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KINETICS OF ZINC EVAPORATION IN INERT AND REDUCING GASES

The article presents the results of studies on the rate of zinc evaporation in the atmosphere of helium and carbon monoxide (II) carried out with the thermogravimetric method. The estimated values of zinc streams were compared with the values determined based on theoretical relationships.

Keywords: evaporation, flux, zinc, thermogravimetric analysis

1. Introduction

The phenomenon of evaporation of metals from liquid alloys accompanies all high-temperature processes of extraction metallurgy as well as refining processes. The intensity of this process depends on many factors, the most important of which is the type of melting device (geometric factor), the nature of the process (technological factor), alloy composition as well as the gas atmosphere (chemical factor) [1-5]. Knowing the value of the equilibrium vapor pressure of a volatile metal can determine the maximum rate of evaporation using the Langmuir equation which correspond to a perfect vacuum conditions. To determine the value of the evaporation rate for higher pressures, it is necessary to carry out measurements. The obtained experimental results for strictly defined conditions are a source of information about the nature of phenomena occurring in an open system containing a condensed phase (liquid metal or its alloy) – a gas phase (atmosphere in a melting aggregate).

The paper presents the results of research on the evaporation of pure zinc in the atmosphere of helium and carbon monoxide (II) carried out with the thermogravimetric method.

2. Methodology

The experiments were carried out using the NETZSCH thermal analyzer, the STA 449 F3 Jupiter model and the Mettler TA1 thermometers. Media and heads that equip these devices allow to carry out measurements thermogravimetric (TG) and differential thermal analysis (DTA). In addition, the analyzers were equipped with furnaces operating in various protective atmospheres, enabling measurements to be carried out above 1800 K.

A sample of zinc (analytically pure) of a precisely defined mass was placed in a DTA / TG crucible made of Al_2O_3 . Then the crucible was mounted on the measuring head in the analyzer working chamber.

All measurements were carried out in helium or CO atmosphere with a gas flow of $50 \text{ dm}^3 \cdot \text{min}^{-1}$.

Parameters registered during researches were:

- weight loss, TG ,
- temperature, T ,
- the duration of the experiment, t ,
- gas flow rate, q .

The sample heating program consisted of three main stages:

- heating the sample to the set temperature (948 K, 973 K, 998 K, 1023 K, 1048 K) at a rate of 20 K min^{-1} ,
- isothermal heating of the sample at a given temperature for a period of 30 minutes,
- cooling of the sample to 473 K.

Measurements of the rate of evaporation of zinc was carried out under isothermal conditions. Initial weight of zinc is uniform cca 1000 mg. The zinc vapors condensed outside the measuring system.

3. The researches results

Figure 1-3 presents exemplary TG curves obtained for researches conducted at temperatures of 948 K; 998 K and 1048 K obtained for experiments carried out using the NETZSCH analyzer in helium atmosphere.

On the basis of the obtained TG curves, the mass losses of individual samples in the isothermal range of measurement were determined for each experiment. The results are summarized in Table 1.

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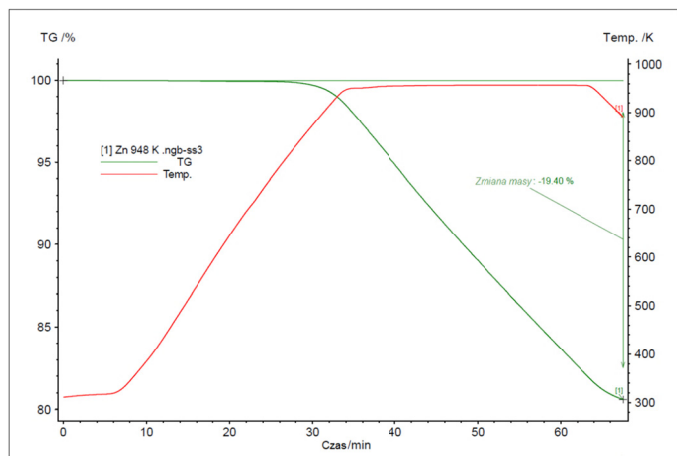


Fig. 1. The change in the weight of the zinc sample during heating up to 948 K

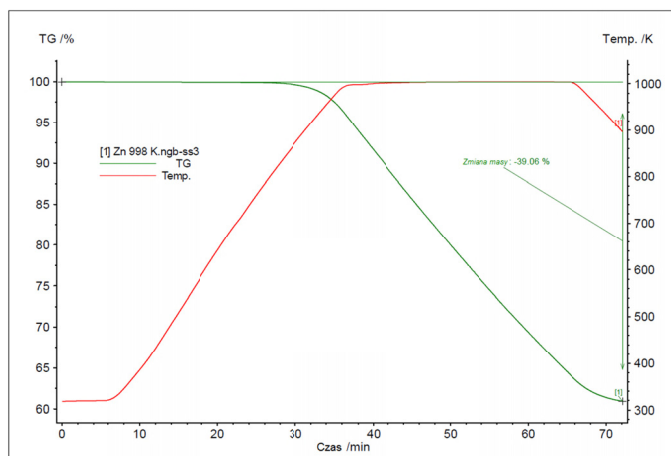


Fig. 2. The change in the weight of the zinc sample during heating up to 998 K

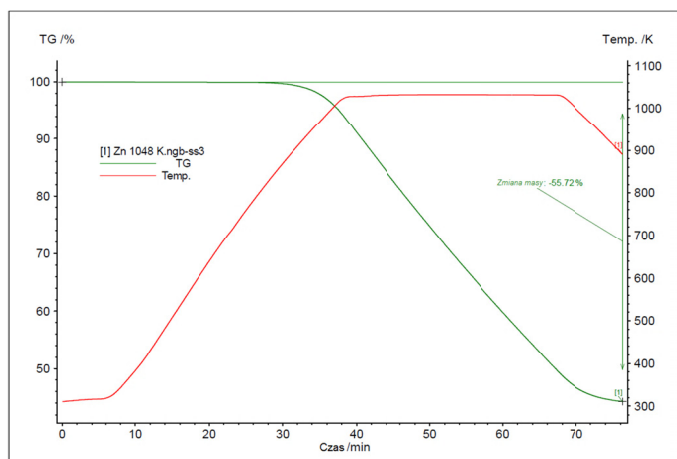


Fig. 3. The change in the weight of the zinc sample during heating up to 1048 K

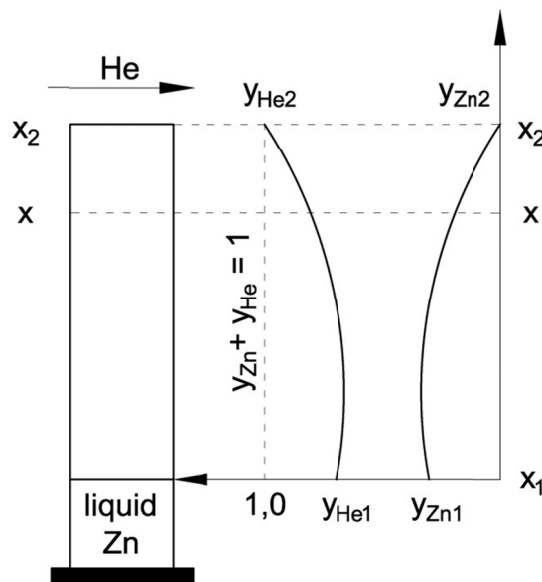


Fig. 4. Distribution of concentration of Zn component diffusing through the inert component (He) in the gas phase

TABLE 1

Changing the mass of the zinc in the range of isothermal heating

No	Temperature of molten zinc, K	Weight loss of the sample under isothermal conditions, %	The rate of weight loss of zinc, mg cm ⁻² s ⁻¹
1	948	17,13	0,34
2	973	25,98	0,50
3	998	34,14	0,65
4	1023	38,19	0,76
5	1048	48,31	0,91

4. Discussing research results

In the analyzed case, zinc evaporates from a bath placed in a high crucible. Above the bath mirror is a gas column – helium or CO with a height of XHe. The same gas flows over the edge of the crucible. It is obvious that with increasing distance X from the metal mirror relative partial vapor pressure of zinc vapor y_{Zn2} decreases and increases the helium relative partial pressure y_{He} , Figure 4.

If we assume an established character of zinc vapor diffusion, its speed through the inert component (helium, CO) define the following relationships [6]:

$$N_{Zn} = \frac{D_{AB}C}{x_2 - x_1} \ln \left(\frac{1 - y_{Zn2}}{1 - y_{Zn1}} \right) \quad (1)$$

$$N_{Zn} = \frac{D_{AB}C}{x - x_1} \ln \left(\frac{1 - y_{Zn}}{1 - y_{Zn1}} \right) \quad (2)$$

where: D_{AB} – diffusion coefficient for the gas mixture, m²/s.

The distribution of zinc concentration in helium in the analyzed measurement system can be obtained from a comparison of these equations.

$$\ln \left(\frac{1 - y_{Zn2}}{1 - y_{Zn1}} \right)^{\frac{1}{(x_2 - x_1)}} = \ln \left(\frac{1 - y_{Zn}}{1 - y_{Zn1}} \right)^{\frac{1}{(x - x_1)}} \quad (3)$$

$$\ln \left(\frac{1 - y_{Zn2}}{1 - y_{Zn1}} \right)^{\frac{(x-x_1)}{(x_2-x_1)}} = \left(\frac{1 - y_{Zn}}{1 - y_{Zn1}} \right) \quad (4)$$

In this case, it can be assumed that

$$y_{Zn2} = 0 \quad (5)$$

then

$$y_{Zn} = 1 - (1 - y_{Zn1})^{\frac{(x_2-x)}{(x_2-x_1)}} \quad (6)$$

The value of partial pressure of zinc vapor at any height from the surface of liquid metal can be appreciated on the basis of the above dependencies. It is determined from dependence:

$$P_{Zn} = P \left[1 - \left(1 - \frac{P_{Zn1}}{P} \right)^{\frac{(x_2-x)}{(x_2-x_1)}} \right] \quad (7)$$

Table 2 presents the vapor pressure of zinc (p_{Zn}) for the temperature of 948 K and 1023 K and the general pressure in the system of 0,1 MPa calculated from the dependence (7). The vapor pressure of saturated zinc was respectively 5264 Pa and 16074 Pa. The calculations were made for the assumed height of the free space of the crucible above the bath $x = 0,6$ m. A graphical interpretation of the change in the vapor pressure of zinc depending on the distance from the surface of the bath is shown in Figure 5.

TABLE 2

The vapor pressure of the zinc above the bath placed in the cylindrical crucible

Distance from the surface of the bath, m	p_{Zn} , Pa		Distance from the surface of the bath, m	p_{Zn} , Pa	
	948 K	1048 K		948 K	1048 K
0*	5264	16074	0,003	2834	8403
0,001	4356	13610	0,004	1823	5627
0,002	3445	10942	0,005	911	2768

* in the calculations the value of the vapor pressure of zinc at the surface equal to the equilibrium pressure was assumed

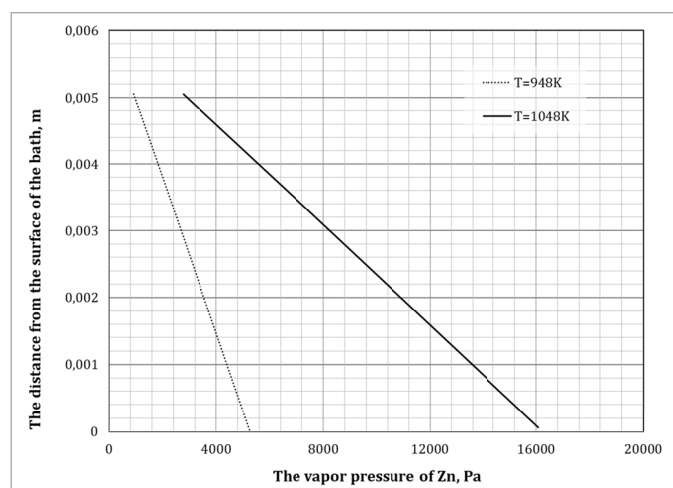


Fig. 5. The pressure of zinc vapors above the surface of the bath

Analyzing the data presented in Table 2 and in Figure 5 can discern that the value of the vapor pressure of zinc decreases with increasing distance from the surface of the bath. Thus, evaporation rate is also decreased with the increase of the amount of free space of the crucible above the bath.

The maximum value of the mass stream of the evaporating metal determines the dependence [7]:

$$\dot{N}_{Max} = \frac{p^o}{\sqrt{2\pi MRT}} \quad (8)$$

where:

p^o – metal equilibrium pressure over the pure melt, Pa,

T – temperature, K,

R – gas constant, $J \cdot mol^{-1} \cdot K^{-1}$.

Using the relationship (8), the values of the maximum flux of zinc evaporating under ideal vacuum conditions were estimated. The zinc equilibrium vapor pressure determined on the basis of the HSC Chemistry program [8] were used for the calculations, Table 2. The values of the N_{max} flux in the temperature range 1023-1073 K were at the level of $12,374-97,139 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.

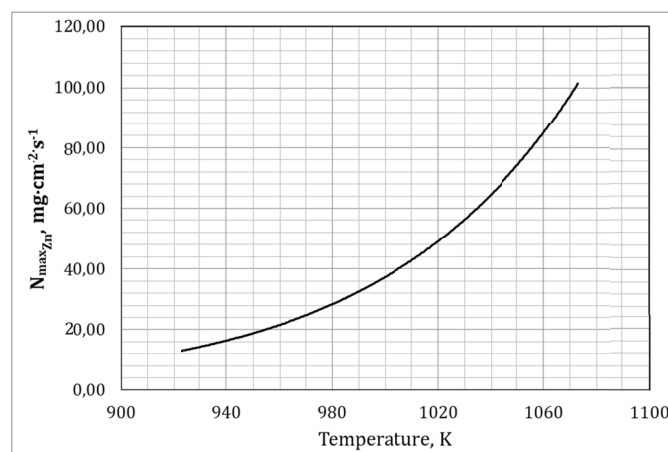


Fig. 6. Effect of temperature on the value of maximum zinc evaporation rate (under ideal vacuum conditions)

The value of the evaporating zinc stream from the bath located in the high crucible under an inert gas atmosphere can be estimated from the dependence [9]:

$$\dot{N}_{Zn} = 2,13 \cdot 10^{-3} P_{Zn}^o \cdot \left(\frac{M_{Zn} \cdot D_{Zn}}{x \cdot T} \right) \quad (9)$$

where:

D_{Zn} – the diffusion coefficient of zinc vapor in the gas, $\text{cm}^2 \cdot \text{s}^{-1}$,

P_{Zn}^o – zinc vapor pressure over a pure melt, Pa,

x – the height of the free space of the crucible above the surface of the liquid metal, cm,

\dot{N}_{Zn} – zinc flux, $\text{g} \cdot \text{cm}^2 \cdot \text{s}^{-1}$.

If we assume that in the analyzed hydrodynamic system the transport of zinc vapors over its bath, in the free space of the crucible, takes place by diffusion, its speed can be determined by analogy to the dependence (1) from the equation:

$$\dot{N}_{Zn} = \frac{D_{Zn-He} \cdot P}{RT(x_2 - x_1)} \cdot \frac{(y_{Zn1} - y_{Zn2})}{\bar{y}_{He}} \quad (10)$$

where:

$$\bar{y}_{He} = \frac{y_{He2} - y_{He1}}{\ln\left(\frac{y_{He2}}{y_{He1}}\right)} \quad (11)$$

Knowing the values of the zinc diffusion coefficients in helium and carbon monoxide (CO) can be determined from the dependence (9) and (10) values of the zinc evaporation rate.

The value of the gas phase diffusion coefficient for the analyzed systems of zinc vapor – helium and zinc vapor – CO was determined using the dependence of Hirschfelder, Curtis and Bird derived from the kinetic theory of gases [10]. This theory takes into account the existence of intermolecular forces described by using the function Lennard-Jones. This equation is valid in principle for binary mixtures of monatomic non-polar gases. However, they can also be used for mixtures of non-polar non-polar gases as well as for non-polar gas – polar gas mixtures. The existence of only one atomic gas form for the majority of metals can be assumed with great accuracy. However, in metallurgy there are also elements whose number of atoms, e.g. aluminum, copper, lead, silver, zinc and tin, have a number of diatomic particles. In most cases the number of polyatomic particles in pairs of these elements is very small. Assuming mononuclear construction of pairs of these elements does not commit a greater error in the calculation. This relationship has the form:

$$D_{AB} = 5,954 \cdot 10^{-24} \sqrt{T^3 \cdot \left(\frac{1}{M_A} + \frac{1}{M_B}\right)} \cdot \frac{1}{P \cdot \sigma_{AB}^2 \cdot \Omega_{AB}} \quad (10)$$

where:

- D_{AB} – diffusion coefficient for the gas mixture, $m^2 s^{-1}$,
 - T – temperature, K,
 - P – general pressure, Pa,
 - M_A, M_B – molar mass of components A and B , $kg mol^{-1}$,
 - σ_{AB} – constant interaction force gas molecules, m,
 - Ω_{AB} – function describing the properties of gases A and B .
- Constant σ_{AB} calculated from dependencies [11]:

$$\sigma = \frac{\sigma_A + \sigma_B}{2} \quad (11)$$

where: σ_A, σ_B – constant forces for gaseous components A and B , m.

Ω_{AB} value of the function can be counted out of the equation Ninja

$$\Omega_{AB} = 1,075 \cdot \left(\frac{k \cdot T}{\varepsilon_{AB}}\right)^{-0,1615} + 2 \cdot \left(\frac{10 \cdot kT}{\varepsilon_{AB}}\right)^{-0,74 \cdot \log(10 \cdot k \cdot T \cdot \varepsilon_{AB}^{-1})} \quad (12)$$

where:

- k – Boltzman's constant, $J K^{-1}$,
- ε_{AB} – constant interaction force gas molecules, J.

ε_{AB} estimated value of the constant depending on the [12]:

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \cdot \varepsilon_B} \quad (13)$$

where: $\varepsilon_A, \varepsilon_B$ – constant forces for gaseous components A and B , J.

The values of the coefficient of zinc diffusion in helium and carbon monoxide calculated from the relationship (10) are summarized in Table 3.

TABLE 3

Values of zinc vapor diffusion coefficient in helium and carbon monoxide

Temperature, K	The diffusion coefficient of zinc D_{Zn-g} , $cm^2 \cdot s^{-1}$	
	D_{Zn-He}	D_{Zn-CO}
948	5,90	1,50
973	6,15	1,60
998	6,40	1,65
1023	6,68	1,70
1048	6,91	1,75

Table 4 summarizes the data determined from the experimental values of the rate of evaporation of zinc in helium and CO. As TG1 the results obtained on the basis of researches carried out using the Mettler analyzer and as the TG2 the results obtained on the basis of researches on the Netzsch analyzer were determined. Figures 7 and 8 present a graphical interpretation of the obtained results in comparison with the values of the zinc evaporation rates estimated from dependences (9) and (10).

TABLE 4

Values for evaporation of zinc in helium and carbon monoxide

Temperature, K	The rate of evaporation of zinc, $mg \cdot cm^{-2} \cdot s^{-1}$		
	Zn-He (TG1)*	Zn-He(TG2)**	Zn-CO(TG1)*
948	0,39	0,34	0,28
973	0,55	0,50	0,47
998	0,98	0,65	0,58
1023	1,21	0,76	0,66
1048		0,91	

* – researches carried out using the Mettler analyzer

** – research carried out using the Netzsch analyzer

5. Conclusions

On the basis of researches carried evaporation rate of zinc showed that the rate of this process in a helium atmosphere is greater than the evaporation rate under an atmosphere of carbon monoxide (II). In the analyzed temperature range 948-1023 K, the determined rate of zinc evaporation in helium atmosphere was in the range of 0,34-1,21 $mg \cdot cm^{-2} \cdot s^{-1}$. For the process carried out in the atmosphere of carbon monoxide (II), these values were at the level of 0,28-0,66 $mg \cdot cm^{-2} \cdot s^{-1}$. The determined value of evaporation rates for some temperatures vary slightly from the

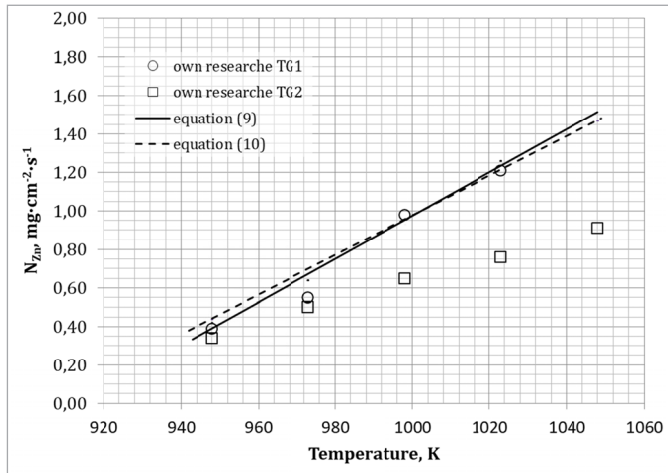


Fig. 7. The evaporation rate of zinc in helium atmosphere

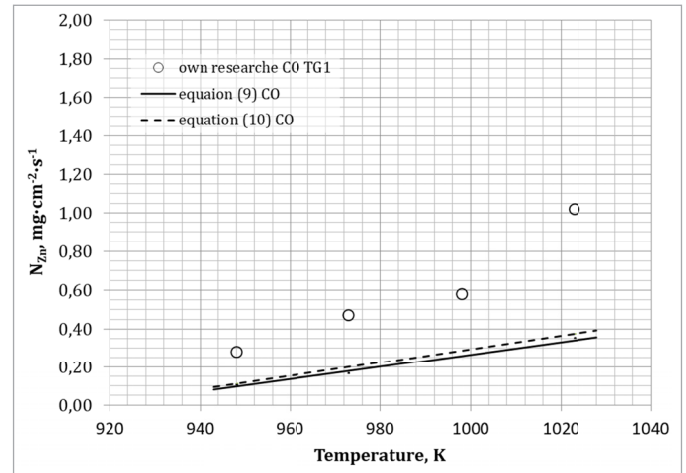


Fig. 8. The evaporation rate of zinc in CO atmosphere

values determined from the theoretical dependence. This may be due to the error made when estimating the actual value of the free space of the crucible above the metal bath. From a kinetic point of view, the analyzed evaporation process can be roughly regarded as quasi-diffusion and therefore the obtained results of experiments can be considered as correct. This is confirmed by the fact that the estimated values of the coefficients of diffusion of zinc vapor in helium is higher than the diffusion of zinc vapor into carbon monoxide (II). The significant influence of the type of atmosphere used on the speed of the zinc evaporation process indicates that it is determined by the phenomena of mass transport in the gas phase.

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