INFLUENCE OF THE ENRICHMENT OF NATURAL GAS WITH HYDROGEN ON THE HYDROGEN SOLUBILITY OF DIFFERENT COPPER QUALITIES AND THE HEAT BALANCE

[1]Lars FELKL, [2]Olaf SCHWEDLER, [3]Alexandros CHARITOS

[1]TU Bergakademie Freiberg, Institute for Non-ferrous Metallurgy and Purest Materials, Freiberg, Germany, EU, lars.felkl@inemet.tu-freiberg.de

[2]KME, Hettstedt, Germany, EU, olaf.schwedler@kme.com

[3]TU Bergakademie Freiberg, Institute for Non-ferrous Metallurgy and Purest Materials, Freiberg, Germany, EU, alexandros.charitos@inemet.tu-freiberg.de

Abstract

Through the rising amount of hydrogen in natural gases provided by the suppliers technical questions about the process control based on the off-gas composition as well as about the supply of the necessary process heat come up. But also the hydrogen solubility plays a significant role in many processes in which solid or liquid metals like copper are produced. This research aims to provide answers to these questions. The changed off-gas composition of the hydrogen enriched natural gas when combusting in a shaft smelting furnace calculated in this study as well as the changed heat output. As it is important that during the combustion the necessary process heat for the melting of the copper cathodes can be provided or if an additional heat source or a higher volume of input gas is needed. For the modelling of the gas combustion special attention is paid to the components oxygen and carbon monoxide as well as the in the gas atmosphere remaining hydrogen. Based on that to be expected hydrogen solubility in different copper qualities is modelled in a thermodynamically software solution. The results are compared to other studies which aimed for the hydrogen solubility with a specific look on the dependency of hydrogen solubility on oxygen solubility.

Keywords: Metallurgy, copper, hydrogen, heat balance, solubility

1. INTRODUCTION

The extension in the usage of hydrogen in the metallurgical industry comes with advantages like the reduction of carbon dioxide emissions but bears also new questions about the technological implementation in current processes. For example: When rising the amount of hydrogen in natural gas like it is done in the European Union some processes in which the gas directly contact with a metal phase the changed gas atmosphere will influence the properties of the processed metal phase. When melting the cathodes of the copper refining electrolysis in a shaft furnace the gas has two tasks: bringing in of the heat via its own combustion as well as produce a reductive atmosphere to prevent the re-oxidation of the molten copper phase. As hydrogen enriched natural gas is suitable to fulfill both tasks but hydrogen and natural gas bear different reduction potentials as well as energy densities. This will influence process parameters like the gas flow into the process as well as from the process to maintain the necessary level of reduction potential in the gas atmosphere and heat input but also the amount of off-gas. A rising content of hydrogen in the input gas also raise the question about the influence on the solubility of hydrogen in the liquid copper phase for this has a direct influence on the surface quality as well as the corrosion stability of copper pre-products and products. For a rising hydrogen content in the molten copper phase a rising hydrogen content in the solidified copper can be assumed. The fact that the hydrogen solubility in solidified copper phases is quite lower than in the molten ones is problematic: The hydrogen which is precipitated from the copper during solidification is precipitated as gaseous hydrogen which is forming gas bubbles. The gas bubbles are mostly located near grain boundaries and lattice defects as twins

[1]. These bubbles can also be found near the surface of the copper pre-product which should be used for hot or cold rolling. During the rolling process the entrapped bubbles are flatened but stay visible that after the mechanical treatment is finished the surface quality is lowered through the entrapped bubbles. On the other hand the hydrogen which is remaining is the combusted gas solution and which will partially solute in the copper phase can also react with the soluted oxygen which would lead to the formation of steam. This reaction can take place in the liquid copper phase but also in the solidified copper phase (where the oxygen is present in form of Cu_2O), which would also lead to the formation of gas bubbles mostly located at grain boundaries. This mechanism is called „hydrogen embrittlement" or less formal also named as „hydrogen sickness". It could be shown that this mechanism occur in copper qualities which contain more than 0.01 wt% oxygen [2]. The limitation of the soluted amount of hydrogen is therefore necessary. The solubility of hydrogen in the liquid and the solidified copper phase is influenced by the composition of the copper phase itself [3] as well as by the partial pressures of hydrogen and oxygen in the corresponding gas atmosphere [4]. The solubility of hydrogen in a liquid copper phased is directly depends on the soluted amount of oxygen in this copper phase [5].

2.   SUBSTANCES AND MODELLING

In this present study a combustion of a natural gas solution is modelled which is gradually enriched with a rising hydrogen content. The modelling of the combustion and the solubility of the reaction products in the copper melts is conducted by using version 8.2 of FactSage™, a thermodynamic modelling software, while the databases FactPS and FScopp are utilized to calculate the needed equilibria [6].The composition of the combusted gas is of special interest as the combustion fulfills beside the necessary heat production for the melting of copper cathodes another purpose: to ensure a reducing atmosphere during the cathode melting. Therefore the combustion has to be under-stoichiometric ($\lambda < 1$) that some carbon monoxide (p(CO) = 1.5 %) remains which can be measured and used for process and combustion control. The solution of natural gas and hydrogen ($x(H_2)$ varied from 0 % to 95 %) is to be brought to reaction and equilibrated at two different temperatures (1200 °C and 1300 °C) and the created gas solutions are separately set in equilibrium at two different copper-gas-ratios with two different copper qualities (see **Table 1**).

For the combustion modelling an exemplary gas composition generalized from the monthly analysis of gas supplier of one of the last years which composition is given in **Table 2**. As reaction partners during modelling the hydrogen is assumed as pure and the needed oxygen originates from air with composition is simplified to 79 vol.% nitrogen and 21 vol.% oxygen. The reaction products are set in equilibrium with 1 kg of the respective copper quality at the two above mentioned temperatures and at two different gas-copper-ratios: 0.1 mol gas per 1 kg Cu-melt and 10 mol gas per 1 kg Cu-melt.

Table 1 Chemical composition of the two used copper qualities in at.% for Cu and in wt.ppm for other elements

quality	Cu	O	P	S	Ag	Fe	Ni	Sn	Pb	Others
Cu-OF	99.997	1.2	0.1	6.0	12.3	0.3	1.3	0.5	2.4	5.9
Cu-ETP	99.982	156.0	0.1	3.5	11.7	1.3	4.3	0.3	1.3	1.5

Table 2 Chemical composition of the input gas (natural gas) before combustion in at.%

CH_4	N_2	CO_2	C_2H_6	C_3H_8	C_xH_y	H_2	O_2
92.57	1.30	1.06	4.24	0.56	< 0.27	< 0.01	< 0.01

3.   RESULTS OF COMBUSTION MODELLING

The results of the combustion modelling of the different solutions of natural gas and hydrogen are given in **Table 3** for a combustion at 1200 °C and in **Table 4** for a combustion at 1300 °C. In both combustion cases it can be seen that at a fixed carbon monoxide content of 1.5 % the steam partial pressure increase by around

35 % while increasing the content of hydrogen in the input gas solution from 0 at.% to 95 at.%. On the other hand the partial pressure of carbon dioxide is dropping by 91.4 % at 1200 °C or by 91.8 % at 1300 °C. The oxygen partial pressure is decreasing to 0.7 % of its initial value at both temperatures. Other components such as hydrogen methane as well as other hydrocarbons are increasing as the combustion is increasingly moving away from complete combustion. As the comparison of **Table 3** and **Table 4** is stating the equilibrium temperature shows a significant influence on all equilibria resulting from the combustion of the gas mixtures. At higher temperatures the equilibria are shifted toward the side of the combustion products which results in a more complete combustion and less remaining input materials.

Table 3 Composition of the off-gas solution (corresponds to partial pressure at 0.1 MPa total pressure) after combustion, at 1200 °C (given: highest or most important components, no radicals, $p(CO) = 1.5\ \%$)

	Part of hydrogen on fuel gas stream										
	0%	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	95 %
H_2O	1.84 E-01	1.88 E-01	1.93 E-01	1.99 E-01	2.07 E-01	2.15 E-01	2.26 E-01	2.40 E-01	2.56 E-01	2.71 E-01	2.49 E-01
CO_2	8.75 E-02	8.47 E-02	8.14 E-02	7.74 E-02	7.27 E-02	6.69 E-02	5.95 E-02	5.00 E-02	3.71 E-02	1.91 E-02	7.57 E-03
H_2	1.29 E-02	1.37 E-02	1.46 E-02	1.58 E-02	1.75 E-02	1.98 E-02	2.34 E-02	2.95 E-02	4.25 E-02	8.72 E-02	2.03 E-01
CH_4	1.07 E-12	1.24 E-12	1.47 E-12	1.88 E-12	2.36 E-12	3.30 E-12	5.16 E-12	9.78 E-12	2.73 E-11	2.24 E-10	3.04 E-09
O_2	3.42 E-10	3.20 E-10	2.96 E-10	2.68 E-10	2.36 E-10	2.00 E-10	1.58 E-10	1.12 E-10	6.17 E-11	1.12 E-11	3.56 E-12

Table 4 Composition of the off-gas solution (corresponds to partial pressure at 0.1 MPa total pressure) after combustion, at 1300 °C (given: highest or most important components, no radicals, $p(CO) = 1.5\ \%$)

	Part of hydrogen on fuel gas stream										
	0%	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %	95 %
H_2O	1.85 E-01	1.89 E-01	1.95 E-01	2.01 E-01	2.08 E-01	2.17 E-01	2.28 E-01	2.42 E-01	2.59 E-01	2.75 E-01	2.55 E-01
CO_2	8.72 E-02	8.43 E-02	8.10 E-02	7.71 E-02	7.23 E-02	6.65 E-02	5.91 E-02	4.96 E-02	3.67 E-02	1.86 E-02	7.14 E-03
H_2	1.12 E-02	1.18 E-02	1.26 E-02	1.37 E-02	1.51 E-02	1.72 E-02	2.03 E-02	2.57 E-02	3.72 E-02	7.78 E-02	1.88 E-01
CH_4	2.11 E-13	2.45 E-13	2.91 E-13	3.60 E-13	4.68 E-13	6.54 E-13	1.03 E-12	1.96 E-12	5.56 E-12	4.81 E-11	7.32 E-10
O_2	6.23 E-9	5.83 E-9	5.38 E-9	4.87 E-9	4.29 E-9	3.63 E-9	2.87 E-9	2.01 E-9	1.10 E-9	2.83 E-10	4.18 E-11

The liberated heat from the combustion of one mole of the different fuel gas streams is plotted as a function of the hydrogen content in the combustion gas in **Figure 1**. The liberated heat differs from the calorific values of the modelled gas mixture as the liberated heat can be understood as the heat which is liberated by the combustion but is not required for preheating the input gas mixture as well as the air for combustion. It can be seen that the liberated heat is lower at a higher temperature although the combustion is more complete than at lower temperatures. The explanation for this can be found in the fact that a greater amount of heat is needed to preheat the fuel gases to the higher temperature. Furthermore is the liberated heat decreasing with an increasing hydrogen content in the combustion gas mixtures. It can be easily explained as the calorific value of methane which is the dominant component in the natural gas is higher as the calorific value of hydrogen [7].

The difference between the liberated heats at constant hydrogen content in the combustion gas mixtures is decreasing with an increasing hydrogen content as the molar heat capacity of hydrogen is lower than these of methane.
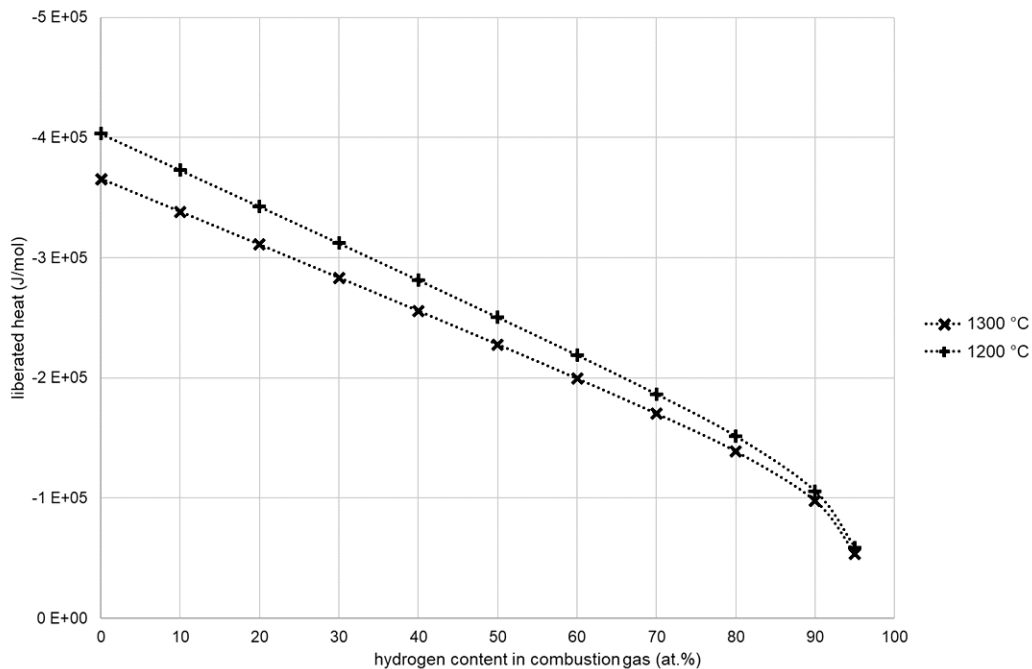

Figure 1 Connection between liberated heat during combustion and hydrogen content in combustion gas at 1200 °C and 1300 °C

4.   RESULTS OF SOLUBILITY MODELLING

After the composition of the combusted gas mixture is achieved, these „off-gases" are set in equilibrium with two different copper qualities who mainly vary regarding their oxygen content. While the OF-copper is quite low in oxygen the ETP-quality contains more than 100 times the amount of oxygen as the OF-quality. The results of the equilibration of the combusted gases and the copper melts are plotted in **Figure 2** for the OF-quality and in **Figure 3** for ETP-quality. In both figures the soluted hydrogen content is plotted as a function of the soluted oxygen content in the copper phase. It can be seen that at a given oxygen content the hydrogen solubility is increasing with increasing temperature, a bevaviour also described in [5]. Furthermore in all cases the hydrogen solubility is increasing with a rising hydrogen content in the fuel gas stream as this lowers the remaining oxygen content on the combusted gases. Through that the oxygen solubility in the liquid copper in lowered as gas solubility in liquid metals is directly proportional to the square root of the respective gas (Sieverts law). **Figure 2** states that the amount of combusted gas produced at 1200 °C has no significant influence on the hydrogen solubility in OF-copper. When equilibrating the combustion products calculated at 1300 °C the amount of gas phase shows that with a higher amount of combusted gas the amount of oxygen and hydrogen soluted in the copper phase is increased. The comparison with **Figure 3** shows differences in ETP-copper: The solubility for oxygen and hydrogen seems to be the same as in OF-copper at 1200 °C and 10 mol combusted gas in equilibrium. At a lower gas amount in equilibrium the amount of soluted oxygen is higher and therefore the hydrogen solubility is lower than in ETP-copper with 10 mol or in OF-copper. With a rising amount of combusted gas the oxygen content in the copper phase can be lowered. The same effect can be observed at 1300 °C: For 10 mol as gas amount the curves for OF-copper and ETP-copper seem similar but as the oxygen content soluted in ETP is higher, because of the higher input oxygen content of the copper phase, the hydrogen solubility is lower bringing 0.1 mol combusted gas in equilibrium with ETP-copper.
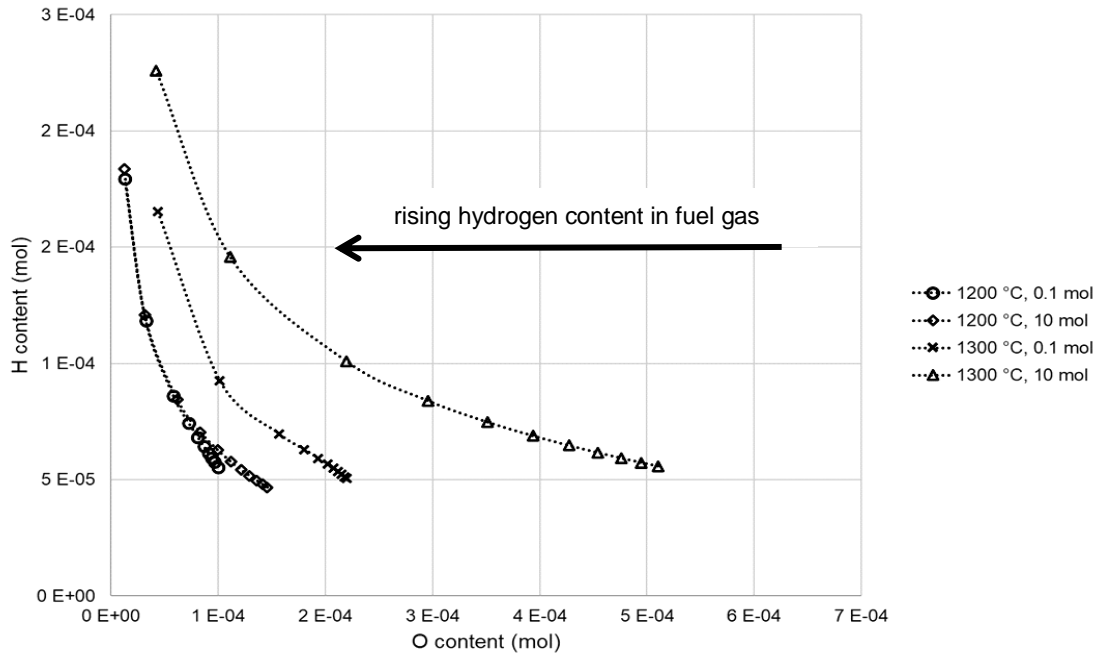
Figure 2 Solubility of hydrogen in liquid OF-copper as function of soluted oxygen at 1200 °C and 1300 °C when varying the amount of combusted gas solution (solubility of hydrogen and oxygen in pure copper for comparision)
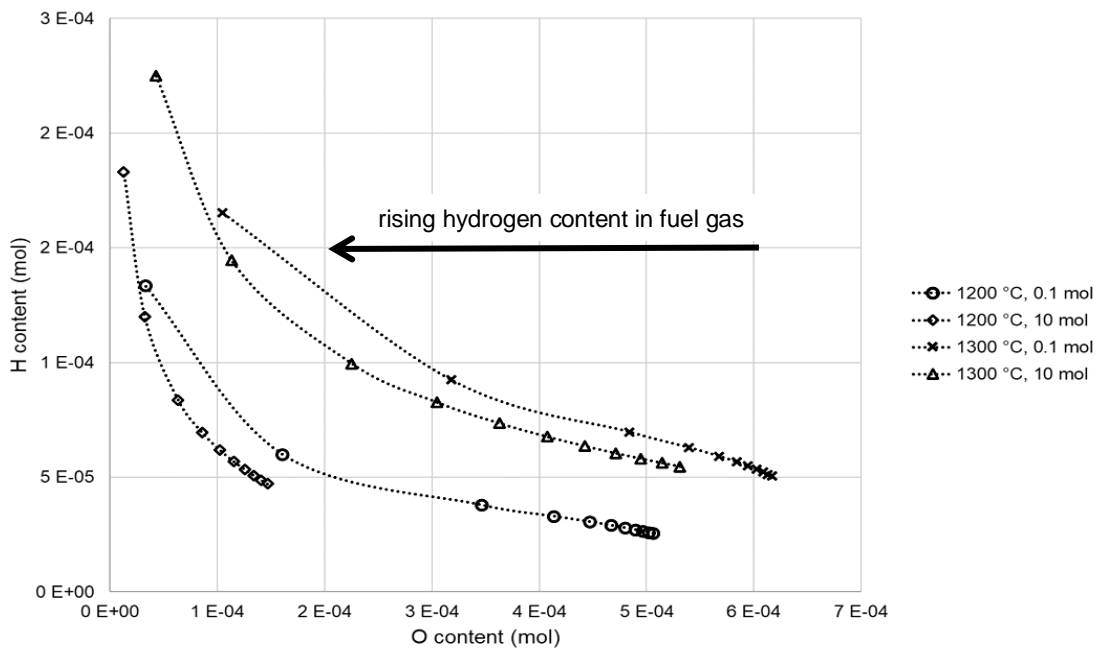

Figure 3 Solubility of hydrogen in liquid ETP-copper as function of soluted oxygen at 1200 °C and 1300 °C when varying the amount of combusted gas solution (solubility of hydrogen and oxygen in pure copper for comparision)

5.   CONCLUSION

The compositions of the combusted fuel gas mixtures were thermodynamical calculated and show that at higher temperatures the combustion take place more completely and therefore more combustion products are formed and less remains of the input components were predicted. This effect is intensified as the proportion

of hydrogen in the combustion gas mixture increases. The liberated heat during combustion which is not otherwise used for the combustion reaction, for example for the preheating of the to be combusted fuel gas mixtures, is decreasing with an increasing content of hydrogen. When equilibrating the combusted gases with liquid copper alloys it can be shown that at 1200 °C as well as at 1300 °C the predicted oxygen and hydrogen solubility does not differ when using higher amounts of gas (10 mol). At lower gas amounts the oxygen richer ETP-copper should solute less hydrogen as at higher gas amounts because of its higher initial oxygen content in the copper phase.

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