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# Oxidation Kinetics of Tungsten Carbide- 20cobalt Composite using Non-Isothermal Thermal Analysis

S. T. Aly
Chemical Engineeering Department
Egyptian Academy for Engineering and Advanced Technology (EAE&AT), Affiliated to Ministry of Military Production, Cairo, Egypt

N. F. Abdel Salam
Chemical Engineering Department
Faculty of Chemical Engineering, Cairo University, Giza, Egypt

K. H. Hamad
Chemical Engineeering Department
Egyptian Academy for Engineering and Advanced Technology (EAE&AT), Affiliated to Ministry of Military Production, Cairo, Egypt

S.M.S.Abdel-Hamid
Chemical Engineeering Department
Egyptian Academy for Engineering and Advanced Technology (EAE&AT), Affiliated to Ministry of Military Production, Cairo, Egypt

***Abstract*- This study presents non-isothermal analysis of the oxidation behavior of tungsten carbide 20% cobalt powder. This was done to further understand and quantitatively model of this process. The effect of heating rate from 5 to 20 °C/min on the oxidation behavior was examined. The specimens were heated in air from ambient temperature up to 1000 °C using the aforementioned heating rates. XRD was used to assess the phases present in the original powder as well as specimens heated to different temperatures. The phases present in the green powder were WC, W2C and metallic cobalt, while the phases appearing at 600 °C were WC, $WO_3$ and $CoWO_4$ and those present at 1000 °C were $WO_3$ and $CoWO_4$. Kinetic calculations were carried out, the value of activation energy was calculated at different conversions using the Flyn – Wall – Osawa method, and the average value was about (255 kJ/mole). The corresponding activation energy values calculated by the Coats – Redfern method were lower (140 kJ /mole).**

***Keywords:* Cobalt, Kinetics, Oxidation, Thermal, Tungsten carbide***

## 1. INTRODUCTION

Tungsten carbides are considered hard materials, so they can withstand cutting, abrasion, penetration, and scratching, yet they are brittle; cobalt is a soft material yet it is tough so great strain can be applied but tearing or breaking is not encountered. Therefore, it can be concluded that tungsten carbide- cobalt composites combine hardness and toughness [1].

Liquid phase sintering of WC-Co composites are made by cementing carbide grains (WC) in a binder matrix of cobalt metal (Co). In high temperatures, WC is soluble in cobalt and has excellent wetting characteristic by the liquid cobalt binder, this leads to optimum densification during liquid phase sintering, which produces a nearly non-porous structure called cemented tungsten carbide [2].

There is a wide range of applications for cemented tungsten carbide because of its excellent wear resistance, such as sand blast, cutting tools, seals in slurry pumps and some component parts in the oil industry [3-5].

The high temperature properties determine the quality of a cemented carbide grade. When hard cemented carbides are used as cutting tools in air, their oxidation resistance affects their working efficiency and lifespan [6–8]. The negative point is that these composites tend to oxidize at relatively low temperatures. Thermal analysis has been used widely to follow the oxidation behavior of metal oxide mixes and composites [9, 10]. Oxidation reactions for these materials mostly described by the following reactions:

$$Co + 0.5O_2 \longrightarrow CoO \quad (1)$$

$$WC + 2.5O_2 \longrightarrow WO_3 + CO_2 \quad (2)$$

The formation of CoO and $WO_3$, can partially combine to yield $CoWO_4$ [11].

The oxidation kinetics of WC–Co composites was studied by Larikov et al. [12] using different compositions and porosity in the temperature between 700 to 1,000 °C in air. The increase in mass regarding these alloys fits a parabolic law. It was determined that the alloy WC–6Co with 15 % porosity at 780 °C has a rate constant of 760 $g^2\ m^{-4}\ s^{-1}$.

The oxidation behaviour of WC-Co sintered carbides with 3–5 μm grain size of WC and 6–15 vol.% of cobalt have been studied in air in the temperature between 650–800 °C by F. Lofaj and Yu. S. Kaganovskii [13] they found that the apparent activation energy of the dimension and weight gain kinetics were within 32 kJ $mol^{-1}$ to 67 kJ $mol^{-1}$, and they proposed that the process is controlled by the reaction at the interface. The oxidation rate is inversely proportional to mean size of WC grains and directly proportional to cobalt content.

L.del Campo et al. [14] investigated oxidation of uncoated WC-based carbides in the range of 450 and 800 °C. They found an unusual decrease of the oxidation rates between 528 and 630 °C. Instead of the normal increase when the temperature increases. The activation energy was found to be 119 ± 8 kJ/mol below 528 °C, however above 630 °C it was found to be 208 ± 8 kJ/mol.

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Thermogravimetric experiments were performed by M.Aristizabal et al. [15] and confirmed that the oxidation resistance of WC–Co increases with their metallic content. They reported that when isothermal or the isoconversion method was used to calculate the activation energies, it suggests that the surface chemical reaction controls oxidation, and activation energies increase with temperature between 650 and 800 °C.

S.T. Aly et. al studied [16] the oxidation behavior of WC-20Co hot-pressed compacts rather than powders in the temperature between 700–850 °C. They follow up the mass with time at different constant temperatures. They reported that oxidation of both cobalt and WC with the formation of $WO_3$ and $CoWO_4$ take place and controlled by chemical reaction at interface. The activation energies for the two steps of oxidation were reported to be 157 kJ $mol^{-1}$ and 205 kJ $mol^{-1}$, respectively.

L. Chen et al [17] carried out the oxidation experimental of WC–Co cemented carbides at 500 °C in air. They observed that in the beginning, the O content in Co phase increases rapidly, and then stabilize after oxidation of 20 min. On the other hand, The O content in WC phase was not changed. Additionally, a direct parabolically relation was found between the thickness of oxide scales of Co phase and the oxidation time.

The oxidation behavior of WC-12Co was investigated by M.Erfanmanesh et al. [18] using thermogravimetric analysis X-Ray Diffraction and scanning electron microscope. The relation between time dependence of weight gain and WC-Co coating was found to be linear. They reported that, this behavior is related to the reaction-controlled and diffusion-controlled oxidation processes in the WC-Co. The apparent activation energy was found to be about 98.3 kJ/mol.

## 2. RAW MATERIAL & EXPEROMENTAL WORK

The studied WC-20Co powder has particle size of 20-120 µm with density of 13.5 gm/cm. This powder was analyzed using Shimadzu TGA-50H and DTA-50 type thermal analyzer. The temperature ranges were between room temperature and 1,000 °C for TG and for DTA. Exothermic peaks represented as maxima, while endothermic ones represented as minima. Oxidation phases were identified by X–ray diffraction.

## 3. RESULTA AND DISCUSSION

### 3.1. X – RAY DIFFRACTION OF WC – 20CO POWDER

The purchased tungsten carbide + 20% cobalt powder was subjected to XRD analysis to establish its mineralogical constitution. Fig. 1 shows the results obtained. Three phases were detected: WC, $W_2C$ and metallic cobalt. XRD is applied also to samples after heating to 600°C, fig. 2 and 1000°C, fig. 3. The phases detected at 600°C are WC, $WO_3$ and $CoWO_4$ and those present at 1000 °C were $WO_3$ and $CoWO_4$.

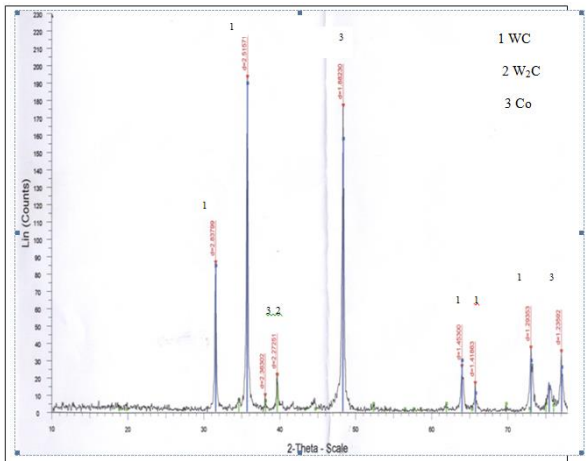


Fig. 1. XRD pattern of WC + 20% Co powder

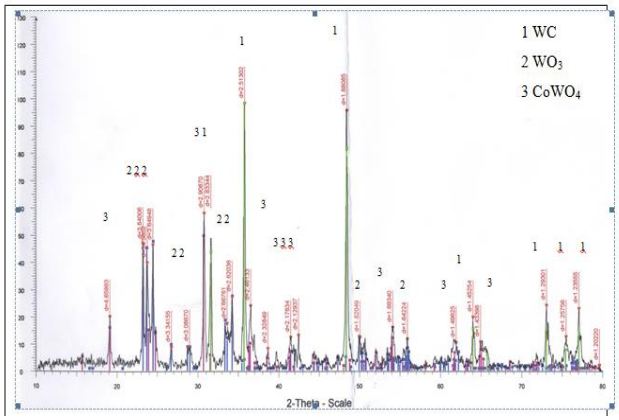


Fig. 2. XRD pattern of WC + 20% Co powder heated up to 600 °C

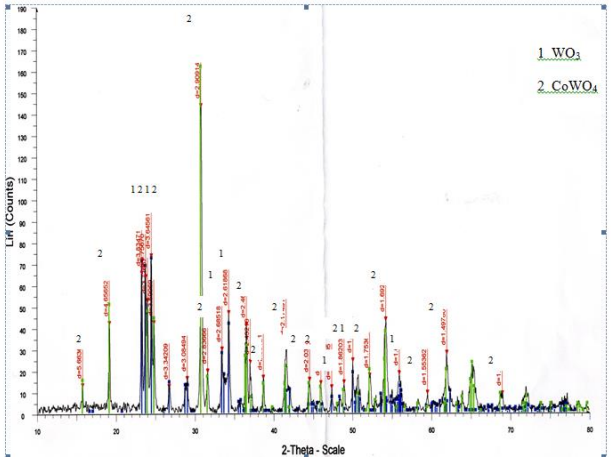


Fig. 3. XRD Pattern of a sample heated to 1000°C

### 3.2. TG AND DTA RESULTS

Different heating rates from 5-20°C/min were performed. Fig. 4 shows the results obtained for percent change in weight. It appears that an increase in heating rate is linked with an increase in the corresponding temperature at any degree of conversion.

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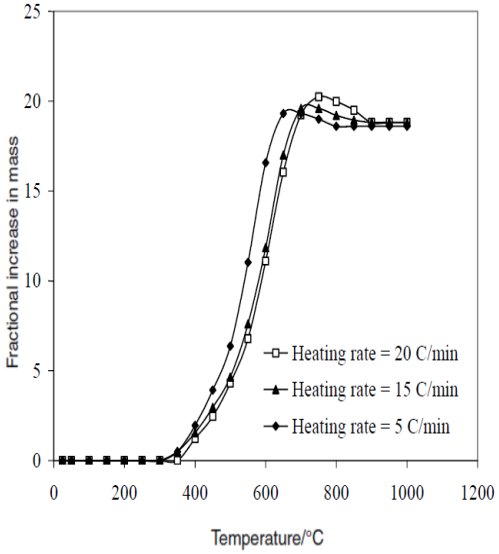


Fig. 4. TG of powder Sample at Different Rates

Fig. 5 shows the results of DTA obtained at two different heating rates (5 and 10°C/min.). The two curves are very close with a slight temperature shift in case of higher heating rate. Two exothermic peaks appear on these curves: the first peak is very sharp occurring at about 300 – 320 °C (depending on the heating rate). The second peak is completed at about 700 °C. This is in excellent agreement with the TG curves in Fig. 4 which show that oxidation is completed at the two aforementioned heating rates at about 700 °C. The first peak corresponds to oxidation of cobalt followed by oxidation of tungsten carbide [19] while the second relates to final oxidation of remaining WC to $CoWO_4 + WO_3$.

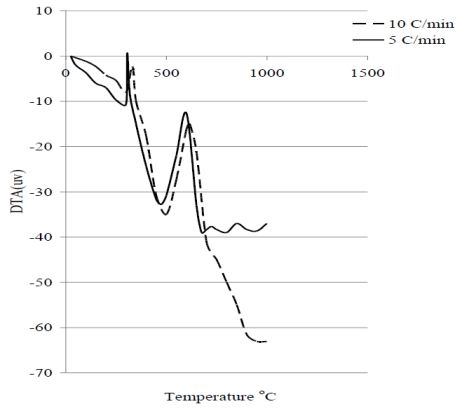


Fig. 5. DTA of powder sample at low heating rates

Higher heating rates show a somewhat different behavior. Fig. 6 shows the curves obtained at heating rates of 15 and 20 °C/min. While a first sharp peak appears at about 340 °C at a heating rate of 15 °C/min, this peak splits into three close consecutive peaks ranging from 340 to 420°C at a heating rate of 20 °C/min. These peaks correspond to the oxidation of cobalt to CoO followed by the beginning of oxidation of tungsten carbide to WO3 and CoWO4. However, it seems that too high a heating rate does not complete this oxidation step. This would explain the second peak showing up at about 575 °C for both heating rates. Such peak did not appear in Fig. 6at lower heating rates. This probably corresponds to oxidation of remnant tungsten carbide to yield CoWO4. Finally full oxidation is completed as evidenced by the third peak occurring at about 750 °C at a heating rate of 15°C/min and at 860 °C at the heating rate 20 °C/min. These figures check well with the TG data of Fig. 4.

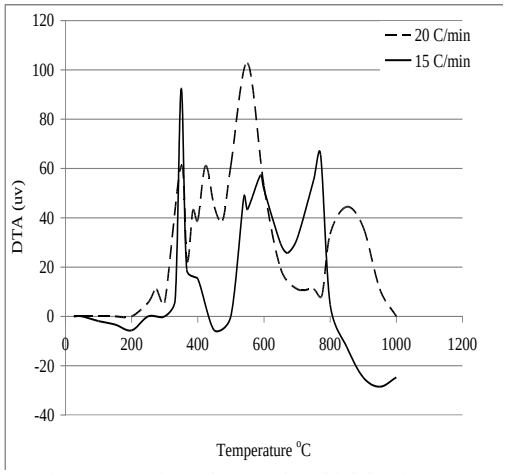


Fig.6. DTA of powder sample at high heating rate

## 4. KINETICS RESULTS

Oxidation kinetics was studied using two methods: the Flynn – Wall – Osawa (FWO) isoconversional method [20, 21] and the Coates – Redfern method [22].

### 4.1. Flynn – Wall – Osawa method [Osawa, 1965; Flynn and Wall, 1966]

In this method, equation (3) was used.

$$\ln B = K - K'.\frac{E}{R.T} - \ln f(x) \qquad (3)$$

Fig. 7 shows the results obtained by FWO) isoconversional method on plotting ln B, where B is the rate of heating, against 1/T for three conversions: 0.1, 0.14 and 0.17 for the studied powder. The three lines obtained are nearly parallel.

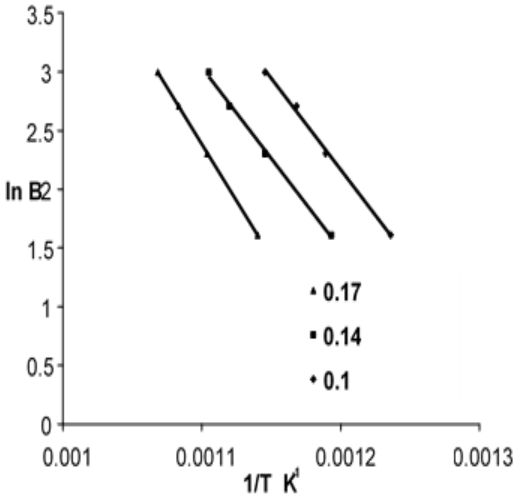


Fig.7. Flynn – Wall – Osawa plot

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Their slopes correspond to 0.4567 E/R, where E is the activation energy in the range of temperatures 550 – 750 °C the results obtained for activation energy average of 255 kJ/mol. These values are in fair agreement with those obtained by Voitovitch et al [23] and Aristizabal et al [15] for WC+25% Co and 16% respectively (235 kJ/mol). It should be noted that these values were obtained on a temperature range where full oxidation to $WO_3$ + $CoWO_4$ are operative. If a lower range was chosen (for gain in weight up to 400 °C), the results would have been different owing to the fact that at low temperature oxidation of cobalt prevails.

4.2. Coats – Redfern method [Coats and Redfern, , 1964]
The following equation was used

$$\ln \frac{f(x)}{T^2} = C - \frac{E}{R.T} \qquad (4)$$

The Coats – Redfern method relies on writing a kinetic function f(x) corresponding to an assumed controlling step. If this assumption is correct, then a plot of ln $f(x)/T_2$ versus 1/T should results in a straight line of slope =E/R
In applying this method we use the formal definition of conversion:

$$x = \frac{W - W_0}{W_\infty - W_0} \qquad (5)$$

Fig. 8 shows this plot at different heating rates taking in consideration the assumption that the controlling step is chemical reaction at interface. This assumption is justified by the fact that almost parallel straight lines were obtained. The calculated value of activation energies for the three lines had an average value of 140 kJ/mol

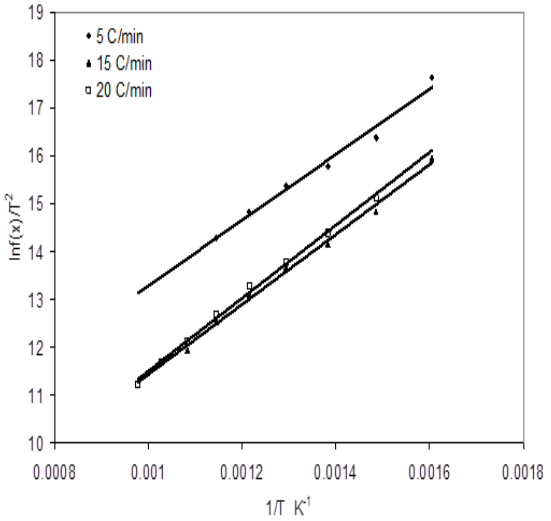


Fig.8. Coats - Redfern plot (Assuming chemical reaction to control)

## 5. CONCLUSION

The calculations of non-isothermal thermal analysis of tungsten carbide 20% cobalt powder shows that oxidation of cobalt takes place from temperatures as low as 200°C and produces CoO and $Co_3O_4$ below 465°C.Immediately follows the oxidation of $WO_3$ and subsequent formation of $CoWO_4$ at about 600°C The oxidation of WC-20Co causes gain of weight of about 20% . The values of activation energy at conversions (0.1, 0.14, 0.17) obtained by using Coats-Redfern method are very different from those obtained using Flyn-Wall-Osawa method, because the first method is restricted to isothermal analysis.

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