T. WOJTAL

ISSN 0543-5846
METABK 61(3-4) 653-656 (2022)
UDC – UDK 546.811-541.451:66.094.1:661.96:536.5=111

THE INFLUENCE OF TEMPERATURE ON THE SPEED OF REDUCTION OF TIN OXIDE WITH ARGON- HYDROGEN MIXTURE

Received – Primljeno: 2021-12-03
Accepted – Prihvaćeno: 2022-03-10
Original Scientific Paper – Izvorni znanstveni rad

Recently, the usage of hydrogen in the processes of metal extraction has been a very important challenge to metallurgic industry. Replacing conventional reductor, taking into consideration CO_2 emission restrictions will enable maintaining and developing this branch of industry. The results of the research on tin oxide SnO reduction using hydrogen given as a mixture Ar – 5 % vol.H_2 in temperature range 773 – 873 K. are shown in this article. The tests were conducted using thermogravimetric method. It is demonstrated that with the rise of a temperature in the analyzed range the speed of reaction rises as well and the obtained degree of reduction varies from 40 to 99,5 %. Stabilization the weight change in the tested sample thermogravimetric (TG) was reached after from 25 min for 773 K to 15 min for temperature 873 K.

Key words: tin oxide; reduction; hydrogen; temperaturs; thermogravimetry (TG)

INTRODUCTION

Majority of metals appear in the natural environment mainly as compounds with oxygen, sulphur and rarely with halogenated compounds. Whereas in recyclable materials, like slag, sludge and dust, metals appear mainly as oxides. To retrieve metals in the process of pyrometallurgic extraction based on reducing these compounds, coal is used in the form of a coke or breeze. Their role in these processes may be seen in two different aspects: energetic and reductive. The former, materials have the function of a fuel. When combusted the heat is obtained necessary to warm the input in a metallurgical aggregate, its melting, as well as to course of different endothermic reactions necessary to the proper realization of a given technology process [1]. Reducing aspect of applying coke or breeze in the indicated processes is related to the course of reducing reactions of oxides included in the input. For many years researches have been targeted on the usage of alternative materials that will enable to replace natural carbonaceous raw materials in metal receiving processes. It is caused mainly due to environmental and economical reasons. It is connected (among others) to the fact of significant supply limitation of coal in the EU and increasing costs related to CO_2 emission. Different kinds of biomass are offered as alternative reductors as well as fine- grained carboniferous wastes created in the processes of enriching and reprocessing coal [2 – 9].

Nowadays, hydrogen has very limited usage in pyrometallurgic processes of receiving widely used materials. It is, however, used to receive: tungsten, molybdenum, platinum, germanium or rhenium. As a gas reducer hydrogen has a number of advantages compared to solid reducers. The main is enhancing the speed of the process resulting in the better mass exchange between a gas reducer and reducing metal compound. Additionally, water is a product of reducing metal oxides with hydrogen therefore its usage may proceed to significant limitation od CO_2 emission. Taking into account increasing concern of limiting the greenhouse effect and having hydrogen as an agent reducing metal oxides, it can be assumed that its usage in pyrometallurgic processes may gain in importance in the future. In the article the researchon reducing tin oxide with a mixture of argon-hydrogen is presented. The research was carried out with thermogravimetric method.

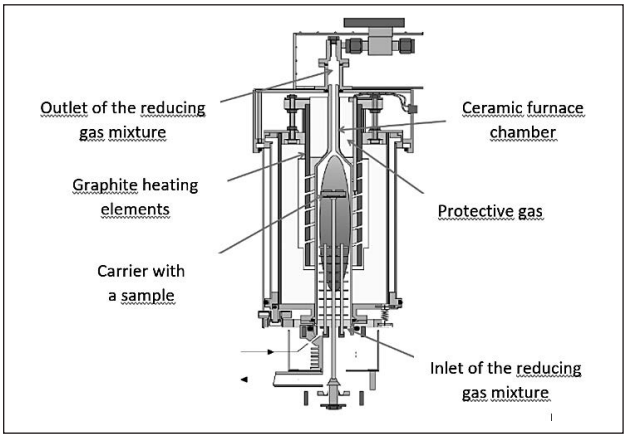

Figure 1 Scheme of leaching stand

T. Wojtal: Silesian University of Technology, Faculty of Material Science, Katowice, Poland
Corresponding author: tomasz.niemam@gmail.com

RESEARCH APPARATUS

An analyzer STA 449 F3 Jupiter brand NETZSCH was used in the research. It was used to thermogravimetric analysis (TGA) and enables simultaneous differential thermal analysis (DTA).

The analyzer equipped with microweight was measuring continuous mass loss of the sample during the experiment and the furnace chamber, where the corundum carrier with the sample was placed diagonally to the heated reactor tube (Figure 1) [10].

EXPERIMANTAL METHODOLOGY

Before every experiment scales together with the furnace chamber was blown with gas argon to prevent entering reactionary environment of gases that could have substantially affect parameters. Weighted amount of the sample used in the experiment was 400,0 mg ± 2,0 mg. Weighted powder was placed in a melting pot on a corundum carrier (made of Al_2O_3), and mounted on a thermoscale connected to a recorder. To measure the speed of SnO reduction with hydrogen with insignificant level of external effects of mass transfer , the speed of hydrogen flow through the reactor was set on 2,5 ml/ min and argon 47 ml/min. The research was carried out at 773 – 873 K.

RESULTS OF RESEARCH

Based on thermodynamic analysis it was assumed that reduction process proceeds according to the equation:

$$SnO_{(S)} + H_{2(G)} \rightarrow Sn_{(S)} + H_2O_{(G)} \qquad (1)$$

Then free enthalpy DG_T [11] was marked for the reaction (1). Obtained results were shown in a graphic form in Figure 2. Obtained results indicate that in case of tin oxide reduced with hydrogen, the change of sign is noticed at 744 K.

For the obtained test results conducted with the usage of thermoweight on the Figures 3 – 5 sample curves TG were demonstrated for the experiments carried out respectively in temperatures 773 K, 813 K and 873 K.

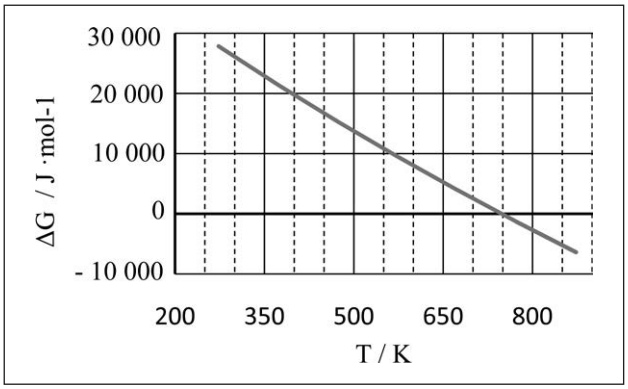

Figure 2 The change of free enthalpy reduction reaction SnO with gas hydrogen H_2 In temperatures 273 K – 873 K.

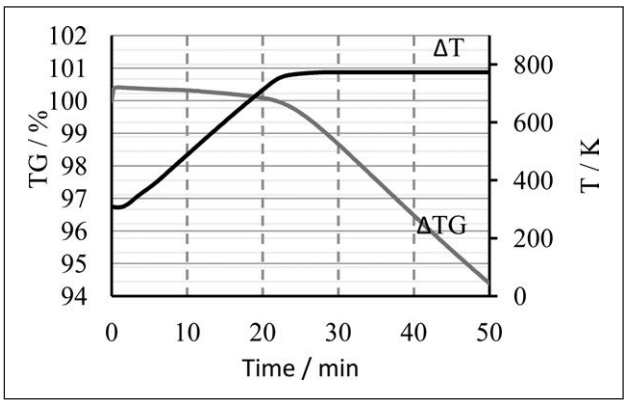

Figure 3 The change of mass sample (TG) received for the experiment conducted in 773 K.

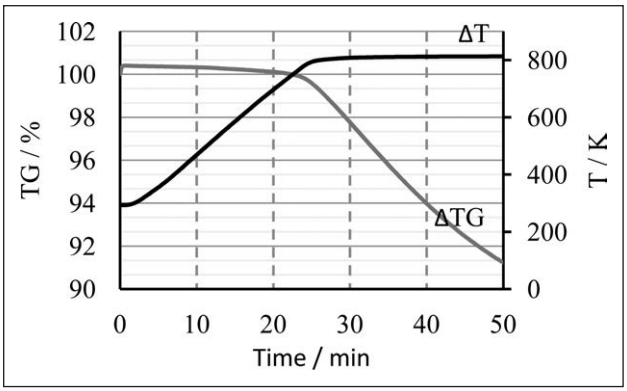

Figure 4 The change of mass sample (TG) received for the experiment conducted in 813 K.

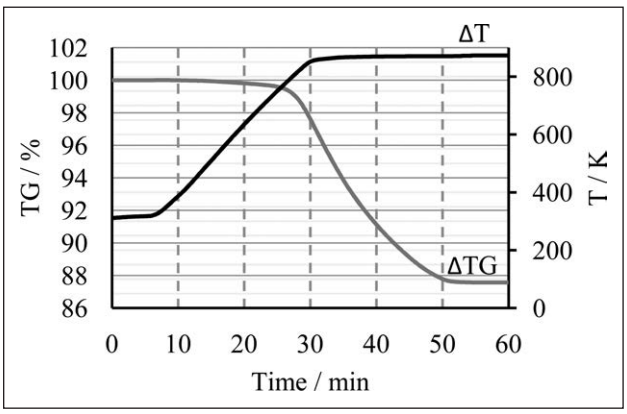

Figure 5 The change of mass sample (TG) received for the experiment conducted in 873 K

To describe the speed of analyzing process of dependence mass change in time according to dependance:

$$v = \frac{\Delta m}{\Delta t} \qquad (2)$$

where**:** Δm – mass loss sample/mg; Δt – time change range, min

Whereas the data described as a degree of overreaction is shown according to:

$$\alpha = \frac{\Delta m}{m_0 - mr} \qquad (3)$$

where**:** m_0 – initial sample weight, [mg]; m_r – weight loss sample after total reduction/mg

Figure 6 shows the received, during the research, reduction process speed change with described dependance (2). In the Tables 1 – 3 there are compiled received experiment data for tests conducted in temperatures 773 K, 813 K and 873 K. Figure 7 shows the overreaction degree coefficient during the process.

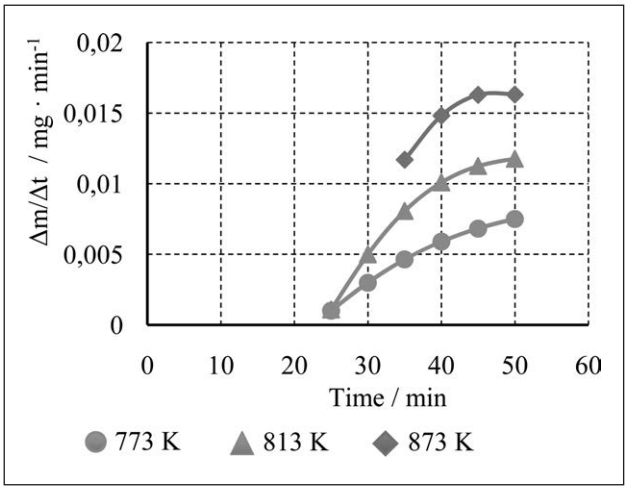

Figure 6 Sample mass change in time in dependence of temperature.

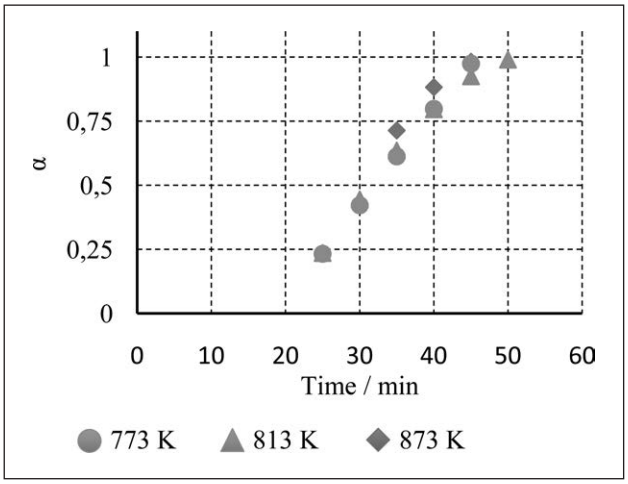

Figure 7 The change of overreaction degree α in function of time lasting reduction process (complete setting)

Table 1 **Sample mass change (TG) received for experiment conducted in temp. 773 K**

Temperature	Time	Instantaneous mass sample	Sample weight loss	Overreaction degree
T / K	t / min	m / mg	Δm / mg	α
293	0	401,600	0,065775	---
768	25	400,080	0,232507	0,066
773	30	396,227	0,422216	0,232
773	35	391,843	0,612792	0,422
773	40	387,439	0,797958	0,613
773	45	383,160	0,974469	0,798
773	50	379,081	0,065775	0,974

Table 2 **Sample mass change (TG) received for experiment conducted in temp. 813 K**

Temperature	Time	Instantaneous mass sample	Sample weight loss	Overreaction degree
T / K	t / min	m / mg	Δm / mg	α
293	0	402,300	0,043043	---
793	25	400,658	0,235845	0,043
808	30	393,303	0,444217	0,236
811	35	385,354	0,634791	0,444
812	40	378,084	0,796215	0,635
813	45	371,926	0,925186	0,796
813	50	367,006	0,989986	0,925

Table 3 **Sample mass change (TG) received for experiment conducted in temp. 873 K**

Temperature	Time	Instantaneous mass sample	Sample weight loss	Overreaction degree
T / K	t / min	m / mg	Δm / mg	α
293	0	401,000	0,492650	---
867	35	376,436	0,713483	0,493
869	40	365,425	0,882453	0,713
870	45	357,	0,982030	0,876
873	50	352,035	0,492650	0,982

CONCLUSIONS

Conducted thermodynamic analysis demonstrates that values of reaction of reduction tin oxide with hydrogen free enthalpy changes its sign in temperature 744 K, it shows that this reaction can be carried out in relatively low temperature range. Based on the research on thermogravimetric process of reduction tin oxide SnO with mixture of Ar and 5 % vol.H_2 it is demonstrated that the higher temperature the faster the analyzed process is car-

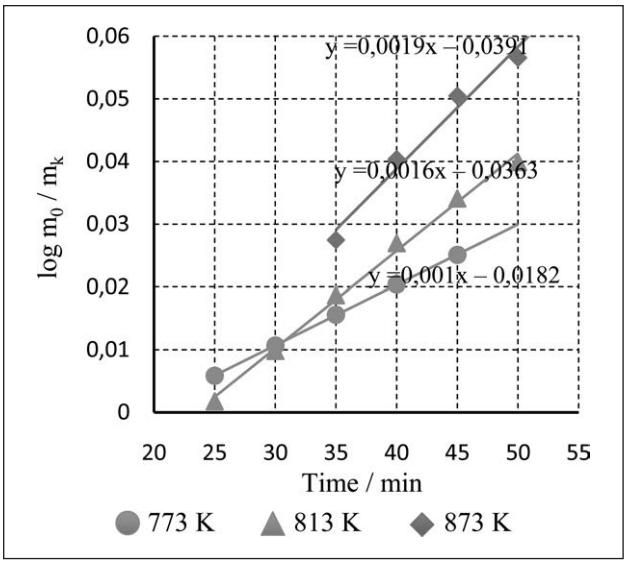

Figure 8 Estimation of sample mass weight change in reduction process of tin oxide SnO with hydrogen in dependance on temperature process.

ried out (Figure 6) By way of example, the value of overreaction degree α after 10 minutes from reaching the temperature 773 K was 0,422 and after 20 minutes it reached 0,798. For temperatures 873 K these values were 0,876 and 1, respectively. For temperature 773 K time to obtain total reduction was about 25 minutes and in temperature 873 K less than 20 minutes.

In case of conducted research on reaction process the sample weight change can be described by linear dependence:

$$\log \frac{m_0}{m_k} = ax + b \qquad (4)$$

in case where direction components of tilt angle of trend line allows to reflect the temperature influence on the speed of the process.

Acknowledgements:

This article was financed by Silesian University of Technology as a part of Statutory Research BKM-567/RM2/2021 (11/020/BKM21/0084)

REFERENCES

[1] A. Łędzki, A. Klimczyk, R. Stachura, M. Bernasowski: Rola własności koksu w wybranych piecach szybowych, Hutnik Wiadomości Hutnicze 82 (2014) 11, 765 - 768

[2] L. Lu, X. Li, M. Mahoney, Z. Zang, Biomass Materials for Metallurgical Application. Adv. Mater. Sci. Eng. 2018 (2018), 1

[3] R. Findorak, J. Legemza, M. Fröhlichova, G. Fabriciová, M. Džupková, New utilization of specific biomass: Lignin in the iron ore sintering process, Metals, 10 (2020) 1170, 1 - 17

[4] M. Alwaeli, The implementation of scale and steel chips waste as a replacement for raw sand in concrete manufacturing. J. Clean. Prod. 137 (2016), 1038 – 1044

[5] J. Łabaj, L. Blacha, A. Smalcerz, R. Findorak, M. Niesler. Utilization of waste coal flotation concentrate for copper matte smelting, Engineering Science and Technology, an International Journal, 24 (2021) 4, 996 – 1004

[6] V. Trinkel, N. Kieberger, N.T. Bürgler, H. Rechberger, J. Fellner, Influence of waste plastic utilisation in blast furnace on heavy metal emissions Journal of Cleaner Production, 94 (2015), 312 – 320

[7] C. Wang, P. Mellin, L. Nilsson, M. Larsson, Injecting different types of biomass products to the blast furnace and their impacts on the CO_2 emission reduction, AISTech, 1 (2015), 1525 – 1534,

[8] M. Niesle, J. Stecko, J. Łabaj, A. Smagór, L. Blacha: Application of waste anthracite dust in the process of copper matte smelting. Metalurgija, 21 (2021) 1, 11 – 17

[9] J. Łabaj, L. Blacha, M. Jodkowski, A. Smalcerz, M. Frohlichova, R. Findorak: The use of waste, fine-grained carbonaceous material in the process of copper slag reduction. J. Clean. Prod., 288 (2021), 1 – 10

[10] NETZSCH-Gerätebau GmbH, Operating Instructions Simultaneous TG-DTA/DSC Apparatus STA 449 F3 Jupiter®

[11] HSC 6.1 Termochemical database

Note: The responsible for English language is mgr Agata Kafel.