Reduction Kinetics of Co_3O_4 Powders by Hydrogen Plasma and Hydrogen Gas at Low Temperatures

Maria Cristina Yukiko Nakayama[a], Estefano Aparecido Vieira[a], Ramiro Conceição Nascimento[a],

Adonias Ribeiro Franco Júnior[a], Jaime Alberto Sanchez Caceres[a]*

[a]Instituto Federal do Espírito Santo, Vitória, ES, Brasil.

The reduction of cobalt oxide (Co_3O_4) powders was studied using hydrogen plasma (HP) and hydrogen gas at low temperatures. The reduction experiments were performed in a pulsed plasma reactor at 540 V, 532 Pa, under atmospheres of 100% hydrogen at a flow rate of 300 cm^3/min, with varying times up to 60 min, and temperature range of 523–653 K. The results showed that the reduction of Co_3O_4 powders occurs in two steps: $Co_3O_4 \rightarrow CoO \rightarrow Co$, when using either HP or hydrogen gas. At lower temperatures, hydrogen plasma provided a significant increase in reduction kinetics compared to gas, since atomic hydrogen is a more powerful reductant than molecular hydrogen due to the increase in the density of crystalline defects provoked by the impact of ions incidents contained in plasma. The values for the activation energy were determined to be 35.4 kJ/mol for plasma and 90.8 kJ/mol for gas, and the kinetic equation that best fits to both experimental data was $[1 - (1 - \alpha)^{1/3}]^2 = k.t$.

Keywords: *Reduction, cobalt oxide, hydrogen gas, hydrogen plasma.*

1. Introduction

Cobalt (Co) is an important strategic metal present in the composition of various iron alloys and non-ferrous alloys. Besides their use in prosthetic or dental implant structures, the Co-based alloys also find application in tribological coatings and high temperature resistant components, such as turbine blades and non-welded steel pipe manufacturing mandrels[1].

The metallic Co is a by-product from the extraction of nickel (Ni) or copper (Cu), contained in concentrates generated by hydrometallurgical, pyrometallurgical and electrometallurgical processes[2]. Many studies on the reducibility of cobalt oxide (Co_3O_4) have demonstrated that the metal can alternatively be produced using gaseous reductors. For instance, Khoshandam et al.[3] and Shirchi et al.[4] have obtained it from the decomposition of Co_3O_4 in argon atmosphere followed by its complete reduction in methane (CH_4) atmosphere, and more recently Cetinkaya and Eroglu[5] attempted experiments at the temperature range of 700–900 K, with ethanol (C_2H_5OH) at different flow rates. Studies conducted by Gallegos and Lopez[6], Bustnes et al.[7] and Lin and Chen[8] have shown that metallic Co is also obtained when hydrogen gas is used as a reducing agent.

In a recent study of the effect of hydrogen flux rate on the reduction kinetics of Co_3O_4, using cold or hydrogen plasma (HP), Sabat et al.[9] found that the reduction of Co_3O_4 occurred at temperature as low as 823 K and in two steps: $Co_3O_4 \rightarrow CoO \rightarrow Co$. They reported that the values for the activation energy when using HP are lower than those for the gas reduction process determined by[6-8]. According to these researchers, the activation energy decrease could be attributed to the plasma excited molecules which make the reduction reaction faster.

The novelty of the present paper is that a comparative study concerning the reduction kinetics of Co_3O_4 powders at lower temperatures (523–653 K) was performed using both reducing agents, that is, hydrogen gas and hydrogen plasma at low temperatures.

2. Materials and Methods

The powder samples used in this investigation were of 99.1% pure−Co_3O_4 and particle size less than 45 μm (−325 mesh). All the reduction experiments were performed in an SDS Soluções mod Thor 500 pulsed plasma set up, shown schematically in Figure 1. Basically, it comprises the following parts: a vacuum chamber made of stainless steel (316 SS) whose inner wall is cylindrical in shape with approximately 0.5 m diameter and 0.75 m height; a rotary pumping system to get ultimate pressure of 1 Pa (without injecting gas) and 10–1000 Pa (with working gas); a hydrogen gas supply system; an electric power supply to produce plasma discharge; an electric power supply for separate heating; and a measurement and control unit (flow rate, pressure, temperature, d.c. power, and pulse width).

The powder samples are placed at the centre of the chamber on five stainless steel (SS) holders on the cathode that, in turn, is connected to the d.c. power supply (650 V and 3.4 kHz). The SS holders which also proceed to form the cathode (-) are electrically insulated from the surrounding anodic (+) chamber. In either gas or plasma experiments, the powder samples possessed a total weight of 1,000 mg (± 0.1 mg), surface area and bed height of approximately
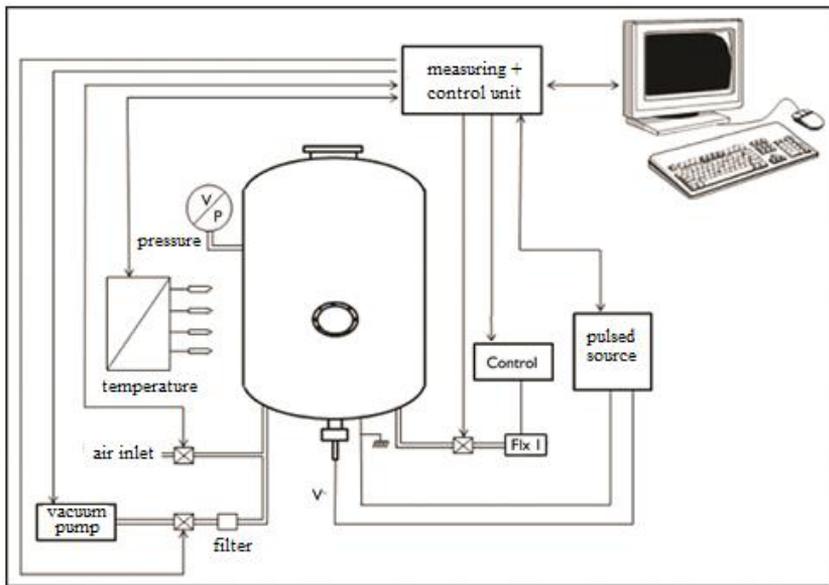
Figure 1. Schematic of the pulsed plasma reactor used in the reduction experiments.

1×10^{-2} m² and 2×10^{-3} m², respectively. After placing the samples in the holders, the chamber is closed and evacuated up to a pressure of about 10 Pa. The pressure is controlled by a solenoid valve. Prior to the reduction, a preheating is made by a resistive heating system, raising the temperature at the rate of 10°C/min up to the working temperature (523, 573, 623 or 653 K), which avoids an early reduction of the samples. The temperature measurements are taken from an empty-holder, positioned at the same level of the powder samples, by a chromel–alumel thermocouple. When reaching the working temperature, the hydrogen gas (99.999% pure) at a flow rate of 300 cm²/min is inserted into the vacuum chamber, and the reduction time starts to be counted.

In the case of plasma reductions, the plasma source is switched on immediately after switching off the heating source, generating the plasma that covers the entire cathode surface and, consequently, the powder samples. According to the literature[10,11], reactor configurations similar to those used in this work provide a ratio of hydrogen atoms / hydrogen molecules as well as a ratio of hydrogen ions / hydrogen molecules of about 10^{-4}. The bombardment of the electrically positive hydrogen ions against the (-) cathode keeps the temperature previously reached by the auxiliary heating system. So, the reactive species in the plasma are able to cause the reduction from the surface of the powder bed.

When attaining the scheduled time (10 to 60 min), the reduction experiment is completed, by closing the gas valve at the same time that the power supply is switched off, keeping the samples inside the chamber under vacuum till they cooled to room temperature.

For calculation of the reacted fraction, it was used for every reduction experiment, which were divided into five austenitic stainless steel AISI 316L crucibles with dimensions of 25 mm in diameter, 5mm in height and 3mmin wall thickness weighed with a digital scale with an accuracy of 0.1×10^{-6} kg. The difference in mass of the crucible containing the sample before and after was associated with the extraction of oxygen, which was withdrawn from the reactor via a vacuum pump in the form of water vapor. Thus, the reacted fraction, α, was calculated according to Equation 1:

$$\alpha = D_m/m_o \tag{1}$$

where: $D_m = m_a - m_t$, with m_a being the initial weight of the sample and m_t is the weight at an instant t; and m_o is the initial weight of oxygen in the sample.

X-ray diffraction (XRD) was used for identifying the reduction products and both light microscopy and scanning electron microscopy were used for characterizing the Co_3O_4 powder before and after the experiments.

3. Results and Discussion

Figures 2 to 5 successively show the development of the reduction process of Co_3O_4 powders after gas and plasma experiments performed at temperatures from 250 to 380 °C, and up to 60 min.

Powder particles prior to gas reduction consist basically of Co_3O_4 as shown in Figure 2. In the gas reduction experiments, at 250 °C, Figure 2a, it is clearly noted that in the times analyzed, there was no complete reduction of Co_3O_4.

For plasma reduction, at 250 °C, Figure 2b, It is observed that after 60 min the Co_3O_4 disappeared, only the presence of CoO and metallic Co being identified.

For 250 °C-reduced samples, using both reducing agents and for reduction times of 10 min and 20 min, metallic Co (α-Co) and cobalt monoxide (CoO) is identified in addition to Co_3O_4, as shown in Figure 2b and 2c.

After 30 min, Figure 2d, it is noted that there is an increase in the Co/Co_3O_4 ratio. For 40 and 50 min, there is an even greater increase in the Co/Co_3O_4 ratio.

For reduction times of 40 and 50 min, there is an even greater increase in the ratio between the intensities of the metallic cobalt peaks and those of its oxides. After 60 min, the presence of Co_3O_4 is no longer evident, with onl CoO and the metallic cobalt α-Co being detected. Therefore, up to 60 min of reduction, Co_3O_4 is reduced to CoO and α-Co.
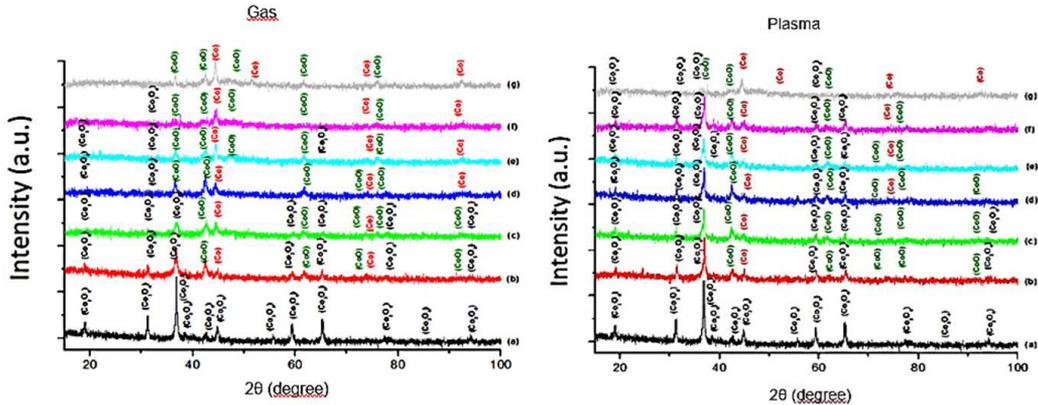
Figure 2. XRD patterns for Co_3O_4 powders after after reduction by gas and plasma at 250 ºC in reduction times of 10 min (a), 20 min (b), 30 min (c), 40 min (d), 50 min (e) and 60 min (f).
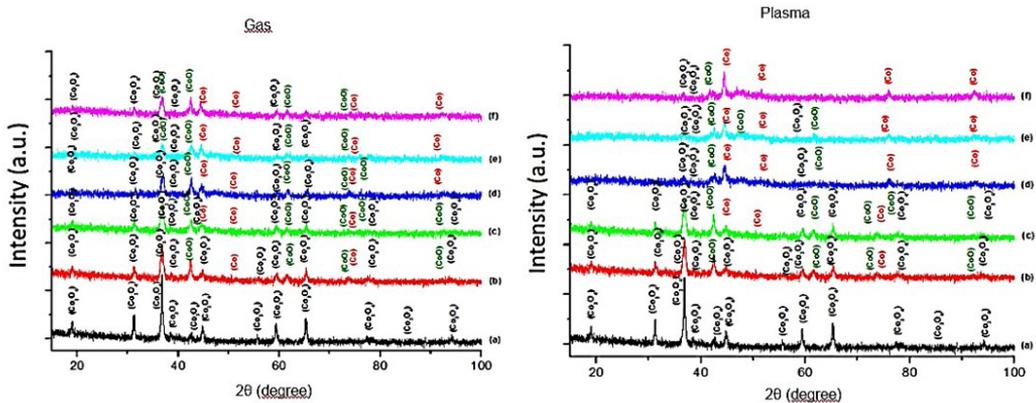

Figure 3. XRD patterns for Co_3O_4 powders after after reduction by gas and plasma at 300 ºC in reduction times of 10 min (a), 20 min (b), 30 min (c), 40 min (d), 50 min (e) and60 min (f).

Figure 4. XRD patterns for Co_3O_4 powders after after reduction by gas and plasma at 350ºC in reduction times of 10 min (a), 20 min (b), 30 min (c), 40 min (d), 50 min (e) and 60 min (f).
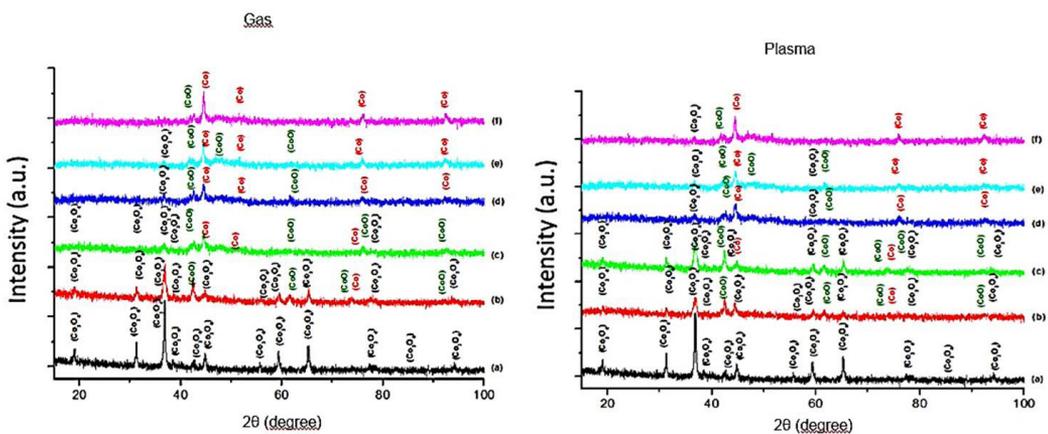
Due to the increase in the intensity of the Co peaks and the decrease in the CoO peaks, it appears that the reduction kinetics were increased when using plasma. After 60 min the presence of Co_3O_4 is no longer evident, and only CoO and α-Co are detected.

Therefore, up to 60 min reduction, the wolly conversion of Co_3O_4 into CoO and α-Co occurs. It is concluded that at a temperature of 250ºC, plasma as a reducing agent significantly increases the reduction of Co_3O_4 to Co-α, leaving very little amount of CoO to be reduced.
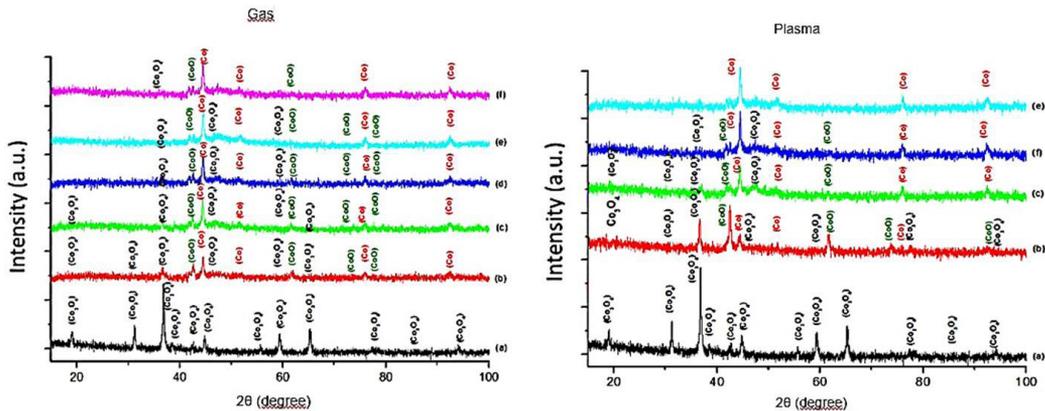
Figure 5. XRD patterns for Co_3O_4 powders after after reduction by gas and plasma at 380 ºC in reduction times of 10 min (a), 20 min (b), 30 min (c), 40 min (d), 50 min (e) and 60 min (f).

For a reduction temperature of 300ºC, as shown in Figure 3b-f, after just 20 min the intensities relative to the Co-α phase are already greater than those of the oxides. Comparing the diffractogram in Figure 3c with that shown in Figure 3d, it can be seen that the reduction kinetics increases significantly with the increase in temperature from 250ºC to 300ºC. After 20 min, the presence of a very small amount of Co_3O_4 phase is evident. When using plasma, after 40 min, the reduction process is practically in the second stage of CoO→Co.

For a reduction temperature of 350ºC, Figure 4b-c, when plasma is used, in addition to the Co_3O_4 peaks, the presence of a small amount of metallic Co and CoO is identified. After 30 min of reduction, Figure 4d, it is noted that there is a very large increase in the ratio between the intensities of the peaks related to metallic cobalt (Co-) and that of the oxides (CoO). After 40 min, the presence of only metallic Co is evident, which indicates that the reduction fraction of 1.0 has already been reached. Comparing the diffractograms in Figure 4f (gas and plasma), it is inferred that the use of plasma promotes a significant reduction in temperature of 350 ºC, after about 30 minutes, the process is in the second reduction stage.

In 40 min, the reduction was complete. Therefore, between 30 and 40 min, the presence of CoO and Co is preponderant.

Figure 5 shows the evolution of the phases present in cobalt oxide powders after hydrogen plasma reduction experiments at a temperature of 380 ºC, for times of 10 to 40 min. Just as was seen at temperatures of 250, 300 and 350ºC, at a temperature of 380ºC there is a progressive evolution of Co_3O_4 reduction with increasing reduction time.

Analyzing the XRDs, it is evident that from 20 minutes onwards the second stage is preponderant when using plasma. After 30 min of reduction, Figure 5d, the presence of metallic Co and traces corresponding to the CoO phase are evident. Comparing Figure 5d with Figure 5d, it is concluded that the increase in temperature from 350 to 380ºC favors the reduction of Co3O4, since the presence of this oxide is no longer detected.

In Figure 5e it can be seen that the only phase detected is Co-α, which indicates that the plasma reduction carried out at a temperature of 380 for 40min is already sufficient to provide reduction fraction values, a, close to 1.0. Comparing Figure 5e with Figure 4e, it is concluded that after 40 min, at a temperature of 380ºC, the use of plasma as a reducing agent allows the reduction kinetics of cobalt oxide to be increased, given that it is not the presence of Co_3O_4 nor CoO was detected.

In the same way as was observed when using only hydrogen gas as a reducing agent, the reduction steps can be represented as follows:

$$Co_3O_4 \rightarrow CoO \rightarrow Co$$
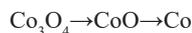
Therefore, from the analysis of the diffractograms, it is concluded that cobalt oxide (Co_3O_4) is initially reduced into cobalt monoxide (CoO) and subsequently reduced into metallic cobalt.

Figure 6 shows the reduction fraction, α, as a function of the reduction time for Co_3O_4 powder after the reduction experiments using both hydrogen gas and hydrogen plasma. At 250 ºC, note that the reduction is not completed by hydrogen gas and hydrogen plasma. However, the reduction process was enhanced by hydrogen plasma, as previously shown in the XRD analysis. At 300 ºC and 50 min, it is noted that plasma allowed to get reduction fractions above 0.9. In contrast, reduction fractions of only 0.6 are obtained when gas was used. At 350 °C or 380 °C, when using plasma, the reduction practically was completed after 30 min. On the other hand, under hydrogen, the reaction only completed only after 50 min. The kinetic equation that best fit the data presented in Figure 6 was $(1 - (1 - \alpha)^{1/3})^2 = k.t$ (Jander interdiffusion model), where: α is the reduction fraction, k is the rate constant [s^{-1}], and t is the reaction time [s].

For different temperatures, Figure 7(a) and (b) shows the experimental data fitted to the mentioned Jander interdiffusion model, where the values for k, obtained by the slope of each straight, are shown in Tables 1 and 2.

Therefore, in the range of temperatures studied, the gas reduction rate of Co_3O_4 is not linear, showing parabolic behavior. It is observed that the kinetics tend to increase with both temperature and reduction time. It can be concluded that for both low and high temperatures, the gas reduction kinetics are controlled by the interdiffusion mechanism.
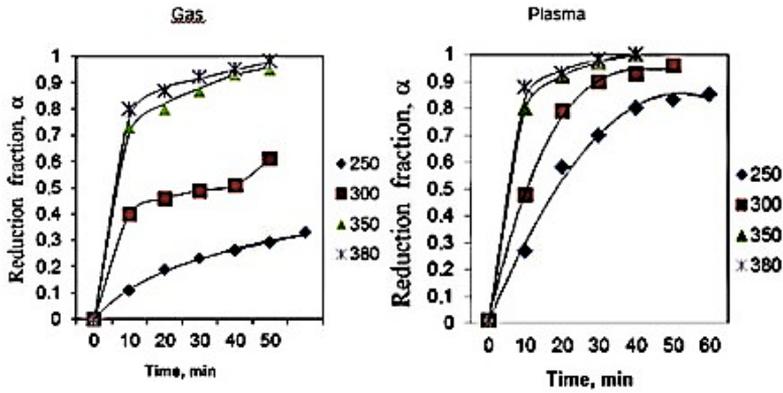
Figure 6. Variation of the reduction fraction of the Co_3O_4 powder as a function of the reduction time for hydrogen gas and hydrogen plasma.
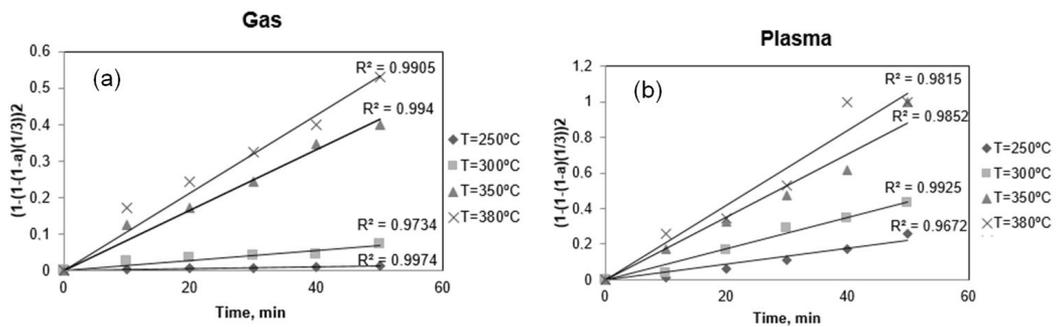

Figure 7 - Plots $(1 - (1 - \alpha)^{1/3})^2 = k.t$ versus Co_3O_4 reduction time, where the dots are experimental data and lines are the fitted data, for (a) hydrogen gas and (b) hydrogen plasma.

Table 1. Reaction rate constants reducing Co_3O_4 to gas as a function of temperature.

T (°C)	T (K)	1/T (10^{-3}), (K-1)	K (min^{-1})	Ln k
250	523	1.91	0.002	- 8.517
300	573	1.75	0.0014	- 6.571
350	623	1.61	0.0089	- 4.791
380	653	1.53	0.0107	- 4.538

Table 2. Reaction rate constants for plasma Co_3O_4 reduction as a function of temperature.

T (°C)	T (K)	1/T (10^{-3}), (K-1)	K (min^{-1})	Ln k
250	523	1.91	0.0044	- 5.426
300	573	1.75	0.0087	- 4.744
350	623	1.61	0.0177	- 4.034
380	653	1.53	0.0205	- 3.863

The same procedure for determining the rate constants (k) of gas reduction was adopted, choosing the model proposed in the literature to which the experimental data were best adjusted.

Jander's diffusion equation proved to be more suitable for experiments carried out at temperatures of 300, 350 and 380ºC, while the chemical reaction equation is the one that best describes the data from the reduction experiments at a temperature of 250ºC.

At temperatures from 300 to 380ºC, there are possibly two mechanisms acting (interdiffusion and chemical reactions) due to the inflection observed in the respective curves, from longer times onwards. However, due to the lack of data for short times, only the diffusion mechanism was considered for temperatures between 300 and 380ºC.

As at low temperatures there is difficulty in the occurrence of diffusion, which means that this is not the controlling mechanism of the process, the high reaction speed must be associated with the plasma species. As they allow the generation of vacancies that facilitate the penetration of hydrogen, there is an increase in the reduction kinetics, contributing to the thickening of the reduced layer.

For temperatures of 250ºC, the mechanism that prevails is that of a chemical reaction. Therefore, for lower temperatures, the reduction kinetics tend to be controlled by the chemical reaction mechanism.

From Figure 7, the values of the reaction constants (k) were determined, which are presented in Table 1 and 2. It is worth remembering that for the reduction experiments at a temperature of 250ºC, the reaction constant was determined considering the diffusion model while for temperatures of 300, 350 and 380ºC the constants were determined using the interdiffusion model.

The Figure 8 compares the activation energy values for reduction of cobalt oxide by hydrogen plasma and hydrogen gas. The activation energy value of 35.38kJ/mol, which is the first experimental data provided to the literature using hydrogen plasma as a reducing agent, is about 2.5 times lower than that of gas, 90.76 kJ /mol. This denotes that when using plasma, temperature has little influence, and reduction can be carried out at low temperatures with high reduction speed,
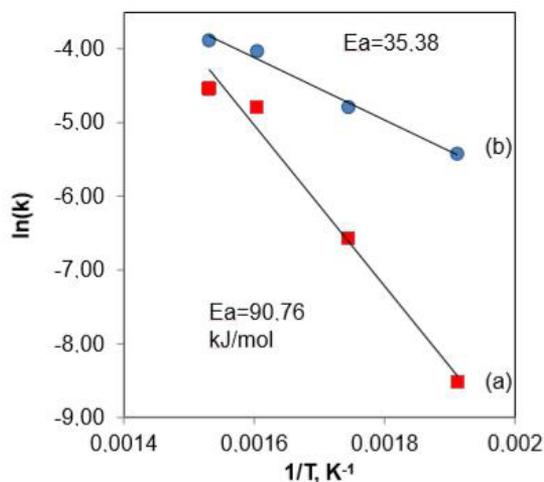
Figure 8. Arrhenius plots - activation energy for the reduction of cobalt oxide (Co_3O_4) by: (a) hydrogen gas and (b) hydrogen plasma.

unlike gas reduction. Bustnes et al.[7] present an activation energy for the reduction of cobalt monoxide by hydrogen of 54.3 kJ/mol, Section 3.5.2. Khoshandam et al.[3] obtained an activation energy of 155.9 kJ/mol for the reduction of cobalt monoxide by methane, Section 3.5.1. Therefore, this suggests that the plasma process, as it has a lower activation energy for reduction, can be used at low temperatures with yields, in terms of reduction fraction, equal to those of gas carried out at high temperatures.

The activation energy values obtained via hydrogen gas and plasma reduction were respectively 90.8 kJ/mol and 35.4 kJ/mol. At all temperatures investigated, the kinetics of reduction via plasma were favored when compared to that via gas reduction, notably at temperatures of 250°C and 300°C. This shows that the main plasma species (H atoms and H^+, H^{2+} and H^{3+} ions according to Mendez et al.[12], Hancock and Sharp[13], Gonoring et al.[14]) played a fundamental role in these temperatures. It is worth noting that such species are smaller in size than the H_2 molecule, which must have facilitated the diffusion of such species on the surface of the oxide under reduction, which seems to be in accordance with the Jander equation used in this work. The faster kinetics reduction cobalt oxide at low temperature is associated the reducing species action derived molecular hydrogen present in plasma and the vacancies generation during ion bombardment[13,14].

4. Conclusions

- When hydrogen gas or hydrogen plasma is used, cobalt oxide (Co_3O_4) is initially reduced into cobalt monoxide (CoO) and subsequently reduced into metallic cobalt: $Co_3O_4 \rightarrow CoO \rightarrow Co$
- At 350 °C or 380 °C, when using plasma, the reduction was practically completed after 30 min. On the other hand, under hydrogen, the reaction only completed only after 50 min.
- The kinetic equation that best fit the data presented $(1 - (1 - \alpha)^{1/3})^2 = k.t$
- The activation energy values obtained via hydrogen gas and plasma reduction were respectively 90.8 kJ/mol

and 35.4 kJ/mol. These values shown that molecular hydrogen is a good reductant, however, the H and H^+ species present in hydrogen plasma can act as much stronger reductants at low temperatures provoking an increasing the density of crystalline defects due to the impact of incident ions from plasma.

- At all temperatures investigated, the kinetics of reduction via plasma was favored when compared to that via gas reduction, notably at temperatures of 250°C and 300 °C. This shows that the main plasma species (H atoms and H^+, H^{2+} and H^{3+} ions) played a fundamental role in these temperatures, which seems to be in accordance with the kinetic equation of the present study.

5. Acknowledgments

6. References

1. Davis JR, editor. ASM Specialty Handbook - Nickel, Cobalt, and their alloys. Materials Park: ASM International; 2000.

2. Crundwell F, Moats M, Ramachandran V, Robinson T, Davenport WG. Extractive metallurgy of nickel, cobalt and platinum group metals. USA: Elsevier; 2011.

3. Khoshandam B, Jamshidi E, Kumar RV. Reduction of cobalt oxide with methane. Metall Mater Trans, B, Process Metall Mater Proc Sci. 2004;35(5):825-8. http://doi.org/10.1007/s11663-004-0076-7.

4. Shirchi S, Khoshandam B, Hormozi F. Reduction kinetics of cobalt oxide powder by methane in a fluidized bed reactor. J Taiwan Inst Chem Eng. 2015;51:171-6. http://doi.org/10.1016/j.jtice.2015.01.030.

5. Cetinkaya S, Eroglu S. Synthesis of cobalt powder by reduction of cobalt oxide with ethanol. J Miner Met Mater Soc. 2018;70(10):2237-42. http://doi.org/10.1007/s11837-018-2799-y.

6. Gallegos NG, Lopez JP. Kinetic study of cobalt oxides reduction by hydrogen. Mater Chem Phys. 1988;19(5):431-46. http://doi.org/10.1016/0254-0584(88)90036-3.

7. Bustnes JA, Sichen D, Seetharaman S. Kinetic studies of reduction of CoO and CoWO 4 by hydrogen. Metall Mater Trans, B, Process Metall Mater Proc Sci. 1995;26(3):547-52. http://doi.org/10.1007/BF02653872.

8. Lin HY, Chen YW. The mechanism of reduction of cobalt by hydrogen. Mater Chem Phys. 2004;85(1):171-5. http://doi.org/10.1016/j.matchemphys.2003.12.028.

9. Sabat KC, Paramguru RK, Pradhan S, Mishra BK. Reduction of cobalt oxide (Co_3O_4) by low temperature hydrogen plasma. Plasma Chem Plasma Process. 2015;35(2):387-99. http://doi.org/10.1007/s11090-014-9602-9.

10. Sabat KC. Formation of CuCo alloy from their oxide mixtures through reduction by low-temperature hydrogen plasma. Plasma Chem Plasma Process. 2019;39(4):1071-86. http://doi.org/10.1007/s11090-019-09963-y.

11. Silveira IS, Vieira EA, Nascimento RC, Franco AR Jr. Redução direta de pós de hematita por plasma frio de hidrogênio. Tecnol Metal Mater Min. 2014;11(4):346-54. http://doi.org/10.4322/tmm.2014.050.

12. Mendez I, Gordillo-Vázquez FJ, Herrero VJ, Tanarro I. Atom and ion chemistry in low pressure hydrogen DC plasmas. J Phys Chem A. 2006;110(18):6060-6. http://doi.org/10.1021/jp057182+.

13. Hancock JD, Sharp JH. Method of comparing solid-state kinetic data and its application to the decomposition of kaolinite, brucite, and $BaCO_3$. J Am Ceram Soc. 1972;55(2):74-7. http://doi.org/10.1111/j.1151-2916.1972.tb11213.x.

14. Gonoring TB, Vieira EA, Nascimento RC, Franco AR Jr. Kinetic analysis of the reduction of hematite fines by cold hydrogen plasma. J Mater Res Technol. 2022;20:2173-87. http://doi.org/10.1016/j.jmrt.2022.07.174.