PROPERTIES OF HARD ALLOYS SINTERED FROM METALLIC CARBIDES

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Abstract: The TiC or TaC alloys, the simple WC-Co alloys with the same cobalt content are much more resistant to bending and breaking and feature improved electrical and heat conductivity. The oxidation resistance of the simple WC-Co alloys is considerably lower which results in a pregnant tendency for chip welding and low resistance. Hardness is affected by micro-porosity, granulation of WC phase, purity and composition, extent of homogenization of the liquid and carbons. The magnetic saturation increases with higher Co contents; it is worth mentioning that bigger grain alloys have a force considerably lower than that of fine grain ones.

Key words: heat conductivity, hardness, density, porosity, hard alloys

1. Introduction

The excessively high sintering temperature results in a lower density which further negatively affects the mechanical strength. Due to overheating and granulation growth by recrystallization an acute decrease in the bending ultimate strength occurs.

Under or de-carburated materials also containing fragile phases η, feature poor ultimate strength. The max values taken by the bending ultimate strength are reached at Co 20 - 25 % and suddenly decrease with high Co contents. At theses compositions there are no contact bonds among the carbons, the carbon crystals being individual and surrounded by the Co metallic mass.

The alloys mainly used for short chip material cutting (cast iron, porcelain, etc) are alloys of WC-Co type, in some cases with small additions of other carbons. The same compositions but of different granulometric classes are also used for pieces exposed to wear (wire drawing, moulds, etc).

The higher performance of the WC-Co alloys in short chip machining applications is accounted for by its very good heat conductivity which is 2-3 times higher than that of fast steels.

The alloys WC-Co, WC-TiC-Co, are mainly used for short chip material cutting and wear -resistant piece applications [1]. The hard- alloys producers can resort to a wide range of possibilities to achieve variation of the properties of a WC-Co composition and thus they can adapt their products to the particular types of tools they may choose to manufacture [2].

The present metallography technique allows for a correct identification and evaluation of hard sintered carbons structures. The metallography approach is an indispensable method of investigation and control in industry.

2. Researches and experimental results

The experimental tests have shown certain features previously identified as requirements for a good quality deposit layer, which are: high compression strength, good impact resistance, good resistance to high temperatures and thermal shock, fine surface roughness, pure layer structure combined with equal grain size, deposition of materials with continuous change of composition, regarding the increase of deposit layer (sandwich layers), deposition of materials impossible to obtain through other procedures, almost unlimited opportunity to choose deposition materials, good adherence between basis material and deposit layers.

The reaction will be possible thermodynamically if the calculated concentrations (partial pressures) of the reactants, under equilibrium conditions, are less than their original concentrations.

The calculation of the equilibrium concentrations from the equilibrium constant involves a good choice of the number of gas spaces.
which can be higher than two and the number of independent relations. A relation implies the equilibrium expression depending on the free standard reaction energy and temperature. The other relation consists in that the system pressure is the sum of the partial pressures. If some reactants possess more than one valence state, the reaction should contain the reactant under its most stable valence state.

After making all the calculations the entire range of deposition parameters (temperature, pressure, gas initial composition) is obtained.

The phases coming from the vapor which contain the diffusion element and the carrying gas pass through three main stages; vapor formation, transportation and deposition. These stages differ in terms of chronology and make up a whole process. According to its essence, such a process is a chemical transport reaction expressed by the solid substance interaction \( A \) with the gas or vapors \( B \).

Upon conveying the gas, two processes are possible: isotherm, without forced flow; anisotherm, with forced flow. With the latter process, saturation with gas diffusion by contact-free procedure is reported.

In the case of two alloys having the same cobalt content but different WC granulations, it is found that a harder alloys involved finer granulations while milder alloys implies rough granulations.

The cobalt, which takes the form of very fine inclusions with alloys 5% Co and 95% WC, is much more agglomerated between the WC crystals along with a slight porosity.

In figure 1 and 2, is illustrated structurally free carbon metallographic appearance in two situations compared with the standard scale.

Thus one can see that it always appears at grain boundaries of carbide WC-Co and that depending on the carbon surplus in the balance of the alloy material, the amount of free carbon as a separate independent phase may be higher or lower.

Macro aspect of the fracture allows accurate observation of the sintered alloy grain size, its color and luster, the presence or absence of free carbon and creating an impression that the exact properties to be expected. Currently simple macrostructure in fracture assessment allows a faster control routine in the production of sintered carbide parts.

An accurate assessment of the microstructure of the sintered alloy requires an appropriate metallographic attack. Preparation of samples for metallographic study is relatively difficult due to the hardness of the material.
Figure 3 illustrates the metallographic structure of the alloy containing 6% Co and 94% WC and average granulation. The basic constituent, WC, is under recrystallization form, called $\alpha_2$, which structurally stable crystals under triangle prismatic shapes of rectangular bases.

As to hardness, there is a tight correlation between the Co content and the WC-Co alloys produced under identical conditions. As shown in figure 4, hardness decreases with the increase in the cobalt content. The sintering temperature and the exposure time along with the type of grinding and mixture homogenizing can decisively affect the sintered metallic carbons alloys [3,4].

![Figure 3: The metallographic aspect of the alloy containing 6% Co and 94% WC, sol. KOH-K$_3$(Fe(CN)$_6$)](image)

Hardness reaches max values with the optimum sintering temperature and then it decreases as a result of carbon recrystallization and alloy super-sintering. An excessive sintering time, even if the temperature is optimum, has the same effect i.e lower hardness. The WC-Co alloy density depends on the Co content and the extent of sintering.

Figure 5 shows the density variation depending on Co content in the alloy; it implies that the real measured density takes values within 0, 5 - 3%, under the theoretical calculated values. This may be accounted for by the residual porosity which is the result of a normal sintering process because of insufficient mixture homogenizing or slight low- or high carburing which may occur with sintering [5,6].

![Figure 5: Alloy density vs Co content](image)

As to the density variation, the specific pressure for pressing the compressed pieces has a lower influence while the sintering conditions, such as the sintering temperature and its being kept at lower values, play a decisive role in determining density (figure 6). Modern methods such as hot pressing or hot iso-static pressing, allow for reaching densities identical to the calculated ones [7].

The breaking/bending strength of the WC-Co alloys increases with the cobalt content but the relation is not lineal [10]. The increase in the breaking/bending strength takes place also in the alloys having more than 20% Co provided these are sintered under special conditions (protected against carburing). With alloys of 10% Co no permanent deformations of the material can be
noticed during the breaking strength test, while they are quite obvious with Co contents higher than 20%.

The compression resistance of the WC-Co alloys, as shown in figure 4 increases with the Co content and then significantly decreases after 4% limit is exceeded [8,9].

The resilience or impact resistance of the metallic sintered carbon alloy is a measure of the mechanical chock resistance. Chock resistance variation vs. temperature is illustrated in figure 7.

The values of this curve have been determined on groove-free samples, 6 x 6 mm cross section, leaning against seats 40 mm distance apart. The curve shape reaches a peak at the optimum alloy – sintering temperature [11]. The elongation strength is quite difficult to determine for such a fragile material like the hard sintered carbon alloy. All the composition WC-Co containing up to 10% Co show no permanent deformation of the material.

It can however be noticed elastic deformations, without plastic deformations, immediately after breaking alloys containing more than 25% can feature a measurable elongation [12,13].

As regards the magnetic properties of the WC-Co alloys, magnetization upon saturation is related to the Co content (the phase $\eta$ - double Co and W carbon) and the force acting upon it strongly depends on sintering extent and the grain size. Thus the magnetic measurements can be of use in quality control [14].

The scope of application of WC-Co alloys is a consequence of their properties. The applications of the metallic alloys depends on their composition according to which there are 4 groups as shown below:

Group I- 97% WC, 3% Co and 95.5% WC – 4.5% Co has the following scope of application: cutting of graphite, ceramics and other metallic...
materials, grinding, accuracy drilling of cast iron, non ferrous material machining, drawing machines.

Group II- 94,5% WC – 5,5% Co and 93,5% WC – 6,5% Co is used for:

a) global granulation sorts (cast iron processing, non-ferrous materials and alloys, synthetic and plastic materials, sensors for wear resistance tools and pieces requiring no high tenacity, drawing machines.

b) fine granulation (machining of gray cast iron, mild cast iron, steels of ultimate strength higher than 1750 MPa, bronze, Si alloys, drawing machines.

Group III – 91% WC – 9% Co, 89% WC – 11% Co, 87% WC – 13% Co used for machining wood, synthetic resin, easy machining of steels, brass and bronze grinding, plates for agriculture tools, wear pieces calling for high tenacity.

Group IV – 85% WC – 15% Co, 80% WC – 20% Co, 75% WC – 25% Co, 70% WC – 30% Co used for: wear resistant parts calling for high tenacity (cutting tools etc.).

3. Conclusions

Hardness is affected by micro- porosity, granulation of WC phase, purity and composition, extent of homogenization of the liquid and carbons. The excessively high sintering temperature results in a lower density which further negatively affects the mechanical strength.

The max values taken by the bending ultimate strength are reached at Co 20 - 25 % and suddenly decrease with high Co contents. At theses compositions there are no contact bonds among the carbons, the carbon crystals being individual and surrounded by the Co metallic mass.

Due to over- heating and granulation growth by re-crystallization an acute decrease in the bending ultimate strength occurs. Under or de-carburated materials also containing fragile phases η, feature poor ultimate strength.

The compression resistance first increases with the Co content then considerably decreases after the Co 4% is exceeded.

The resilience of a Co 6% alloy increases with temperature and reaches a max value at 1600°C.

The elongation vs compression resistance ratio is estimated as 1: 3 while the elongation resistance vs ultimate strength ratio is three times higher that that of steel.

The magnetic saturation increases with higher Co contents; it is worth mentioning that bigger grain alloys have a force considerably lower than that of fine grain ones.

4. REFERENCES


[9] Constantinescu, S.,Orac L.,Wear resistance of chemical vapour deposition coatings, 4th International Conference Welding in Maritime Engineering , BRAC - SPLIT-Croatia 13 -16. 05. 2009, brancko.bauer@fsb.hr


