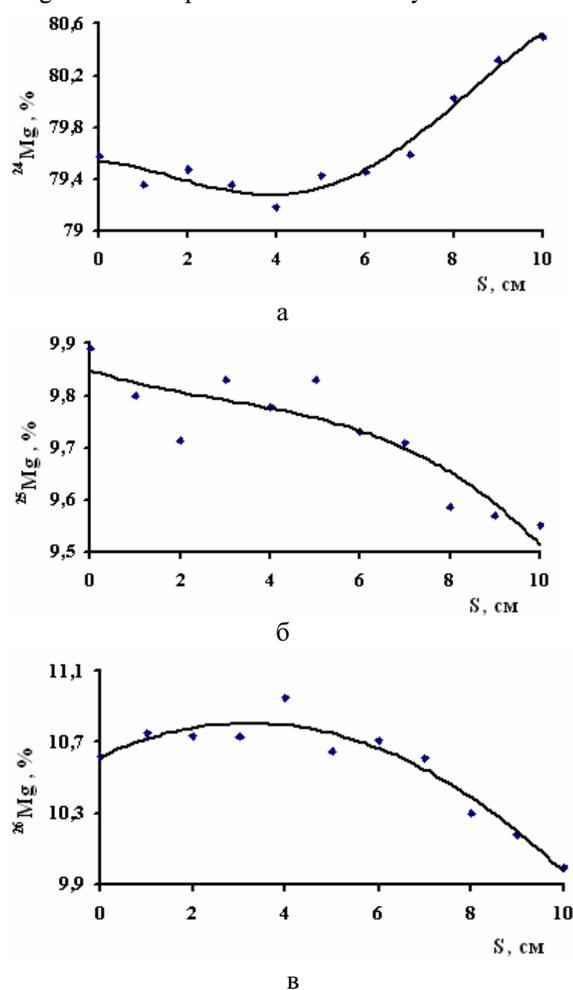


Fig. 3. Change in magnesium isotope composition by ingot length S : a) ^{24}Mg ; б) ^{26}Mg ; B) ^{25}Mg

As it is known [4] ion salvation in solution is determined by the character and ratio of all types of interaction in the solution – ion-ion, ion-molecule and intermolecular interactions. Salvation contributions for ionic systems are estimated by considering the following processes: 1) formation of cavity in solvent (contribution of interactions depending on ion size); 2) transfer to the cavity of uncharged particle isoelectronic relative to ion; 3) redistribution of electron cavity between ion and molecules of solvent (contribution from other interaction depending on ion charge).

Evidently, interaction of magnesium ions with water molecules that is chemical component of hydration makes the greatest contribution into control of magnesium ion diffusion. It is connected with the fact that H_2O molecule is an electro donor and implements donor-acceptor interaction with magnesium ions mainly by mechanism cation – solvent. At insignificant content of H_2O molecules (as it is seen from chemical formula there are six molecules of H_2O in crystalline hydrate of magnesium chloride) all of them or the most part of them are coordinated to magnesium ion. As the radius of formed particle exceeds ion radius then their diffusion decreases that affects the efficiency of isotope division.

In this paper magnesium isotopes division by the method of floating-zone refining with influence of constant magnetic field or continuous current was studied on molten zone. The results of the experiments are given in Table 1. The samples for analysis were selected from the initial zone of crystallization after 30 stages; traverse speed of molten zone during the experiments was always constant and amounted to 3 cm/h.

Table 1. Change of $MgCl_2 \cdot 6H_2O$ isotope composition in the process of floating-zone refining at the influence of constant magnetic field or continuous current on molten zone, %

Experiment conditions	Isotope			
	^{24}Mg	^{25}Mg	^{26}Mg	
Original composition	79,58±0,03	9,8±0,02	10,62±0,02	
Floating-zone refining	79,35±0,04	9,87±0,04	10,75±0,04	
Floating-zone refining + magnetic field (0,3 T)	79,26±0,04	9,83±0,04	10,89±0,03	
Floating-zone refining + continuous current (0,65 A/cm ²) (direction of zone motion is indicated by the arrow)	−→+	79,2±0,02	9,63±0,05	11,19±0,03
	+→−	79,31±0,05	9,84±0,03	10,82±0,05

As it is seen from the Table data the segregation coefficients increase both at the influence of constant magnetic field and continuous current. Continuous current flowing through the ingot at crystallization influences most of all on magnesium isotope segregation. Increasing enrichment by isotope ^{24}Mg is observed at the direction of molten zone motion from negative electrode to a positive one. Changing current polarity insignificant increase of isotope separation effect occurs.

It should be also mentioned that at presence of continuous current a greater motion of ^{25}Mg isotope with molten zone than at common floating-zone refining is observed.

The obtained results may be explained in the following way. According to [3] to determine effective distribution coefficient the expression of Barton, Prim and Slihter may be used:

$$K = \frac{1}{1 + \left[\left(\frac{1}{K_0} \right) - 1 \right] e^{-f\delta/D}},$$

where K_0 is the equilibrium distribution coefficient, f is the crystal growth rate, δ is the thickness of diffuse layer before crystallization front, D is the diffusion coefficient.

It follows from the equation that the difference of effective distribution coefficient K from equilibrium distribution coefficient K_0 is the greater the more the diffusion coefficient D and less the thickness of diffuse layer δ before crystallization front. It is known [3] that mixing process influences significantly the efficiency of zone refining. Taking into account the fact that diffuse layer thickness δ depends on mixing intensity (at weak mixing of the melt $\delta \sim 10^{-1}$ cm, at rapid mixing $\delta \sim 10^{-3}$ cm) then the influence of magnetic field and continuous current on changing $MgCl_2 \cdot 6H_2O$ isotope composition in conditions of floating-zone refining may be connected with more intensive mixing of the melt before crystallization front.

Besides, in the case of combined action of floating-zone refining and current electro transfer may also influence the increase of segregation coefficient [5]. Light isotopes travel first of all with molten zone due to their comparatively high diffuse mobility. This allows making a conclusion that decreasing ^{25}Mg concentration in the initial zone of crystallization at continuous current overlapping is connected with the phenomenon of electro transfer.

Coefficients of segregation of magnesium isotopes $^{24}Mg/^{26}Mg$ obtained while using different physicochemical methods and segregation coefficient obtained in the given paper are given in Table 2.

Table 2. Segregation coefficients of $^{24}Mg/^{26}Mg$ obtained while using different physicochemical methods

Separation method	Segregation coefficient
Amalgam [6]	1,022
Vacuum distillation [7]	1,034
Extraction with crown ethers [8]	1,0017
Ion-exchanging [9]	1,00016
Floating-zone refining	1,0039

Conclusion

At floating-zone refining of $MgCl_2 \cdot 6H_2O$ light isotope ^{24}Mg travels with molten zone. Increasing a number of recrystallization stages and decreasing traverse speed of molten zone the effect of magnesium isotope segregation grows. The enriched areas occupy about 2% of the original material that is the effect has volumetric character. Segregation coefficient of $^{24}Mg/^{26}Mg$ at floating-zone refining equals to 1,004.

When constant magnetic field (0,3 T) or continuous current (0,65 A/cm²) influence molten zone the enrichment factor for ^{26}Mg increases in the first case in ~2 times, in the second case in ~4 times. The largest enrichment value by isotope ^{24}Mg is observed at the direction of molten zone motion from negative electrode to the positive one.

REFERENCES

1. Kherington E. Zone melting of organic substances. – Moscow: Mir, 1965. – 260 p.
2. Brodskiy A.I. Isotope chemistry. – Moscow: USSR AS Press, 1957. – 595 p.
3. Pfann V. Zone melting. – Moscow: Mir, 1970. – 366 p.
4. Krestov G.A., Novoselov N.P., Pereygin I.S. et al. Ionic solvation. – Moscow: Nauka, 1987. – 320 p.
5. Fiks V.B. Ionic conduction in metals and semiconductors (electro transfer). – Moscow: Nauka, 1969. – 296 p.
6. Kravchenko A.V., Rylov V.S. Segregation of magnesium isotopes in the system of magnesium amalgam – water solution $MgCl_2$ // Zhurnal Fizicheskoy Khimii. – 1963. – V. 37. – № 4. – P. 910–912.
7. Pugachev Yu.I., Rylov V.S. Segregation of magnesium isotopes at vacuum distillation // Zhurnal Fizicheskoy Khimii. – 1963. – V. 37. – № 3. – P. 691–693.
8. Levkin A.V., Basmanov V.V., Demin S.V., Tsivadze A.Yu. Segregation of magnesium isotopes at extraction with crown ethers // Zhurnal Fizicheskoy Khimii. – 1990. – V. 64. – № 5. – P. 1376–1377.
9. Aaltonen J. Separation of alkaline earth metal isotopes by ion exchange. P. I. Studies on magnesium and calcium // Suomen kem. – 1971. – V. 44. – № 1. – P. 1–3.

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OBTAINING NEODYMIUM FROM MELTS BY ELECTROLYSIS

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The mechanism of electrode reactions at electrochemical obtaining neodymium and neodymium-iron alloy from fluoride oxide systems has been studied. Current-voltage dependences of electrochemical processes in melts containing fluorine salts of lithium, potassium, sodium and neodymium oxide were analyzed. Neodymium current yield values, optimal process variables: current density, temperature, melt composition were determined. Electrolyzers constructions were optimized, experimental-industrial electrolyzer was designed, process instrument flow diagram was developed.

Rare-earth metals are applied year by year in larger quantities in various fields of science and technology. Such rapid growth of consumption is stipulated by many unique physical and chemical properties of these metals and their compounds: optical, magnetic, electrical and others. Flow of scientific and technical researches on studying physical and chemical properties of REM and materials on their basis as well as on applying these materials increases that promotes further rapid development of manufacturing REM and new materials on their basis. Volume of production and use of REM characterizes to a considerable extent the degree of development of country science and technology especially new branches.

Use of rare-earth materials for manufacturing unique high-energy constant magnets on the basis of Sm-Co and Nd-Fe-B was developed more dynamically recently [1]. Literary analysis [2–5] showed that one of the main techniques of obtaining neodymium at the present time is electrolytic neodymium obtaining from oxide-fluoride melts which practically replaced metal-thermy. Applying this technology China became the sole leader in manufacturing rare-earth metals and their compounds: 85 % of manufactured rare-earth production in the world falls on China [2].

The aim of the paper was to develop optimal process diagram of obtaining neodymium and neodymium-iron alloy.

On the basis of known data the composition of the melt [4], Fig. 1: LiF – 76,8 %, NdF_3 – 19,2 %, Nd_2O_3 – 4 % was selected in terms of salt state diagrams being

a part of electrolyte composition. This composition underwent electrolysis. Besides, at present the electrolyte the main component of which is cheaper salt of sodium fluoride than lithium fluoride is tested $Nd_2O_3 + 2C = Nd + CO + CO_2$. At temperature of electrolysis the theoretical voltage of neodymium oxide decomposition was calculated by the reaction (1) slightly differing from that given in the paper [5]. The value of decomposition voltage – 1,6 V given by the authors [5] is larger than one which we calculated but formation of CO_2 by the reaction (1) is not taken into account.

The mechanism of electrode processes proposed by us [3] differs from those known before [6] in multistage and discharge on cathode of $NdOF_2^-$ anions. Though it is rather difficult to solve definitely the question about the character of electrode processes occurring at melt electrolyses it is possible to suppose the existence of the following ions: F^- , NdF_6^{-3} , $NdOF_2^-$, $NdOF_3^{-2}$, Nd^{+3} , NdO_3^{-3} in the melt. The processes occurring in the volume of electrolyte and on electrodes may be presented in the following way:

