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THE CHLORINATIONS KINETICS OF THE CHROMIC OXIDE

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ABSTRACT

Chlorination kinetics of Cr_2O_3 was tried on the thermobalance in the temperature range of 900°-1100°C. Obtained degree of the conversion was estimated gravimetricaly from the amount of the evaporated oxychloride from the following reaction :

$$Cr_2O_3 + 2\ Cl_2 + 0{,}5\ O_2 = 2\ CrO_2Cl_{2/g/}$$

INTRODUCTION

Chromium ores are used in metallurgy namely for ferrochromium and refractory materials production. From the point of the quality are these ores in the most cases not suitable for refractories production. For conditions of the changable oxygen potencial and for high temperatures is content of iron in Cr-ore unsuitable. Therefore in the world are tried chlorination technologies by means of which the content of the impurities of materials for the refractory materials production is decreased.

Review of the literature references concerning abovementioned problem has been made in our former work /1/.

Result of metioned process is that in oxydation conditions chromium is lost due to the evaporation of oxides /2/, oxychlorides /3/ or chlorides/4/.

The aim of the chlorination kinetics study of Cr_2O_3 was to determine the basic kinetics data and on the base of these data to analyse the possibility of decreasing of Cr losses.

EXPERIMENTAL

For the experimental work the Cr_2O_3 powder of the analytical purity was used. The powder particles size dimenos was 100% : - 0,04 mm. After the gaining of the moisture content up to 1-5 %,

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the powder was briqueted under the pressure of 0,5 ± 0,05 MPa to form cylindrical samples. The height of the samples was corrected by the grinding to be equal to the diameter of the samples. The samples were then dried and sintered at 900°C for 1 hour. The gained densities of such treated samples were 45 - 65 % of the theoretical value mentioned in the literature /5/.In the most cases the sample was cylinder heigth and diameter of which were 10,0± 0,3 mm.

The apparutus used in the experiments consisted of the purification lines for gases Cl_2,O_2 and N_2 resp. Required mixture was prepared by the mixturing of these gases. The reached degree of the conversion was estimated gravimetricaly from the silica spring elongation. The rate of the gases flow around the sample was 36 mm s^{-1} by which rate the influence of external diffusion of the reaction products - gaseous oxychloride and chlorides of Cr - was eliminated. The majority of the experiments were realised with the optimal gaseous mixture for CrO_2Cl_2 with the content of 14% Cl_2 and 86 % O_2 as it is recommended in literature /3/.

RESULTS AND DISCUSSION

The study of the temperature influence was excecuted at the temperature 900,1000 and 1100°C resp. with the sample diameter of 10 mm and atmosphere with 14% Cl_2. The same atmosphere was used at 900 and 1000°C for the sample size influence study. The radius of the sample was varied in the range of 0,15 - 0,6 cm. For the obtained time dependance of the conversion degree R the best fulfilment of the linear time dependance was reached by function $1 - / 1 - R /^{1/3}$. The dependances of this function on time are for 1000°C and different contents of Cl_2 in atmosphere shown in fig.1. From the equation valid for the cylindrical samples where height is equal to their diameter :

$$1 - / 1 - R /^{1/3} = \frac{k}{r_o \cdot \varrho_o} \cdot \tau \qquad /1/$$

where $R = \frac{W_o - W}{W_o}$ - conversion degree

r_o - original sample radius, /m/
ϱ_o - original sample density, / kg . m^{-3}/
τ - time,/h/
k - rate constant, /kg . m^{-2}. h^{-1}/

W - sample weight in time ,/kg/

W_o - sample wieght at the beginning, /kg/

the values of k were calculated. Since the dependance of the ln k values on 1/T was linear, the apparent activation energy was estimated by the means of the Arhenius plot.

The influence of chlorine and oxygen content change has been studied at 900° and 1000°C resp. The dependance of k values change on concentration is shown in fig.2. The linearity of this dependance is fulfiled for the function chlorine concentration volume fraction $X_{Cl_2}^{2/3}$ with the exception of the two last values for which the chlorination of Cr_2O_3 takes place and also $CrCl_3$ is formed. The $CrCl_3$ presence in the condesate has been proved during the mentioned experiments.

On the separate influence study base the mathematical relation valid for Cr_2O_3 conversion change dependance in the chlorine atmosphere consisting of chlorine and oxygen has been found as follows :

$$\frac{1 - /1-R/^{1/3}}{\tau} = \frac{0.3077}{r_o \cdot \varrho_o} \cdot X_{Cl_2}^{2/3} \cdot \exp - \frac{6995}{R_p \cdot T} \qquad /2/$$

The validity of this relation has been proved in our former work /1/.

REFERENCES

1. D.Kmeťová et all: The Fe content lowering in Cr-ores./Research work / Košice, Dep.of Nonferrous met., VŠT 1978.
2. W.Kim,G.R.Belton: The Thermodynamics of Volatilization of Chromic oxide.Part 1"Metall.Trans.",Vol.5.,August 1974.
3. N.Sano,G.R.Belton : The Thermodynamics of Volatilization of Chromium oxide,Part 2,The species CrO_2Cl_2."Met.Trans."Vol.5., October 1974.
4. H.Oppermann : Das Reaktionsgleichgewicht 2 $CrCl_3$ + Cl_2= 2 $CrCl_4$ "Zeit.anorg.chem.",359,č.1-2,1963.
5. T.D.Averbuch,P.G.Pavlov : Technologija sojedinenij chroma. Leningrad, 1973.

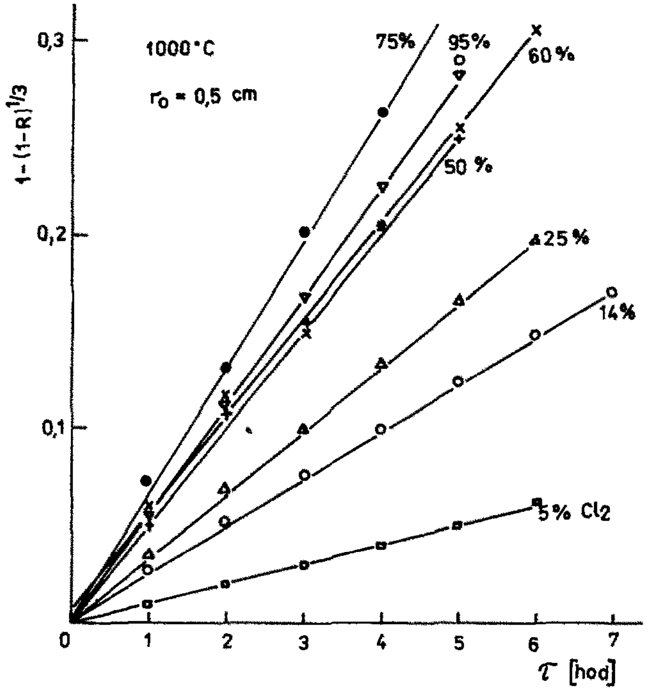

Fig.1.: Relationship of function R versus time.

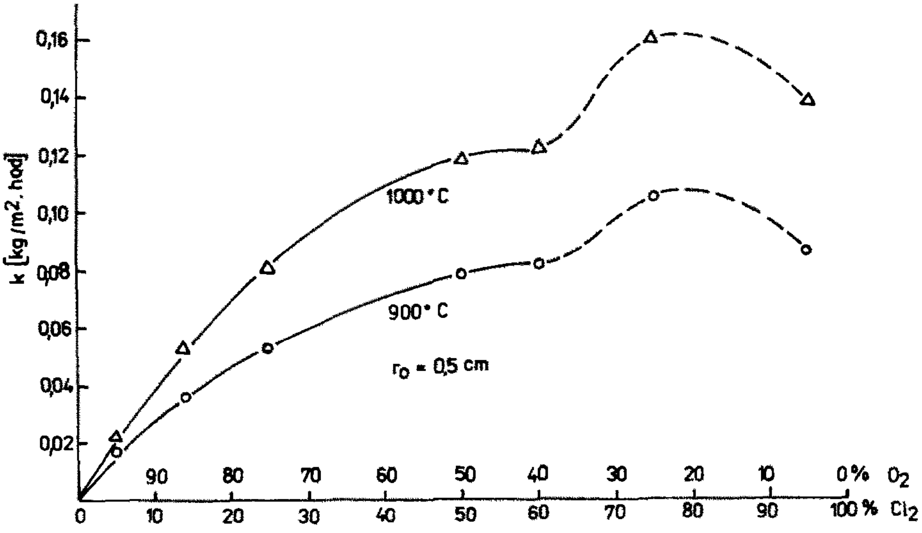

Fig.2.: Relationship of k values change versus atmosphere.