Thermochimica Acta, 95 (1985) 383—388
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

A THERMOGRAVIMETRIC METHOD FOR THE STUDY OF DECOMPOSITION OF LUBRICANTS IN CEMENTED CARBIDE POWDER

Bengt O Haglund

Sandvik Hard Materials, P O Box 42056, S-126 12 STOCKHOLM, Sweden

BACKGROUND

Cemented carbide is a composite material that consists of hard particles of tungsten carbide, titanium carbide and similar carbides embedded in a ductile matrix of cobalt. Such alloys are manufactured by powder metallurgical methods in which the carbide powder is milled together with cobalt. This mixture is then pressed in dies to shape and sintered to full density at high temperature.

To facilitate the pressing and increase the strength of the compacted blank a lubricant is added to the powder before the pressing. This lubricant is decomposed and evaporated in the first step of the sintering cycle, the dewaxing process. The heating rate and furnace atmosphere must be chosen carefully to avoid damage to the blanks due to excessive gas formation and to diminish residues from the decomposition, mainly free carbon. This choice of conditions has up to now been based on trial and error, but it would obviously be much better if it could be based on calculations.

METHOD

The simpliest way to study the evaporation of the lubricant would obviously be to compact a solid piece of the powder and record the weight loss in a thermobalance under a certain gas atmosphere and temperature programme. There are, however, a number of conditions which may vary during such a test, e.g.

0040-6031/85/$03.30

- increasing diffusion distance from this core to the free surface

- uncontrolled temperature changes due to endothermic or exothermic decomposition reactions in the interior of the compact

- change in geometry of the remaining lubricant-containing core

All these factors make the evaluation of the kinetics of the decomposition very complex.

To avoid these problems a method similar to that used by Motzfeldt et al (1) for determination of vapour pressures above 10^{-2} bar has been used. This method allows the study of interdiffusion and viscous flow in capillaries which may simulate the porous outer part of a compact under dewaxing. As we use loose powder enclosed in a bulb the influence of diffusion of the reacting gases in the powder mass may be neglected, at least in the low temperature decomposition region. Furthermore the temperature is measured inside the powder bed and can be kept under control also at high decomposition rates.

The powder to be investigated is enclosed in a cell with a pocket for temperature determination in the bottom. The cell is made of Pyrex glass and after filling the inlet tube is rapidly heated and drawn into a long, narrow capillary. The cell is inserted in the thermobalance furnace, which is then evacuated to less than 0.1 mbar for at least 12 hours at room temperature (or even lower). The furnace and cell is then filled to atmospheric pressure with a suitable gas for simulating the dewaxing process. The gas may be inert or may participate in the decomposition reaction. The measurements may be performed in two ways:

i - The furnace and cell is heated to and held at a constant temperature. The gas pressure is then lowered stepwise and the rate of weight loss is recorded at each step. A variant of this method is, if gases which participate in the decomposition are used, to lower the partial pressure of the active gases by diluting with an inert gas.

ii - The gas pressure inside the furnace and cell is kept constant and the temperature is increased stepwise.

Whatever method is used one will find that the rate of weight loss increases with increasing temperature and decreasing pressure, but not linearly. The curves often show different regions corresponding to different mechanisms of evaporation e.g. slow evaporation and boiling with a not too wide intermediate range. From the temperature dependence of these curves and from the dimensions of the capillary it is possible to determine the decomposition pressure of the lubricant in the powder.

THEORY

The theory behind the application of the method for vapour pressure determination was first treated by Wagner in 1943 (2). Wagner defined two parameters A and B and derived the following equation between the inert gas pressure P_f and the equilibrium vapour pressure P_2^o of the vapourizing substance:

$$\frac{P_f}{P_2^o} = 1 + \exp\left(-\frac{\dot{n}_2}{A}\right) - \frac{\dot{n}_2}{B} \qquad (1)$$

where $\dot{n}_2$ is the rate of weight loss from the substance. The parameter A depends on the dimensions r and l of the capillary and the interdiffusion coefficient D_{12}, the pressure P and the temperature T according to

$$A = \frac{\pi r^2 * D_{12} P}{l * R T} \qquad (2)$$

The parameter B is dependent on the heat transfer coefficient K from the furnace atmosphere to the substance in the cell, the molar enthalpy of vapourization of the substance ΔH_v and the temperature T according to

$$B = \frac{K\ R\ T^2}{\Delta H_v^{\ 2}} \qquad (3)$$

To estimate the heat transfer coefficient it is necessary to know the temperature difference ΔT between the powdery substance in the cell and the furnace atmosphere outside the cell. For this purpose the use of a DTA sample holder has been found suitable, where the reference thermocouple is used for measuring ΔT.

MEASUREMENTS AND RESULTS

Material: For testing of the method cemented carbide powder of grade CR60 was used, which contained 3 weight percent polyethylene glycol, with molecular weight 4000.

Measurements: The decomposition was made in hydrogen in a Mettler TA 1 Thermoanalyzer. The specimen was heated in 10°C steps from approximately 80°C to 230°C. The heating rate between steps was 4°C/min. The dwell time at each temperature level was one hour to ensure quasistatic conditions. The rate of mass loss was calculated from the thermogravimetric curve for each isothermal period.

Results: In Figure 1 the values of rate of mass loss are recorded versus the reciprocal absolute temperature (Arrhenius plot). The ordinate values are corrected for the capillary dimensions, furnace temperature and pressure according to equation 2. As the interdiffusion constant D_{12} is unknown the ordinate values also contain an arbitrary constant k.

The differential thermocouple indicates a temperature difference of +1.2°C between the outer atmosphere and the central part of the powder (extrapolated to zero mass loss rate).

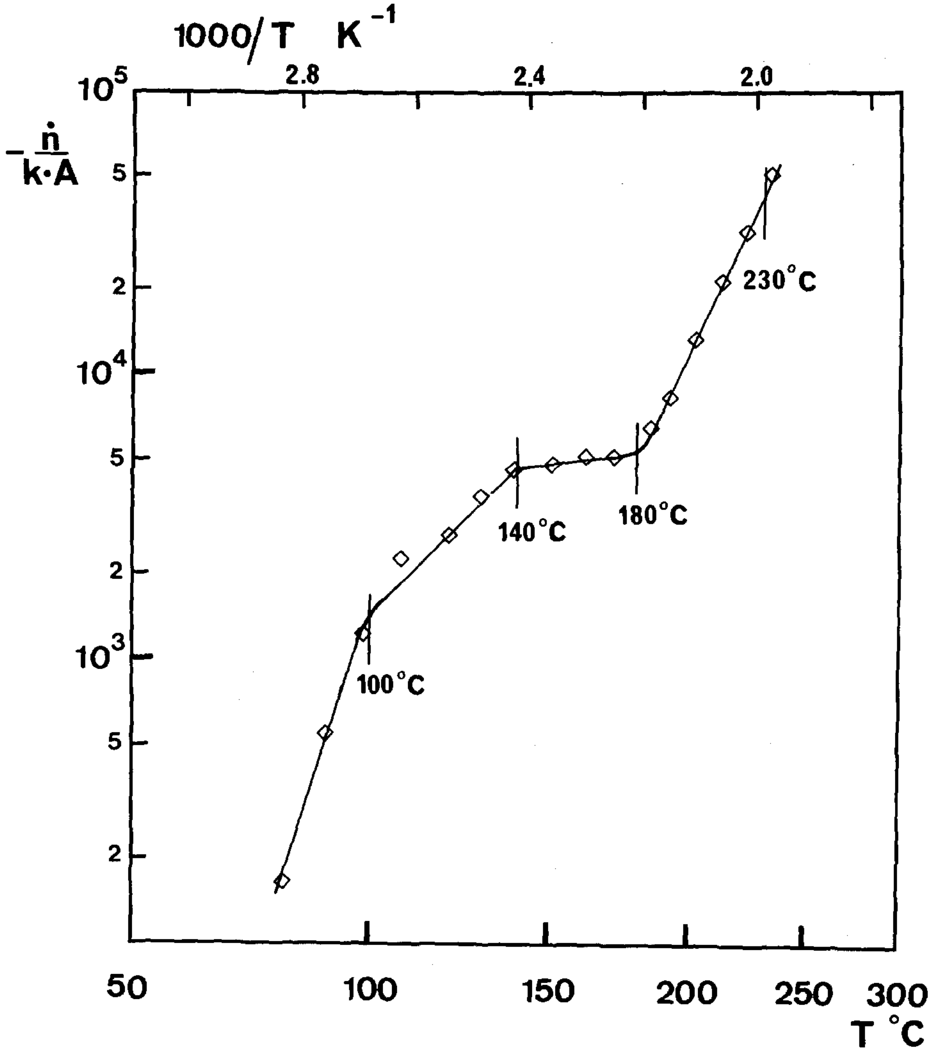

Figure 1. Rate of mass loss of lubricant in cemented carbide powder of grade CR60 versus the reciprocal absolute temperature

It is obvious that the evaporation of this kind of lubricant proceeds according to at least four different process in the temperature range investigated:

80-100°C:	Rapid mass loss, presumably by loss of physically bound water.
100-140°C:	Moderate loss of decomposition products of the lubricant.
140-180°C:	Low rate of mass loss.
180-230°C:	Rapidly accelerated rate of mass loss, presumably with the aid of reaction between hydrogen and polyethylene glycol.

ACKNOWLEDGEMENT

The author is grateful to AB Sandvik Hard Materials for the permission to publish this paper. He is also indebted to Prof. K Motzfeldt for valuable advice, to Dr C Chatfield for helpful criticism and to Mr A Möllare and Mr K-E Thorgren for making the ampoules.

REFERENCES

1. K. Motzfeldt, H. Kvande and P.G. Wahlbeck, Acta Chem.Scand. A31 (1977) p.444-452.

2. C. Wagner, Z. Phys. Chem. 192(1943) p 85-100.