OXIDATION BEHAVIOR OF TUNGSTEN CARBIDE-20COBALT COMPOSITES

By
Engineer \ Soheir Taha Ali Gohaem

A Thesis Submitted to
the Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
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Summary

Oxidation behavior of tungsten carbide cobalt is an important research topic when dealing with WC-Co composite. The lifespan and working efficiency of WC-Co cemented carbide as cutting tools in air are strongly depending on its oxidation resistance. A study of the oxidation process was undertaken to further understand and quantitatively model this process. The effects of key processing parameters (including grain size, heating rate, temperature, and time) on the oxidation behavior were examined.

This thesis deals with the kinetics of the thermal analysis (isothermal and non isothermal) of tungsten carbide 20% cobalt in two material forms: powder without sintering and compacts.

Non isothermal analysis was carried out on the powder using TGA and DTA units. Two parameters were varied; heating rate (5, 10, 15, 20 °C/min) and grain size (45-53, 90-106 um). The specimens were heated in air from ambient temperature up to 1000°C using the aforementioned heating rates for both particle sizes. 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, WO₃ and CoWO₄ and those present at 1000°C were WO₃ and CoWO₄.

Kinetic calculations for non – isothermal runs were carried out and the value of activation energy was calculated at different conversions using the Flynn – Wall – Osawa method. The average value was about (255 kJ/mole) for the two particle size used. The corresponding values of activation energy calculated by the Coats – Redfern method were lower (140 kJ /mole).

Isothermal analysis was carried out on tungsten carbide 20% cobalt cylindrical compacts using an electrical tube kiln. Two parameters were varied: temperature and time. The weight and diameter changes of specimens were recorded. Two specimens were examined using XRD: the first one was kept at 800°C for 45 min and the second was kept at 800°C for 90 min. The pattern for 45 min showed that CoWO₄ and WO₃ with few lines of CoO were detected while the pattern for 90 min showed only the lines of CoWO₄ and WO₃. SEM was also used to investigate the morphology of the external oxidized...
layer. This revealed very high porosity (70%) which was explained by a simple physical model.

Kinetic calculations were performed and the results showed that two stages of oxidation take place; the first stage is presumably related to the oxidation of Co to CoO (and possibly to $\text{Co}_3\text{O}_4$) on the compact surface and the second stage where oxidation proceeds towards the formation of the final oxidation products $\text{WO}_3$ and $\text{CoWO}_4$. The value of activation energy of the first stage was about $(172 \text{ kJ/mol})$ while that of the final stage resulting in the full oxidation of WC was about $243 \text{ kJ/mol}$. It was also proved that the oxidation of WC – 20% Co to $\text{WO}_3$ and $\text{CoWO}_4$ is a chemically controlled reaction throughout all intermediate steps.

Thermodynamic activation functions were calculated for the two stages of oxidation. The values of activation energy are in agreement with that values previously obtained; for the first oxidation step; $\Delta H^+ = 163 \text{ kJ/mol}$, and for the second step $\Delta H^+ = 242 \text{ kJ/mol}$. On the other hand, the values of the entropy of activation $\Delta S^+$ and the values of the free energy of activation $\Delta G^+$ were also calculated at each stage of oxidation.
2- Literature Review

2.1 Introduction

The beginning of tungsten carbide production may be traced to the early 1920’s, when the German electrical bulb company, Osram, looked for alternatives to the expensive diamond drawing dies used in the production of tungsten wire. These attempts led to invention of cemented carbide, which was soon produced and marketed by several companies for various applications where its high wear resistance was particularly important. The first carbide-cobalt grades were soon successfully applied in the cutting and milling of cast iron and, in the early 1930’s, the pioneering cemented carbide companies launched the first steel-milling grades which, in addition to tungsten carbide and cobalt, also contained carbides of titanium and tantalum. By the addition of titanium carbide and tantalum carbide, the high temperature wear resistance, the hardness and the oxidation stability of hard metals were considerably improved, and the WC-TiC-(Ta,Nb)C-Co hard metals are excellent cutting tools for the machining of steel. Compared to high speed steel, the cutting speed increased from 25 to 50 m/min to 250 m/min for turning and milling of steel, which revolutionized the productivity in many industries. The first mining tools with cemented carbide tips increased the life time of rock drills by a factor of at least ten compared to a steel-based drilling tool [Zhu, 2010].

2.2 Properties of Carbides

Carbides of refractory metals have superior physical, mechanical, and chemical properties. They are also distinguished by their extremely elevated hardness and strength, high melting point, and high corrosion-resistance, especially to mineral acids. At room temperature the carbides are negligibly oxidized by the air oxygen. With an increase in temperature, the resistance of carbides to oxidation in air decreases. Table 2.1 gives the temperature when active oxidation begins for different carbides.
Table 2.1 Active Oxidation Temperatures for Different Carbides [Romanova et al 1970]

<table>
<thead>
<tr>
<th>Carbide</th>
<th>TiC</th>
<th>ZrC</th>
<th>TaC</th>
<th>NbC</th>
<th>VC</th>
<th>Mo2C</th>
<th>WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature when active oxidation begins, °C</td>
<td>1100 To 1400</td>
<td>1100 To 1400</td>
<td>1100 To 1400</td>
<td>1100 To 1400</td>
<td>800 To 1100</td>
<td>500 To 800</td>
<td>500 To 800</td>
</tr>
</tbody>
</table>

Chlorine and other halogens begin to react with carbides at temperatures of 500 to 700°C.

2.2.1 Tungsten Carbide

Tungsten carbide is a grey metal powder which slowly reacts with acids. It is resistant to chlorine up to a temperature of 400°C and begins to react with it only at 600 to 800°C. Fluorine already combines with WC in the cold and with a flash. Tungsten monocarbide is slowly oxidized to WO₃ when heated in air or in oxygen. The physical properties of tungsten monocarbide are shown in (table 2.2) [Romanova et al 1970].

Table 2.2 Properties of WC [Romanova et al 1970]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/cm³</td>
<td>15.5 – 15.7</td>
</tr>
<tr>
<td>Melting point K</td>
<td>2870</td>
</tr>
<tr>
<td>Ultimate tensile Strength MPa</td>
<td>35</td>
</tr>
<tr>
<td>Young’s Modulus GPa</td>
<td>7.32</td>
</tr>
<tr>
<td>Elongation</td>
<td>App. 0</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.2</td>
</tr>
<tr>
<td>Compressive Strength MPa</td>
<td>30</td>
</tr>
<tr>
<td>Bending Strength MPa</td>
<td>5.3</td>
</tr>
<tr>
<td>Microhardness MPa</td>
<td>173</td>
</tr>
<tr>
<td>Thermal Conductivity W/m.K</td>
<td>29.3</td>
</tr>
<tr>
<td>Coefficient of Linear Expansion K¹</td>
<td>4.4×10⁻⁶</td>
</tr>
</tbody>
</table>

2.2.2 Cemented Carbide

The main use of tungsten (in the form of tungsten carbide) is in the manufacture of cemented carbide. Cemented carbide, or hard metal as it is often called, is a material made by "cementing" very hard tungsten mono-carbide (WC) grains in a binder matrix of tough cobalt metal by liquid phase sintering [Pastor et al, 2010].
This material is classified technically as a "brittle" material since it exhibits little or no plastic deformation preceding the initiation of a crack. All materials contain some amount of defects in the form of voids, pores or micro-cracks. These defects lead to reduced material strength. In the case of ductile materials such as aluminum, mild steels or copper, the frequency of defects is less critical than in brittle materials. Sintered tungsten carbide exhibits a broader range of scatter-of-fracture stresses, due primarily to the existence of micro-voids, when compared to ductile materials. The value of the stress at fracture can also vary widely with size, stress state (tensile, bending, torsion), shape, and type of loading. Despite the significant variability of the stress at failure, cemented carbide has considerably high strength for what some consider being a cermet material (Ceramic – metal composite) [Jaworska et al, 2006].

The definition of a ceramic material is the marriage of a metal to a nonmetal, for example silicon (metal) carbide (carbon, non-metal), aluminum oxide, silicon nitride or tungsten carbide. A cermet is a composite material composed of ceramic and metallic materials. A cermet is ideally designed to have the optimal properties of both a ceramic, such as high temperature resistance and hardness, and those of a metal, such as the ability to undergo plastic deformation. The metal is used as a binder with oxide, boride, carbide, or alumina. Generally, the metallic elements used are cobalt, nickel, and molybdenum. It is the addition of the metallic binder, i.e. cobalt or nickel that makes the cemented carbide (WC - Co) a cermet and differentiates it from truly brittle materials, that is, the ceramic family of materials [Jaworska et al, 2006].

The combination of WC and metallic cobalt as a binder is a well-adjusted system not only with regard to its properties, but also to its sintering behavior. The high solubility of WC in cobalt at high temperatures and a very good wetting of WC by the liquid cobalt binder result in an excellent densification during liquid phase sintering and in a pore-free structure. As a result of this, a material is obtained which combines high strength, toughness and high hardness [S-Ahmed et al, 1999; John et al 2008].

2.3 Manufacture of cemented carbides

2.3.1 Introduction

The manufacturing process begins with the composition of a specific tungsten carbide powder mixture – tailored for the application. Many more
combinations are possible when the WC powders are milled with a metal binder to produce a graded powder. While Co is most used in contents of 3 to 25 percent by weight, Ni and Cr are used in applications that require enhanced corrosion resistance. Small amounts of other carbides such as titanium carbide (TiC) and tantalum carbide (TaC) may be added to improve wear resistance during the high-speed machining of steels and gray cast iron. Increasing the binder content increases the toughness, but at the expense of hardness [Romanova et al, 1970., Voitovich et al, 1996; John et al, 2008].

2.3.2 Preparation of Mixtures

In the production of hard alloys, there are used carbide powders that are characterized by a very low plasticity. Therefore, to the mixture of carbides and bonding metal are added plasticizing agents that improve the fluidity of the mixture and assure lubrication of the grains, decreasing the friction between them. The plasticizing agent decreases the briquetting pressure required. The specific briquetting pressure largely depends on the quantity and quality of the plasticizing agent used. Plasticizing agents should possess the following properties. They should:

(a) wet the grains of the powder mixture well
(b) easily dissolve in an organic solvent;
(c) be removed without traces of impurities from a compressed briquette on heating it up to a temperature of 600 to 750\(^0\)C
(d) increase the mechanical strength of a compressed briquette;
(e) produce no chemical effect on the components of the mixture;
(f) have no toxic effect on the servicing personnel

The aforementioned requirements are met by the following compounds: a solution of synthetic rubber in petrol, a solution of glycerin in alcohol, paraffin or its solution in petrol, an alcoholic solution of glycol, and oleic acid [Romanova et al, 1970].

2.3.3 Pressing

The pressing or briquetting operation envisages obtaining parts of a predetermined shape. Powder mixtures of carbides with a bonding metal (cobalt) are first pressed into briquettes of various shapes, which are then sintered. The pressing process involves
changes in the structure and properties of powders. Pressing considerably increases
the contact area between particles, imparts the required strength to a briquette, and
disintegrates the conglomerates of particles and sometimes even the particles
themselves. In the course of pressing there may simultaneously occur elastic, brittle,
and plastic deformation of the particles. There are known the following pressing
methods: hydrostatic, nozzle, dross casting (pouring slurries in to provisional
moulds), hot, explosive, and die pressing [Romanova et al, 1970].

2.3.4 Sintering

Sintering is the final manufacturing operation in the production of hard alloys.
The sintering operation consists in heating parts up to a temperature of (0.7- 0.8) of
melting point in vacuum or inert atmosphere, holding them at this temperature for
certain time, and cooling them. The main object of sintering is the consolidation and
strengthening of compressed blanks, which should after this treatment, posses the
specified physical and mechanical properties. When sintering pressed powder, the
following processes take place [Romanova et al, 1970]:
(a) Increase in the mobility of the atoms
(b) Change in the contact surface between the particles
(c) Relieving of the internal residual stresses
(d) Recrystallization
(e) Change in mechanical properties
(f) Change of the surface of the particles
(g) Displacement of the particles.

In the process of sintering hard alloys, some amount of liquid phase in the
form of molten cobalt is formed in the part being sintered. Cobalt wets the tungsten
carbide grains and partially dissolves them with subsequent crystallization on cooling.
Therefore, sintering can be defined as the quantitative and qualitative change in the
contact between the particles, caused by the mobility of atoms at elevated
temperatures.

Sintering is characterized by appreciable consolidation prior to attaining the
temperature of the liquid phase, and by rapid, almost complete consolidation after this
phase has appeared.

Consolidation prior to the appearance of the liquid phase occurs in the solid
phases, and is accompanied by the diffusion of tungsten carbide into cobalt with the
formation of solid solution. The solubility of tungsten carbide in cobalt amounts to about 10 percent. Consolidation after the appearance of the liquid phase may result from the displacement of solid particles under the influence of the surface tension. Moreover, consolidation is facilitated by the process of recrystallization of carbide grains through the medium of liquid or molten cobalt.

In the following sintering stage, the average size of the tungsten carbide grains increases. The rate of growth of the tungsten carbide grains depends on the amount of the liquid phase, which is determined by the cobalt content in the mixture being sintered; therefore, in high-cobalt alloys the average grain size of tungsten carbide grains will be greater than in low-cobalt alloys. WC grains dissolve in the liquid owing to the difference in the surface energy between the fine and the coarse particles, as well as to the difference in the degree to which their crystal lattices approach the equilibrium state [Romanova et al, 1970].

2.3.4.1 Sintering procedure

Parts are sintered in one or two stages in electric furnaces provided with graphite tube, as well as in vacuum furnaces. In two-stage sintering, the pre-sintering operation is effected at a low temperature in the front part of the tube or in a separate furnace. The plasticizing agent is removed in the first sintering stage, and the alloy is formed at elevated temperature in the second stage. The pre-sintering schedule is selected with due regard to the purpose of this operation, the shape and overall dimensions of the part being sintered. The maximum temperature of the final sintering operation mainly depends on the composition of the alloy. For WC-Co alloys it depends on the cobalt content and the granularity of the mixture from which the parts are manufactured. The higher the cobalt content, the lower the sintering temperature. The lower the grain size, the lower the sintering temperature because the surface energy of smaller grain size is higher.
In practice, it is permitted to deviate from the aforementioned temperature schedules. However, when sintering at lower temperatures, the duration of the process is increased. The application of elevated temperature reduces the duration of the process, but rapid changes in temperature may result in cracking of parts of complicated shape. To enable the processes of the consolidation of the alloy and grain growth to be carried out to the full extent, the parts must be kept for a certain period of time in the hot zone of the furnace [Romanova et al, 1970].

2.3.4.2 Applications of sintered carbides in the Metal-Working Industry

Sintered metal carbides play an important part in the industry, particularly in machine-building. The use of carbides in machine-building substantially increases the efficiency of labour, permits to attain an economy in materials and equipment, and ensures a higher production rate. In machine-building carbides are used as a material for making tools that machine metals and non-metal materials by cutting or noncutting shaping. The field of application of carbides is determined by their physical properties, which may vary within certain limits depending on the chemical composition of the carbide and some other factors. The principal properties of carbides that determine their fields of application are hardness, strength, and plasticity. Under certain conditions the thermal conduction and coefficient of thermal expansion as well as wear resistance and cutting capability acquire a great importance [Romanova et al, 1970; John et al, 2008].

2.3.5 Principal Properties of Cemented Carbide

2.3.5.1 Mechanical Properties

(a) Hardness

This is one of the most important properties of cemented carbide. It is the one physical property that thought to be the most important when it comes to abrasion resistance. Hardness is determined by indenting a sample with a diamond penetrator per ASTM standard B-24. Hardness values for cemented carbide are usually expressed in terms of Rockwell "A" or Vickers values [Okamoto et al, 2003].
(b) Density

Density is determined according to the ASTM standard B311. Since cemented carbide is a composite material, and its constituent ingredients have varying individual densities, the density of cemented carbide varies with composition. Combining these materials in varies proportions creates variation in the density of the cemented carbides in line with their composition. A density of 14.5 g/cc is typical for a 10% cobalt binder material. This value is twice the density of 1040 carbon steel, which is an important consideration when weight is a factor in design [Okamoto et al, 2003].

(c) Transverse Rupture Strength

The mechanical strength of cemented carbide is usually determined by this method rather than a tensile test commonly used for steel. The reason for this is that brittle materials are extremely sensitive to misalignment of the tensile test apparatus and sensitive to any notch or surface defect, which would cause a stress concentration and lead to incorrect test results. The transverse rupture strength (TRS) is determined by placing a standard sample (per ASTM B-406, ISO 3327) between two supports and loading it until fracture occurs, as shown in the Figure 2-1. The value obtained is called transverse rupture strength or bending strength and is measured as the load that is needed to fracture the sample. This is shown as load per unit area. The TRS values increase with increasing the binder content and grain size [Okamoto et al, 2003].
The following equation can be used to determine rupture strength:

$$\text{MOR} = \frac{3WL}{2bd^2}$$  \hspace{1cm} (2.1)

Where,

- \( \text{MOR} \) is the modulus of rupture (or rupture strength), MPa
- \( W \) is the fracture load, N.
- \( L \) is the distance between the two supports, mm
- \( b \) is the breadth of specimen, mm
- \( D \) is the thickness of specimen, mm

On the other hand, Table 2.3 indicates the main grades of carbides, composition, principal properties and applications.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Equivalent grade</th>
<th>ISO grade</th>
<th>WC%</th>
<th>Co%</th>
<th>TiC%</th>
<th>TaC%</th>
<th>Other%</th>
<th>Density g/cm$^3$</th>
<th>TRS Mps Min</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU15UF</td>
<td>YG8X</td>
<td></td>
<td>90.5</td>
<td>8</td>
<td></td>
<td>1.5</td>
<td></td>
<td>14.6</td>
<td>3500</td>
<td>For fiberglass reinforced plastics, titanium alloys, hardened steel.</td>
</tr>
<tr>
<td>GF25UF</td>
<td>YG12X</td>
<td></td>
<td>86</td>
<td>12</td>
<td>1.2</td>
<td>0.8</td>
<td></td>
<td>14.1</td>
<td>4000</td>
<td>For grey cast iron &amp; heat resistant alloys.</td>
</tr>
<tr>
<td>GU10</td>
<td>YG6X</td>
<td>K01</td>
<td>94</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>14.85</td>
<td>2700</td>
<td>For non-ferrous precision cutting and wood cutting.</td>
</tr>
<tr>
<td>Code</td>
<td>Type</td>
<td>K</td>
<td>H</td>
<td>T</td>
<td>Rpm</td>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
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<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GU20</td>
<td>YG10X</td>
<td>K20</td>
<td>90</td>
<td>10</td>
<td>14.45</td>
<td>3400 For endmill and drill.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GU30</td>
<td>YG13X</td>
<td>K20</td>
<td>86.5</td>
<td>13.5</td>
<td>14</td>
<td>3500 Excellent wear resistance and toughness, for wood cutting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK02</td>
<td>YG4</td>
<td>K20</td>
<td>96</td>
<td>4</td>
<td>15.15</td>
<td>2300 For hard grey cast iron precision cutting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK05</td>
<td>YG6A</td>
<td>K10</td>
<td>94</td>
<td>6</td>
<td>14.95</td>
<td>2450 For drawing dies and wood cutting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK10</td>
<td>YG6X</td>
<td>K10</td>
<td>94</td>
<td>6</td>
<td>14.95</td>
<td>2500 For general purpose of non-ferrous applications.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK20</td>
<td>YG6</td>
<td>K20</td>
<td>94</td>
<td>6</td>
<td>14.95</td>
<td>2600 For non-ferrous rough cutting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK30</td>
<td>YG8</td>
<td>K30</td>
<td>92</td>
<td>8</td>
<td>14.7</td>
<td>2700 For drawing dies.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GK40</td>
<td>YG9</td>
<td>K40</td>
<td>91</td>
<td>9</td>
<td>14.6</td>
<td>2800 For soft grey cast iron cutting.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF20</td>
<td>YG6</td>
<td></td>
<td>94</td>
<td>6</td>
<td>14.95</td>
<td>2600 High anti-abrasion for mining inserts.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF25</td>
<td>YG8</td>
<td></td>
<td>92</td>
<td>8</td>
<td>14.7</td>
<td>2750 High anti-abrasion and good toughness, for percussion bits.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF25D</td>
<td>YG8</td>
<td></td>
<td>92</td>
<td>8</td>
<td>14.7</td>
<td>2800 For mining and construction inserts.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF35</td>
<td>YG11</td>
<td>K40</td>
<td>89</td>
<td>11</td>
<td>14.45</td>
<td>2900 For wear parts and mining tools.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF40</td>
<td>YG12</td>
<td>K40</td>
<td>88</td>
<td>12</td>
<td>14.4</td>
<td>3000 For heavy roughing non-ferrous.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF45</td>
<td>YG13</td>
<td>K40</td>
<td>87</td>
<td>13</td>
<td>14.2</td>
<td>3100 For wear and light shock resistance.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF55</td>
<td>YG18C</td>
<td></td>
<td>82</td>
<td>18</td>
<td>13.85</td>
<td>3000 For impact resistance forging dies &amp; roll.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF60</td>
<td>YG20C</td>
<td></td>
<td>80</td>
<td>20</td>
<td>13.65</td>
<td>2900 For operations of rolling, drawing, hot pressing and cold moulding.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF65</td>
<td>YG22C</td>
<td></td>
<td>78</td>
<td>22</td>
<td>13.4</td>
<td>2700 For stainless bolt header dies and roll.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF70</td>
<td>YG25</td>
<td></td>
<td>75.5</td>
<td>24.5</td>
<td>13.18</td>
<td>2500 For nut forming dies.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF70A</td>
<td>YG25C</td>
<td></td>
<td>75</td>
<td>25</td>
<td>13.15</td>
<td>2400 For high impact resistance forging dies.</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GD10</td>
<td>YG6C</td>
<td></td>
<td>94</td>
<td>6</td>
<td>14.95</td>
<td>2500 For percussion bits and inserts for hard rock or coal mining.</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GD20</td>
<td>YG8C</td>
<td></td>
<td>92</td>
<td>8</td>
<td>14.7</td>
<td>2700 For percussion bits and mining inserts.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GD25</td>
<td>YG10C</td>
<td></td>
<td>90</td>
<td>10</td>
<td>14.5</td>
<td>2850 For oil bits and mining inserts.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GD40</td>
<td>YG13C</td>
<td></td>
<td>87</td>
<td>13</td>
<td>14.2</td>
<td>3200 Good toughness, for oil bits.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>GD50</td>
<td>YG15C</td>
<td></td>
<td>85</td>
<td>15</td>
<td>14</td>
<td>3100 Good wear&amp; impact resistance, for forming die and oil bits.</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GT20</td>
<td>P20</td>
<td></td>
<td>72</td>
<td>8</td>
<td>8</td>
<td>12.55 1900 Good general purpose for turning and finishing of ferrous metal.</td>
<td></td>
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<tr>
<td>GT30</td>
<td>P20</td>
<td></td>
<td>75.8</td>
<td>6</td>
<td>8</td>
<td>12.9   2100 Excellent general purpose for rough machining of ferrous metal.</td>
<td></td>
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<tr>
<td>GT40</td>
<td>P40</td>
<td></td>
<td>80</td>
<td>5</td>
<td>5</td>
<td>13.1   2200 Good impact resistance, for rough cutting of ferrous metal.</td>
<td></td>
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</tr>
</tbody>
</table>
2.3.5.2 Corrosion Properties

Tungsten carbide particles themselves are resistant to most corrosive media. It is the binder material that is susceptible to leaching in the presence of a strong acid or alkali solution. The binder material will leach from the surface of cemented carbide, leaving a skeletal structure which is unsupported. The carbide particles will then abrade away quite readily, exposing new surface area to be attacked. When binder content is low, the carbide skeleton is denser. Low binder grades show a slightly higher combined wear and corrosion resistance than those grades with higher binder content [Warren et al, 1996].

Straight WC-Co grades are corrosion resistant at neutral pH, (7). This is also true for WC-Co grades that contain additives like titanium carbide (TiC), tantalum carbide (TaC) or niobium carbide (NbC). Certain alloyed titanium carbide/nickel binder based grades possess the highest corrosion resistance down to about pH1. When compared to straight WC-Co grades these grades are brittle and have inferior thermal conductivity. They also hard to grinds and braze, and are only used in specific applications where corrosion and wear resistance are a must and mechanical strength and thermal shock resistance are not as important. When corrosion/wear is a prime design requirement, specially alloyed WC-Ni grades are the best choice. They are resistant down to pH2-3. In certain solutions, where pH value is less than 2, they have proven to be resistant to corrosion. Because they have WC as the hard principle, and nickel and cobalt are similar metals in most respects, their mechanical and thermal properties are similar to those of straight WC-Co grades [Warren et al, 1996].

The pH factor is one of the most important parameters when determining how corrosive a medium will be. Other major influencing factors include temperature and the electric conductivity of the medium. The latter is dependent on the ion concentration, i.e. the amount of dissolved salts in the solution. Therefore, it is hard to simply determine how corrosive a certain medium will be. No general rules apply to all situations, however, it is generally accepted that WC-Co cemented carbides should not be exposed to pH7 or below leaching will occur. For practical grades, it is recommended that tests be conducted with intended medium [Warren et al, 1996].
2.3.5.3 Oxidation of cemented tungsten carbides in air

The oxidation behavior of WC-Co alloys in air has been studied by many investigators [Oakes, 1987; Gummitiskii et al, 1989; Larikov et al, 1990; Reid et al, 1991; Bhaumik et al, 1992; Lofaj et al, 1995; Basu et al, 1996]. It was found that the reactions for these alloys are most likely described by

\[ \text{WC} + 2.5\text{O}_2 \rightarrow \text{WO}_3 + \text{CO}_2 \text{ and } \text{Co} + 0.5\text{O}_2 \rightarrow \text{CoO} \]

and result in gaseous products, namely CO\(_2\) and WO\(_3\), which evaporates at temperatures above 800\(^\circ\)C. Gummitiskii et al [1989] investigated the oxidation kinetics of WC-8Co alloy in air at temperatures from 700\(^\circ\) to 1050\(^\circ\)C. They reported that the oxidation rate at 700\(^\circ\)C was insignificant but became high in the temperature range 900\(^\circ\) to 1000\(^\circ\)C. The oxide layer at the surface of the specimens consisted mainly of WO\(_3\) and CoO. Traces of other tungsten oxides such as WO\(_2\) and W\(_{18}\)O\(_{49}\) were also found below the surface. Larikov et al [1990] investigated the oxidation kinetics of WC-Co alloys of different compositions and porosity in the temperature range from 700\(^\circ\) to 1000\(^\circ\)C in air. They found that the increase in weight for these alloys obeyed a parabolic law. The rate constant at 780\(^\circ\)C for the alloy WC-6Co with 15% porosity was 760g\(^2\)m\(^{-4}\)s\(^{-1}\). An increase in Co content from 4% to 8% was reported to cause a significant decrease in the oxidation rate. The oxide layer was identified as WO\(_3\) on the surface and a mixture of WO\(_3\) and WO\(_2\) below the surface. Lofaj and Kaganovskii [1995] investigated the oxidation kinetics of WC-Co alloys with a 3- to 5-\(\mu\)m grain size and 6%-15% Co content, heated in air over a temperature range from 650\(^\circ\) to 800\(^\circ\)C. The rate of weight gain also followed a parabolic law in this work. In contrast to the findings of Larikov et al [1990] mentioned above, the oxidation rate increased with a decrease in grain size and an increase in cobalt content. The oxidation layer consisted mainly of WO\(_3\) and small amounts of Co, CoO, and WC. An increase in the oxidation rate with a decrease in grain size a decrease in cobalt content was reported by Reid et al [1991] when a WC-6Co alloy was heated in air at 650\(^\circ\)C. Basue and Sarin [1996] investigated the oxidation behavior of WC-Co alloys as a function of cobalt content, temperature, and the flow rate and oxygen concentration of the oxidizing atmosphere. It was reported that the oxidation rate of WC-Co increased rapidly at temperatures above 600\(^\circ\)C and with the oxygen concentration of the atmosphere. An increase in the cobalt content of the alloy led to a decrease in the oxidation rate. The only oxides identified in the scale were WO\(_3\) and CoWO\(_4\).
2.4 Heterogeneous Reactions

Reaction mechanisms are classified as first and second order for most reactions, and third, zero, or fractional order for few reactions. The ordinal number indicates the number of chemical species whose concentrations determine the velocity of the reaction. For fractional order reactions (e.g. 1.5), these probably being compromise values where two mechanisms are operating simultaneously. Sometimes the order of reaction changes as the concentration changes [Gilchrist et al, 1980]. In the case of heterogeneous reactions of current interest, Hilling [1986] emphasized that except in a purely formalistic sense it is hard to see how the concept of order can have much meaning. Large groups of heterogeneous reactions are controlled by diffusion processes which cannot be expressed through a constant order of reaction and indeed, the order of reaction varies throughout the reaction in this respect. So the concentration and order of reaction generally have no significance.

2.4.1 Factors Affecting the Rate of Reaction

The rate of reaction is a function of the system. In homogeneous one phase systems the rate of reaction is a function of temperature, pressure, and composition. In heterogeneous systems (more than one phase with distinct phase boundaries), the rate of reaction at a given time depends basically on three factors, namely the nature of the system, the time of reaction and the temperature. Rate is measured using a suitable parameter which changes with reaction (e.g., total weight of a reactant or product). Uncertainties in kinetic studies can arise of poor and incomplete characterization of the nature of the system.

Factors which lead to complications for real systems involving solid-gas reactions, for example may be summarized as follows [Dixon, 1972].

(a) Presence of impurities in the solid and the gas composition
(b) Attempts at interpreting packed bed reaction using experimental data on single particles of fixed geometry (sphere, cube, etc.)
(c) Multiparticle nature of systems with or without uniform particle size and shape
(d) Reagent starvation and heat transfer problems
(e) Variations in pore structure of solid during reaction
(f) Non isothermal conditions etc...
2.4.2 Activation energy

In 1889, Arrhenius suggested that before a reaction can occur there must be some minimum kinetic energy possessed jointly by two colliding molecules. The minimum quantity of energy that must be available for a collision to lead to reaction is called the activation energy and denoted E. If two molecules collide with less than this critical amount of energy, they will recoil without undergoing chemical change. The activation energy is necessary to rupture bonds between atoms, in a molecule, or between an ion and its salvation shell if the reacting species are in solution. The reason why the rate of chemical reactions are so strongly temperature dependent becomes clear once we recognize the need for a minimum kinetic energy for colliding molecules. As the temperature is increased, the average kinetic energy increases and a greater fraction of molecules have higher kinetic energies [Segal et al, 1985]. The quantity E has the dimensions of energy per mole and is the heat of formation of one mole of the activated molecule. The activation energies of reactions which occur explosively are very low so that the molecules are rather easily brought to a condition in which almost all of them are sufficiently energized for reaction simultaneously. Some reactions are rather easily energized by radiation of a particular frequency which may be in the visible range or near it. Some reactions can be accelerated or even made possible by the use of a catalyst which is a reagent necessary to produce an activated complex of low energy of formation that will enable the reaction to produce at a reasonable rate [Gilchrist et al, 1980].

2.4.3 Dependence of rate of reaction on temperature

Reaction rates increase with temperature. Arrhenius gave the following empirical relationship:

\[ K = A \exp \left( \frac{-E}{RT} \right) \]  \hspace{1cm} (2.2)

Rate constant according to Arrhenius is expressed by a frequency factor, describing the frequency of trials to reach the activation energy barrier, and the exponential term \( \exp \left( \frac{-E}{RT} \right) \) expressing the probability of successful trials.

\[ \ln K = \ln A - \frac{E}{RT} \] \hspace{1cm} (2.3)

Where the parameters E and A are assumed independent of temperature.

E = activation energy J/mol
K = reaction rate constant
R = universal gas constant J/mol.K
T = absolute temperature K
A= frequency factor, it is constant or nearly so.

A is sometimes written as the product ZP where Z is the collision number and P the shape factor for the reaction. P is nearly unity and seldom less than 0.1 for simple molecules but can be very small \( 10^{-10} \) when complex organic molecules are involved [Gilchrist et al, 1980].

From equation (3.3), it is clear that a plot of \( \ln K \) versus 1/T will be linear, with slope \(-E/R\)

Another celebrated theory dealing with reaction rate dependence on temperature is the transition state (the activated complex theory) [Segal et al, 1985].

Consider the hypothetical reaction:

\[ A-B + C = A + B-C \]

Before the reactants A-B and C are converted into the products A and B-C, there is a specific geometric configuration of all three atoms, called the activated complex, which may be denoted A…B…C…, which must be formed before reaction can occur. The state of the system when the activated complex has been formed is called the activated state or the transition state, as it represents unstable combination of all atoms involved in the reaction. Its potential energy pathway results in reaction. If we are dealing with exothermic reaction, the energy of reactants is higher than that of the products. But before the products can be formed the system must acquire additional energy, it must pass through the activated state, Fig (2.2).

The energy that the reactants must acquire to reach the activated state is the activation energy of the forward reaction, denoted \( E_{af} \). For the backward reaction to take place the same activated state must be attained. The activation energy of the backward reaction \( E_{ab} \), is therefore larger than that of the forward one, for exothermic reaction.

\[ \Delta G = E_{af} - E_{ab} \] \hspace{1cm} (2.4)

Note that \( \Delta H \) is negative, as it must be for an exothermic reaction.

For an endothermic reaction, the reactants are at a lower potential energy than the products and they must acquire sufficient energy to reach the activated state before the products can be formed. A reaction with large activation energy is to have a high potential barrier. Such reactions will have slower rates of reaction than others with lower potential energy barriers in which the activation energy is small.
Fig (2.2) Potential energy profile for an exothermic reaction

2.4.4 Selection of A model

For the non-catalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the unreacted-core model and the progressive-conversion model:

2.4.4.1 Unreacted – Core Model [Levenspiel, 1962; Ray, 1993]

According to the unreacted-core model five steps are occurring in succession during the reaction.
1- Diffusion of the gaseous reactant (A) through the film surrounding the solid.
2- Penetration and diffusion of (A) through the blanket of ash to the surface of unreacted core.