

THERMODYNAMIC INVESTIGATION OF OXYGEN/NATURAL GAS COMBUSTION IN SECONDARY ALUMINUM TECHNOLOGY

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Secondary metallurgy of aluminum presents some particularities to be taken into account when designing burners for room type furnaces: low temperature due to the large surface area of contact between recycled materials and reaction products of combustion, energy efficiency, the final quality of alloys obtained. This article shows the studied effects of processing parameters such as type of fuel, fuel to-oxidizer ratio, furnace temperature, and batch water content .

Keywords: LTOF – low temperature oxy-fuel, H₂O_(v), H₂, thermodynamic parameters

1. Introduction

During the last years the environmental protection problem is accentuated as well as the production and energy cost reduction for the companies in the field of metallic scrap recycling or secondary aluminum alloys producing. To increase the melting efficiency for metallic scraps as well as for pollutant quantity reduction in the atmosphere [1, 2], the practical solution is

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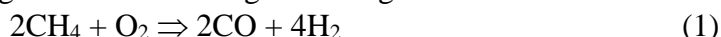
replacing the air-natural gas combustion system with the oxygen-natural gas combustion system – low temperature oxy-fuel, till the flame-less procedure.

In recent decades more articles are published, and the mathematical modeling of the burning process is extensively studied, but the heating systems used in the metallic scrap recycling are less studied. The present study refers to the secondary aluminum alloys to the room type furnaces using as heating system oxy – natural gas burners.

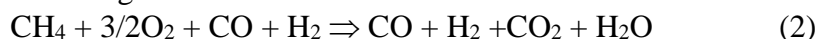
2. Material and methods

Some authors [4] consider that the burning process may be divided in 3 stages, as:

a) the stage I – fuel burning with heat evolving according to the reaction:



b) stage II – fuel burning with heat evolving in the presence of stage I reaction products (CO, H₂), according to the reaction:



c) stage III – elimination in the atmosphere of the reaction products from the stage II (CO, H₂, CO₂, H₂O) after complete oxidation, according to the relationships:



Also, the same authors specify the chemical composition of the reactants (air, natural gas) and the reaction products, as resulting from table 1.

Table 1

The reactants and reactants products at natural gas burning in air presence

C _n H _m (% vol.)	Preheated air (% vol.)	Burned gases (% vol.)
CH ₄ : 87.8%	O ₂ : 19.5%	O ₂ : 1.6%
C ₂ H ₆ : 4.6%	N ₂ : 59.1%	NO: 140 ppm
C ₃ H ₈ : 1.6%	H ₂ O: 15.0%	
C ₄ H ₁₀ : 0.5%	CO ₂ : 6.4%	
N ₂ : 5.5%	NO: 110 ppm	

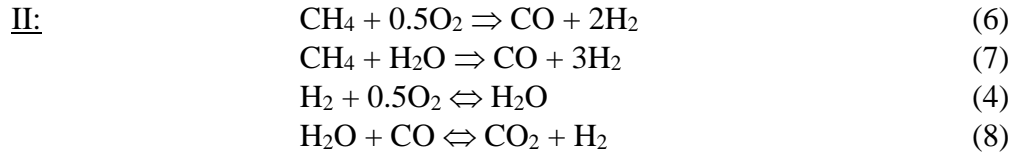
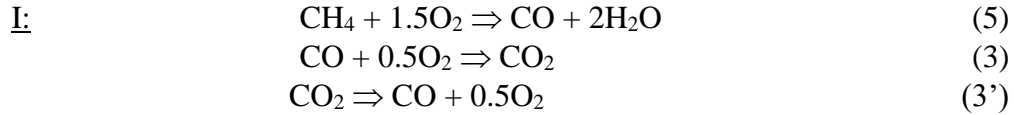
In another article [5], the authors studied the process of natural gas burning in oxygen presence, study indicating a maximum working temperature of 2342°C. The chemical composition of the natural gas has been slightly different in comparison to [4], underlining the following compounds (table 2).

Table 2

Natural gas chemical composition

C _n H _m (% vol.)
CH ₄ : 85.7%
C ₂ H ₆ : 5.4%
C ₃ H ₈ : 2.2%
N ₂ : 5.5%
CO ₂ : 1.2%

From the authors [5, 6] point of view the reaction taking place at natural gas burning in the oxygen presence can be divided in:



The interesting reaction for this study, the natural gas burning in the air presence, at room type furnaces heating used in secondary aluminum metallurgy.

Krzysztof Gosiewski et al [7] considers that the complete natural gas burning process took place by 3 reactions resulting in the table 3.

Table 3

Burning reactions according to some authors [6]		
I) Complete burning to CO ₂	$\text{CH}_4 + 2\text{O}_2 \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	(9)
II) Burning to CO	$\text{CH}_4 + 3/2\text{O}_2 \Rightarrow \text{CO} + 2\text{H}_2\text{O}$	(5)
III) Burning with passing from CO to CO ₂	$\text{CO} + 1/2\text{O}_2 \Rightarrow \text{CO}_2$	(3)
$\text{CH}_4 - \text{reaction II} \Rightarrow \text{CO} - \text{reaction III} \Rightarrow \text{CO}_2$		

Also, in other articles [8] the generally assumed relationships are the ones through natural gas combustion that take place from the production of thermal energy. The authors, after the effected research, affirm that after combustion does not produce molecular or atomic hydrogen.

In another study [9] the authors follow the resulted temperatures, characteristics of the reaction products and the flame at natural gas combustion in the presence of CO₂ and O₂. The combustion study in the presence of some different O₂, CO, CO₂, H₂O_(v), H₂ and CH₄ concentration in the burning mixture had realized other authors in their study [10, 11, 12], following the effects of laminar flowing and turbulence on the temperature, length and the radiant effect of the flame, temperature and the heat transfer by radiation and on the determining the reaction products and their concentration – table 4 and Fig. 1.

Table 4

The reaction products at natural gas combustion in one or more stages				
	1- step global reaction	2- step reaction	2- step reaction	Full dissociation
O ₂ – NG flames	5134	3787	3370	3042
Air – NG flames	2326	2256	2245	2223
Reaction products	CO ₂ , H ₂ O	CO, CO ₂ , H ₂ O	CO, H ₂ , CO ₂ , H ₂ O	> 100 species

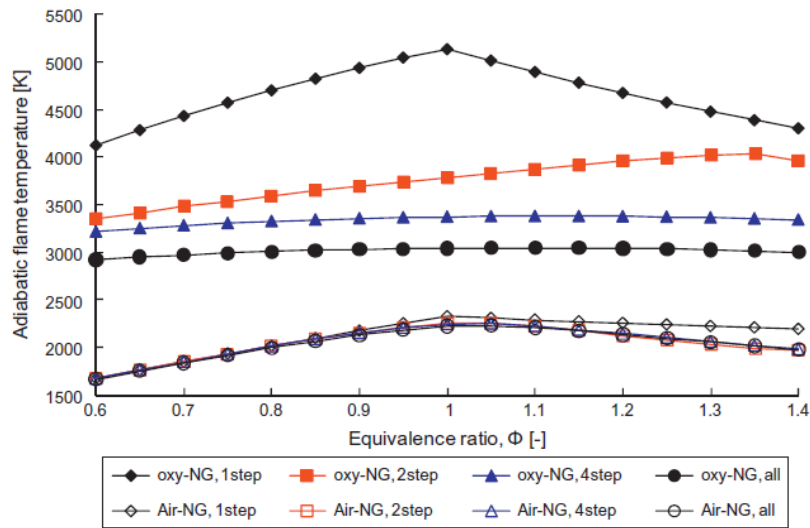


Fig. 1. Flame temperature at different composition in one or more steps [11]

2.1 Thermodynamic study on oxygen-natural gas combustion

The natural gas combustion process is using oxygen but also a combination between O_2 , air, CO_2 and N_2 in different concentrations. For secondary aluminum technology an energy source is necessary which, by the components used, does not interact with the metallic bath or the material from the charge. The most usual heating system is the one with air-natural gas burners or oxygen-natural gas with open flame or a newer one, flameless – low temperature oxy-fuel.

The temperatures reached in the burning process can overcome $1800^\circ C$ but also in the aluminum metallurgy field are not necessarily these kinds of temperatures. Also, there are some restriction imposed by the furnace building materials for aluminum alloys processing - in the furnace vault room type zone the temperature should be between $1000 - 1200^\circ C$.

From specialty literature results that some reactions accepted are taking part of the process. This paper aims to present the thermodynamics calculus in order to establish the order for the reactions.

From the metallurgical point of view the final composition of the burned gases is important as we specify in the prior paragraph, the presence of H_2 or $H_2O_{(v)}$ inside the furnace being undesirable due to their gassing or advanced oxidation of the melt. The variation of Gibbs' energies for reaction (1) ÷ (10) is shown in table 6. For a series from these reactions some thermodynamic data will be present to establish the reaction products compounds.

The main reactions taking place to natural gas combustion are shown in the table below. There are interesting aspects also in the atomic hydrogen in molecular hydrogen transformation (reaction 10).



Determinations have been made with the DELTA 2000-IV apparatus which are intended to highlight the composition of the flue gases.

The measurements which were taken during the combustion process are shown in table 5, not all gases determined by the device are shown.

Table 5

DELTA 2000 IV measurements					
	1	2	3	4	U.M.
Nat. gas light	12.2	12.2	12.2	12.2	%
T-Gas	803.1	497.2	525.2	958.7	°C
T-Amb	30.5	27.7	27	32.5	°C
O₂	0.6	20.3	21	12.9	%
CO₂	11.9	0.4	0	4.7	%
Losses	31	99.9	-	81.2	%
Effic.	69	0.1	-	18.8	%
Nox/0%O₂	8	0	-	10	ppm

Phases of the technological process (table 5): 1. burners at high capacity, furnace door closed; 2. burners turned off, door opened immediately after loading the materials in the furnace (volatile release); 3. burners turned on for heating/melting, O₂ injection for burning volatiles, furnace door closed; 4. burners at maximum power for melting of loaded materials, door closed.

From the composition of the flue gases result 2H/H₂ which form porosity as shown in Fig. 2, and O₂/H₂O_(v) with metallic components of the bath which form oxides as shown in the SEM analysis - Fig. 3.

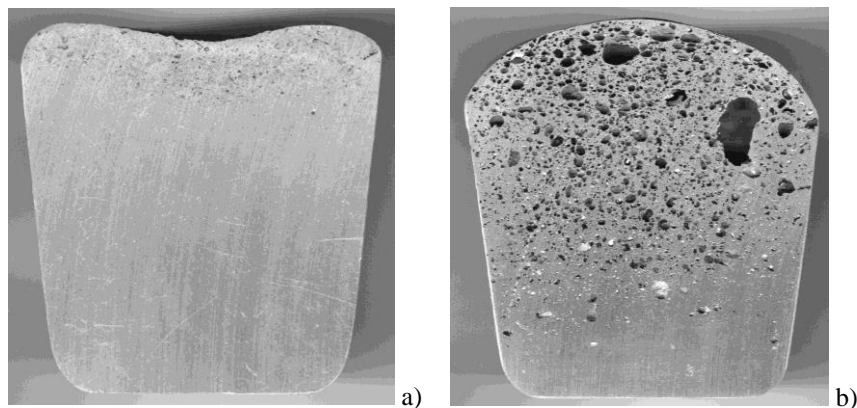


Fig. 2. Porosity formed due to hydrogen - Density Index 37.3
 a) Probe solidified in air, weight 85.70g, density 2.603g/cm³
 b) Probe solidified in vacuum, weight 71.45g, density 1.632g/cm³

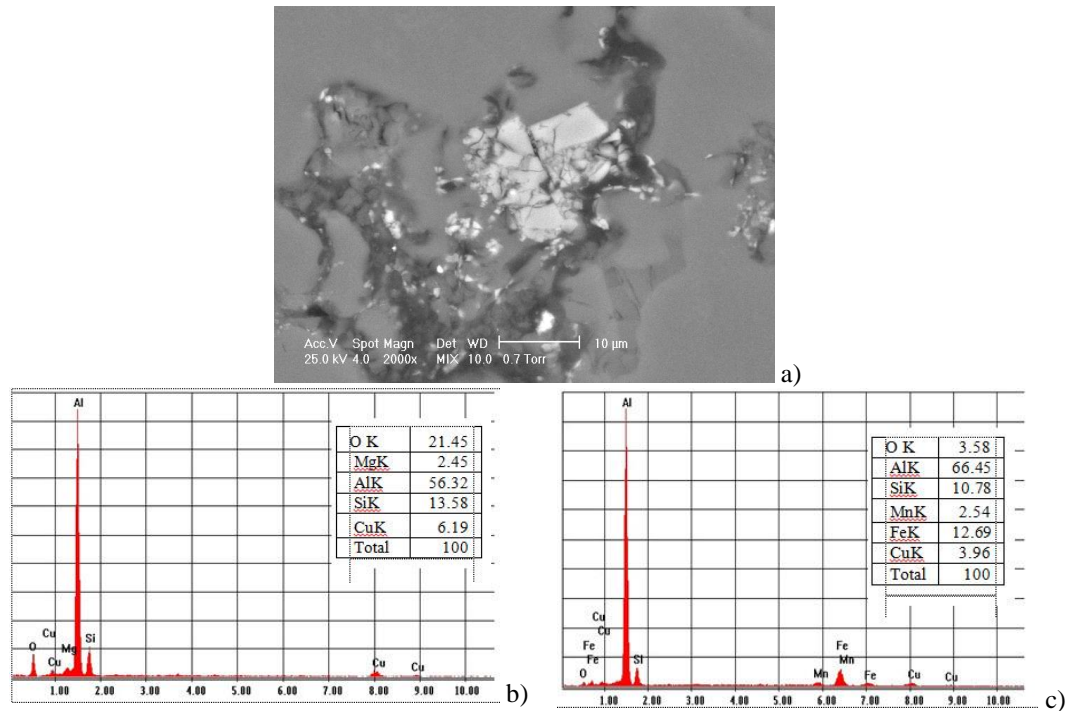


Fig. 3. Oxides formed due to reaction with O₂ and H₂O_(v)

- a) SEM; b) The EDS spectrum of filiform compounds indicating the presence of O, Mg, Al, Si and Cu elements; c) The EDS spectrum of polyhedral compounds that indicate the presence of O, Al, Si, Mn, Fe and Cu elements.

Table 6.

Gibbs energy variations for reaction (1) ÷ (10)

Temperature, °C	ΔG1, kcal	ΔG2, kcal	ΔG3, kcal	ΔG4, kcal	ΔG5, kcal	ΔG6, kcal	ΔG7, kcal	ΔG8, kcal	ΔG9, kcal	ΔG10, kcal
600	-93.0	-143.6	-49.4	-47.7	-142.0	-46.5	1.2	-1.7	-191.3	-82.5
700	-102.4	-144.9	-47.3	-46.4	-144.0	-51.2	-4.8	-0.9	-191.3	-79.8
800	-111.8	-146.2	-45.2	-45.1	-146.1	-55.9	-10.8	-0.1	-191.3	-77.1
900	-121.2	-147.5	-43.2	-43.8	-148.1	-60.6	-16.8	0.6	-191.3	-74.3
1000	-130.6	-148.8	-41.1	-42.4	-150.1	-65.3	-22.9	1.3	-191.2	-71.6
1100	-139.9	-150.1	-39.0	-41.1	-152.1	-70.0	-28.9	2.0	-191.2	-68.8
1200	-149.3	-151.4	-37.0	-39.7	-154.1	-74.6	-34.9	2.7	-191.1	-66.0
1300	-158.6	-152.6	-35.0	-38.4	-156.0	-79.3	-40.9	3.4	-191.0	-63.1
1400	-167.9	-153.9	-32.9	-37.0	-157.9	-83.9	-47.0	4.1	-190.8	-60.3
1500	-177.1	-155.1	-30.9	-35.6	-159.8	-88.6	-53.0	4.7	-190.7	-57.5
1600	-186.3	-156.3	-28.9	-34.2	-161.6	-93.2	-58.9	5.3	-190.5	-54.6
1700	-195.5	-157.5	-26.9	-32.9	-163.5	-97.8	-64.9	6.0	-190.4	-51.7
1800	-204.7	-158.7	-24.9	-31.5	-165.3	-102.3	-70.8	6.6	-190.2	-48.9

From thermodynamic data obtained using the HSC Chemistry 6.0 software, it follows that possible reactions of the data are conducted according to the reaction (1), (2), (5) and (9), as can be seen in Fig. 4.

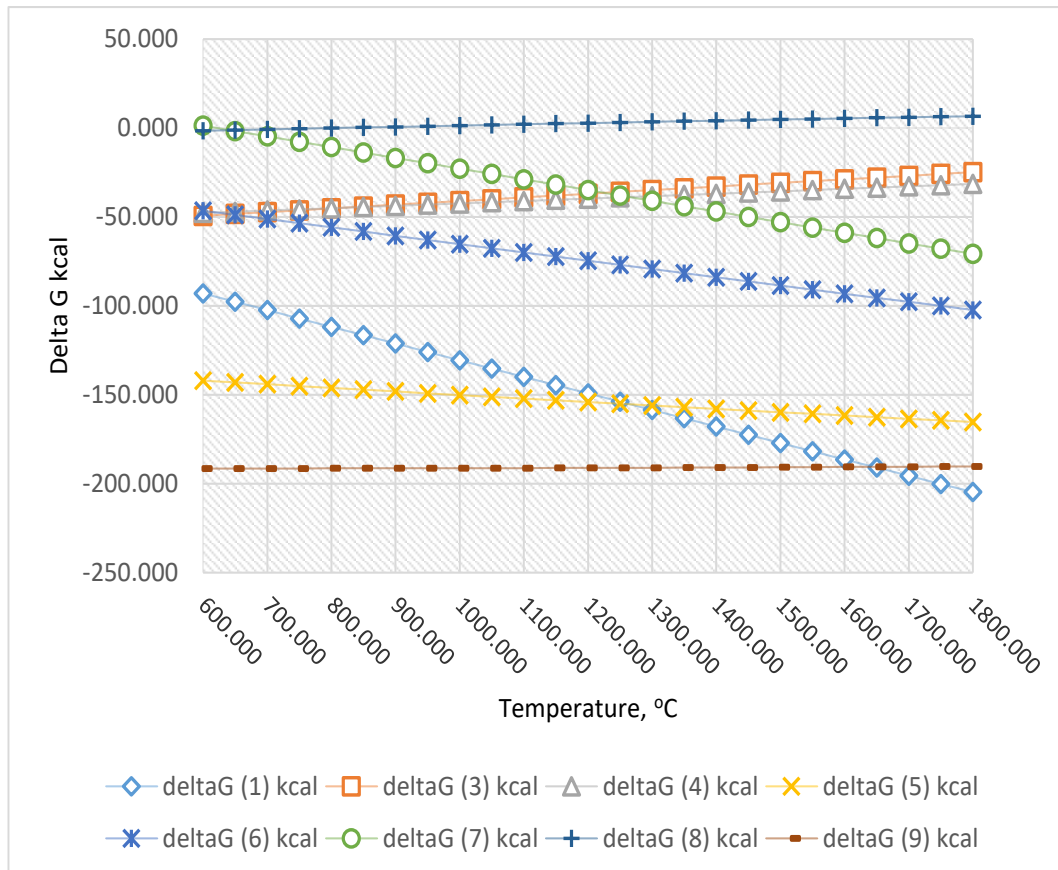


Fig. 4. Variation of standard free enthalpy (ΔG) in the temperature range 600-1800°C for the reactions studied

3. Result and discussion

For the species involved in the reactions (1), (3), (5) and (9), as well as the resulting reaction products for each part reaction was determined by calculation of the temperature variation of the heat capacity, the latent enthalpy and the entropy training. There were also determined using HSC Chemistry program in the temperature range 600°C ÷ 1800°C, Gibbs energy $G^0=f(T)$, $\Delta H_T^0 = f(t)$, $\Delta S_T^0 = f(t)$ and the Ellingham diagram was constructed $\Delta G_T^0 = f(t)$.

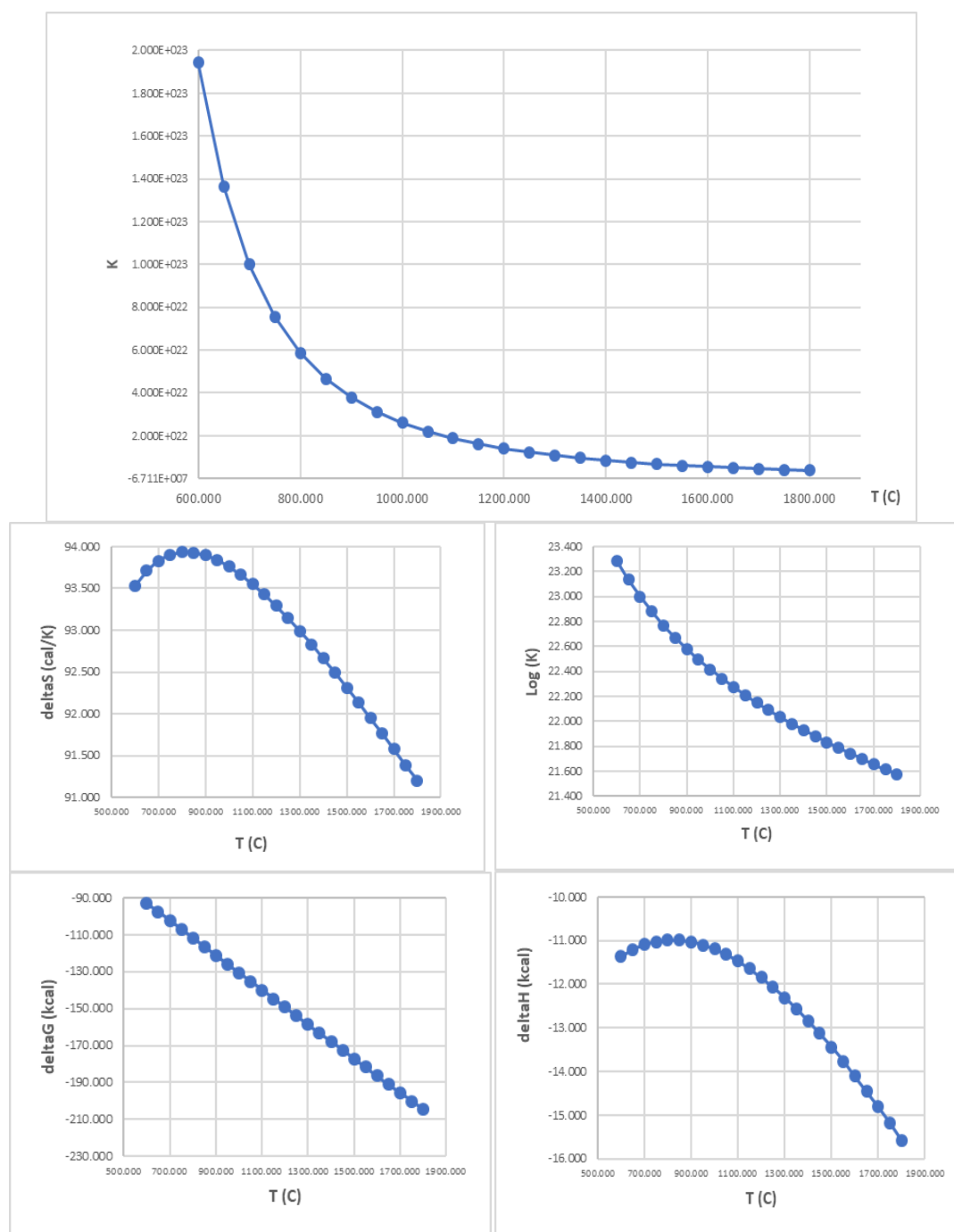


Fig. 5. The variation of the thermodynamic parameters for the reactants and the reaction products, in the temperature range 600-1800°C, for reaction (1)

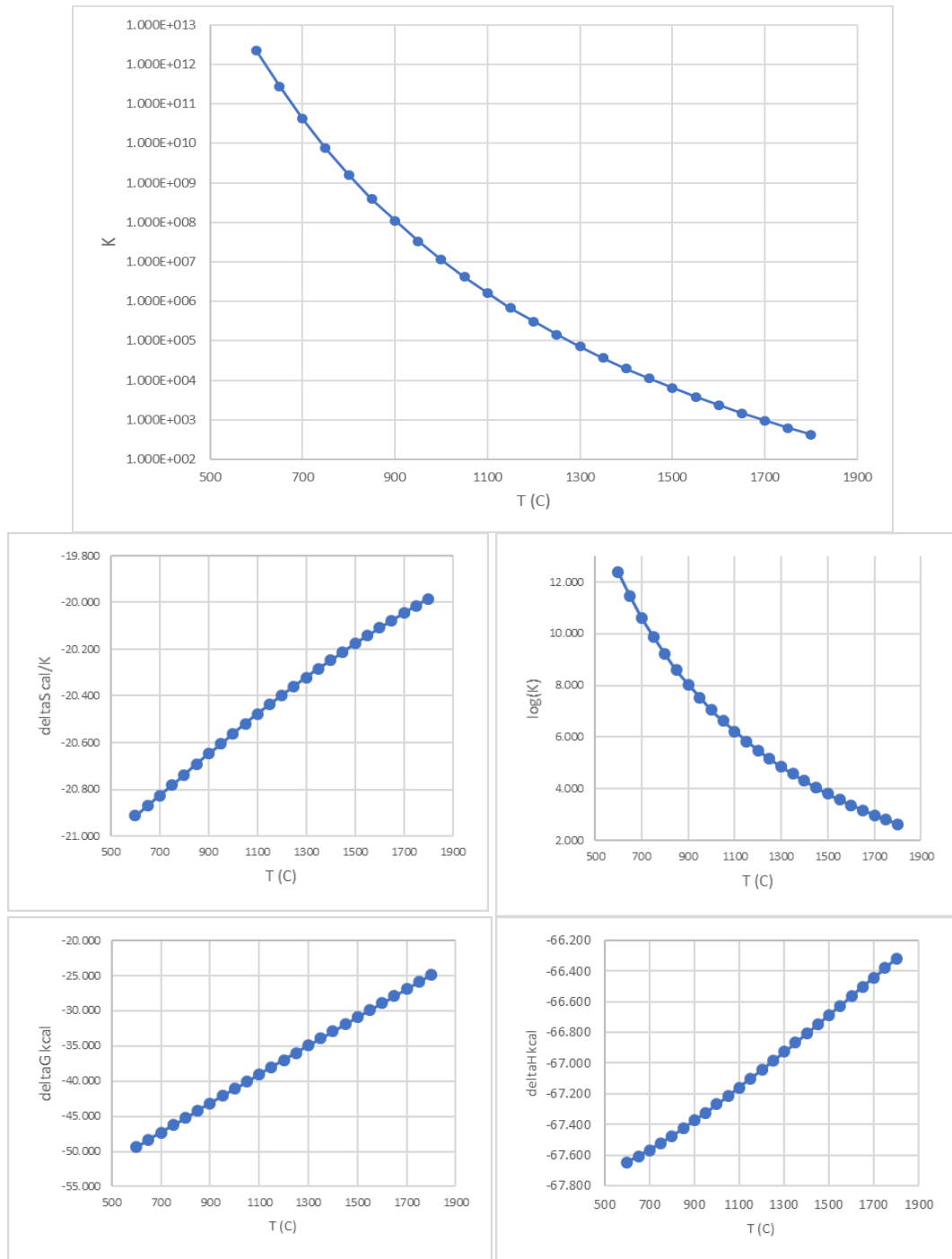


Fig. 6. The variation of the thermodynamic parameters for the reactants and the reaction products, in the temperature range 600-1800°C, for reaction (3)

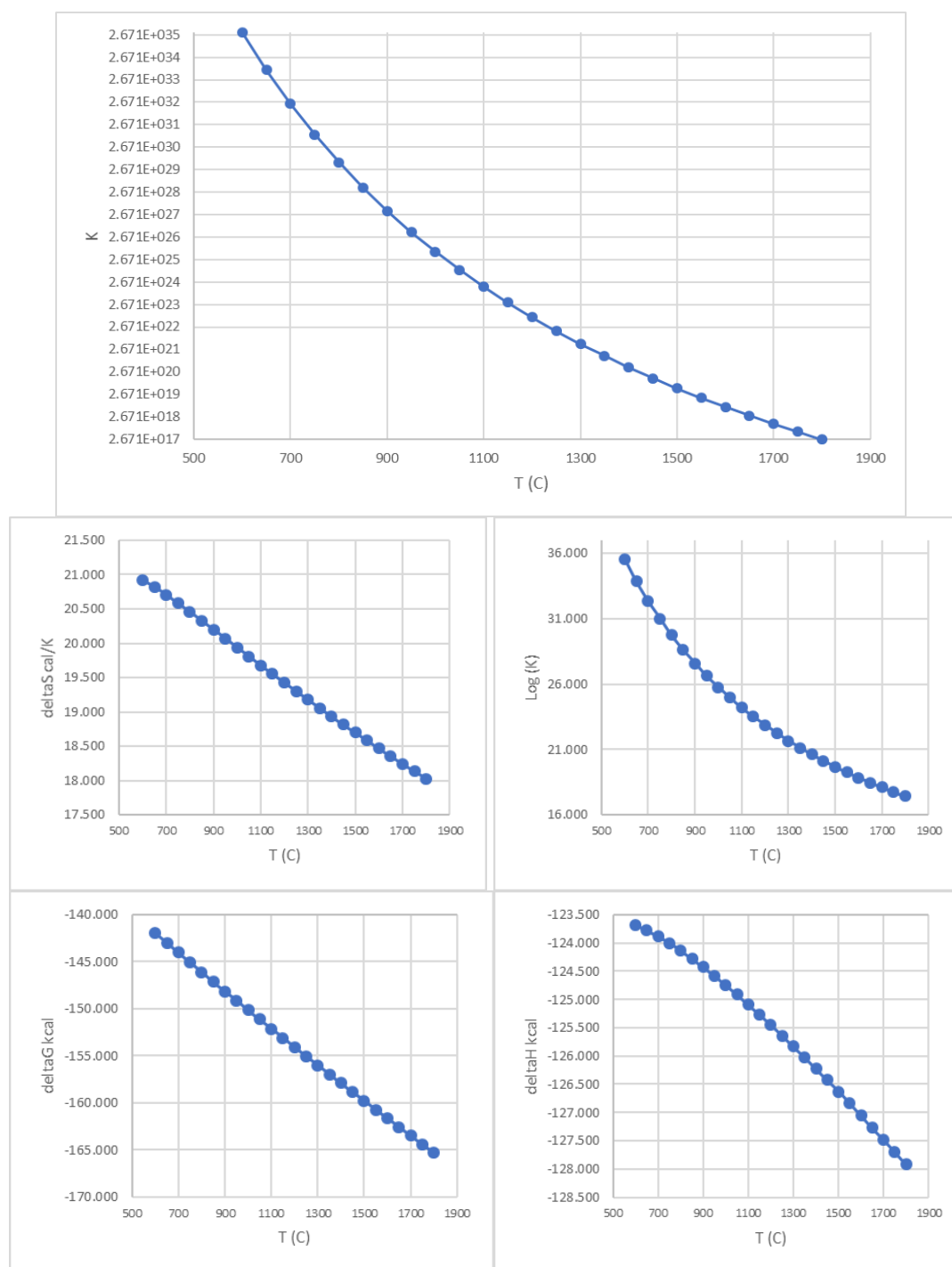


Fig. 7. The variation of the thermodynamic parameters for the reactants and the reaction products, in the temperature range 600-1800°C, for reaction (5)

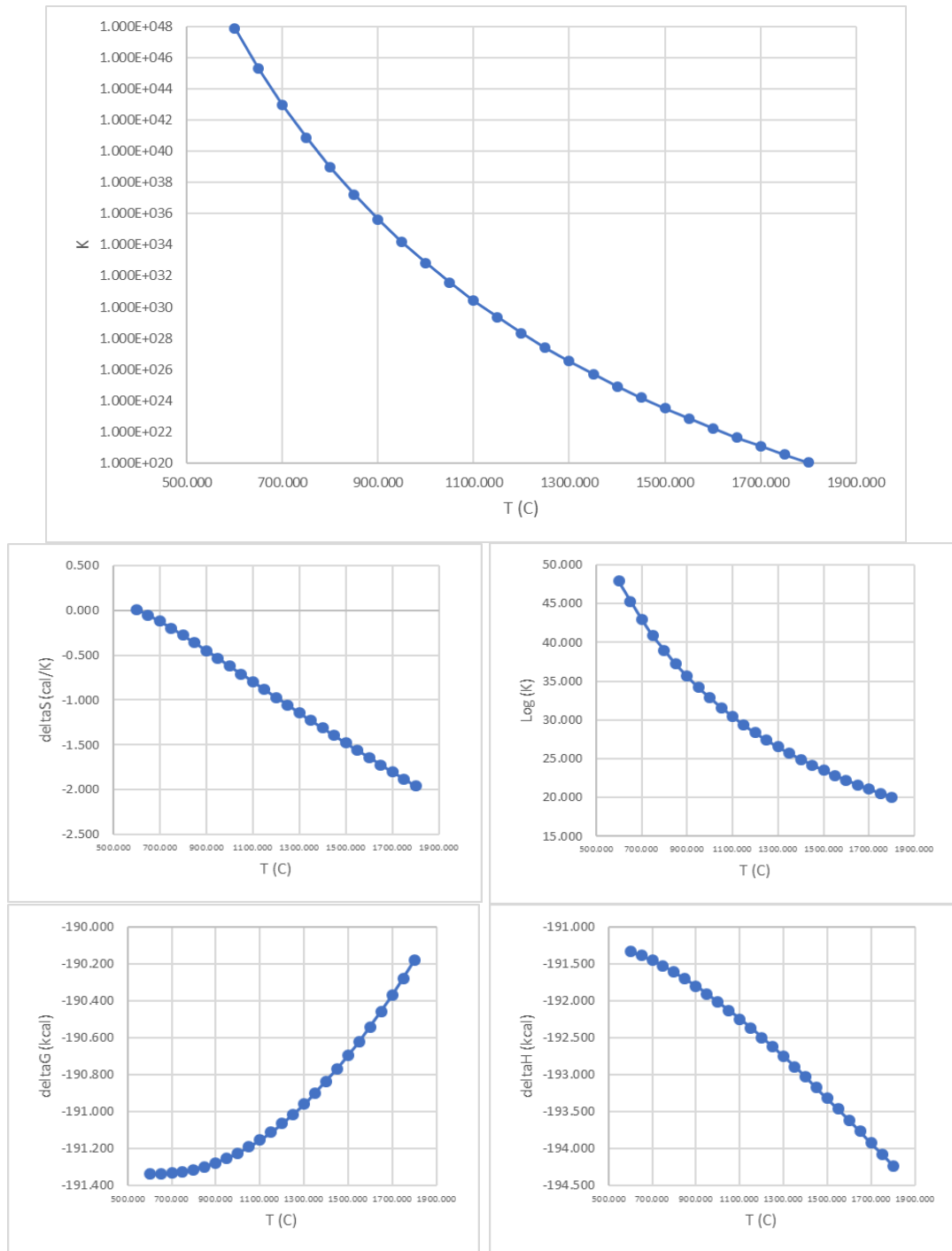


Fig. 8. The variation of the thermodynamic parameters for the reactants and the reaction products, in the temperature range 600-1800°C, for reaction (9)

3.1 Considerations on efficient use of natural gas in non-ferrous metallurgy

Romania has the largest natural gas market in Central Europe and was the first country to use natural gas for industrial purposes [14]. Adherence to the European Union (EU) and transposition of EU law call for increased concern for the efficient use of energy. The Council of Europe called for an energy efficiency action plan to be adopted as a matter of urgency in 2006 to achieve the energy savings target of over 20% by 2020 [15]. As a result, GO no. 22/2008.

However, European Commission estimates, which took into account the 2020 national energy efficiency targets set by Member States in the context of the Europe 2020 strategy, suggested in 2012 that the Union would achieve only half of the 20% target by 2020 [16]. The European Council and the European Parliament have called on the Commission to adopt a new ambitious energy efficiency strategy to capitalize on the considerable potential that exists through a determined action. The result was the adoption of Directive 2012/27 / EC of the European Parliament and of the Council on energy efficiency.

In Romania, Law 121/2014 was adopted which transposes Directive 2012/27 / EC. Its application will stimulate energy efficiency also in the metallurgy sector, which had a final energy consumption in 2013 of 1,782,351 tep / year, ie over 30% of the consumption of energy-intensive industries (companies with consumption of over 5,000 tep / year) [17]. In branch energy consumption, nonferrous metallurgy has a contribution of about 24% [17].

Nonferrous metallurgy has a share of energy in costs of over 30% [17], being the industrial branch in Romania with the greatest impact of energy consumption on costs. In recent years, as a result of the implementation of energy efficiency improvement measures, the energy intensity of the branch decreased to 0.1556 toe / 1000 lei in 2013 [17].

Through the solutions proposed in this article, the authors also intend to optimize the consumption of natural gas in the field of metal waste recycling or the production of secondary aluminum alloys.

4. Conclusions

After the combustion the main reaction products obtained are: CO, CO₂, H₂ and H₂O_(v). From the graph in Fig. 3 we can observe that the most probable reactions are reaction (2), (5) and (9). At higher temperature, over 1200°C the reaction (1) becomes more probable than reactions (2) and (5) and over 1650°C more probable than reaction (9).

In the furnaces commonly used in the secondary aluminum metallurgy we can distinguish, from the temperature point of view, 3 main zones:

1. the burning zone where the temperature can reach 1800°C;
2. the lateral walls zone, of the materials charged form melting, the zone over the melt, where the temperature reaches 700 – 900°C;
3. the free space, space between the burners, melt and walls where the temperatures reaches the level of 900 – 1100°C.

For all the temperatures intervals the reaction products resulted are interesting from the metallic bath quality point of view. The molecular hydrogen and water vapors present in the working atmosphere of the furnace interact with the melt in a negative way.

The present paper underlined the fact that in the furnace H₂ exists and diffuses towards the melts surface and is adsorbed by the melts, diffusing in bulk afterwards.

For secondary aluminum metallurgy, as charging materials are used scraps from the internal combustion motors, hydrocarbons impurities containing parts participating to the combustion process – influence that can be found in the final density index of the alloy.

Managing the development processes of the batches in the secondary metallurgy of aluminum, at temperatures below 1650°C, reduce production costs by reducing the time allocated for degassing the metallic bath, labor costs, costs of products used in degassing (nitrogen, argon, flows).

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