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APPLICATION OF THERMAL ANALYSIS TO MATERIAL SCIENCE
Case-study on hardmetals

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Abstract

Thermoanalytical methods are used for investigation of outgassing and sintering of hardmetals. Shrinkage (DILA), mass loss (TG), gas evolution (EGA - mass spectrometry) and thermal effects (DSC) allow to describe sintering processes. The results may be applied for a better understanding of technological procedures, e.g. for improvements of temperature-time-atmosphere cycles in the production scale.

Keywords: gas evolution, hardmetals, mass loss, outgassing, shrinkage, sintering, TA modelling, thermal effects, up-scaling

Introduction

In this paper topical results of the application of thermoanalytical methods for the investigation of outgassing and sintering of hardmetals are demonstrated. For a better understanding information on hardmetals is presented first. The modelling of technological processes such as sintering requires TA methods which can be used at high temperatures (most of the apparatus at the IKTS can reach 2000°C, a temperature far above that of the usual working conditions of most of the other TA labs).

At the IKTS, research work on hardmetals by means of TA methods is focussed on four special topics (Fig. 1):

- Technological questions (solid-state sintering – liquid-phase sintering, effect of impurities, role of the carbon balance)
- Materials development (effect of doping elements, development of fine-grained hardmetals)
- Theoretical aspects (basic mechanisms)
- Data bases (thermophysical properties).

A few characteristic results are summarized in this paper. More detailed discussions are given in Refs [1–4].

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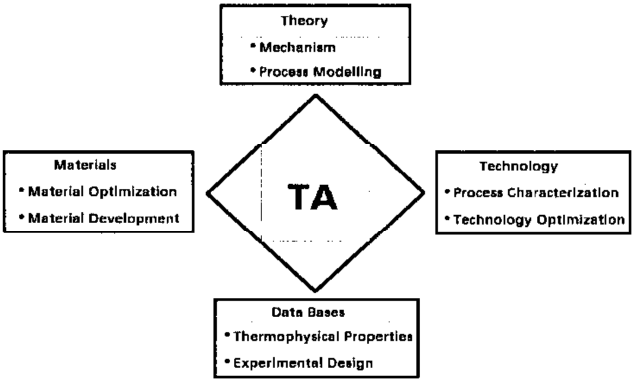


Fig. 1 Materials characterization by TA methods

Hardmetals – an old and new material

Hardmetals have been used for a long time. The first hardmetals were introduced on the market in 1924 by Krupp-Widia. Since then, the materials and the technology have been continually improving. Nowadays much effort is still being put into improving this old and new material.

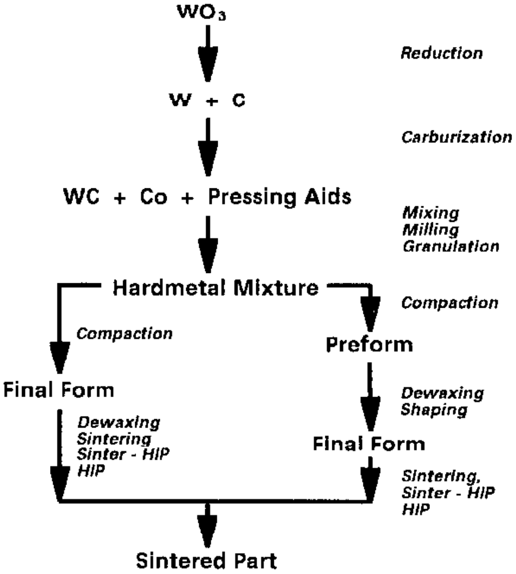


Fig. 2 Scheme of production cycle of WC-Co hardmetals

Hardmetals are used
- for cutting, milling, and drilling;
- as wear parts; and
- for many other applications.

Hardmetals are powder metallurgical parts, meaning that the production route (Fig. 2) begins with powder which is compacted by pressing. The pressed sample with a porosity of 40 to 50 vol% must be densified by sintering to full density with zero porosity. Normally organic pressing aids like paraffin or others are used in order to improve the compaction. These organic compounds must be burned out before closing the pores during sintering.

The simpliest type of hardmetals consist of
- WC as the hard material and
- Co as the ductile binder.

The phase diagram (Fig. 3) shows that during heating the powder mixture there is a solution of W and C in the Co phase. At about 1300°C a eutectic is formed. In the literature the sintering of hardmetals is described as being a prototype for liquid-phase sintering. However, we often find effects during sintering which are far away from the equilibrium states shown in the phase diagrams. There is a considerable interplay between thermodynamics and kinetics.

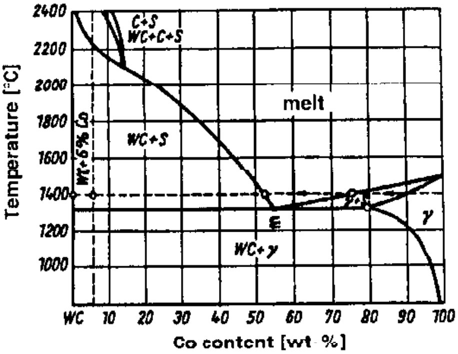


Fig. 3 Phase diagram of WC-Co [5]

Modern developments in hardmetal research tend towards
- new materials,
- new technologies,
- improved properties, and
- reduced costs.

What can be done with TA in the field of hardmetal research? In Fig. 4 the basic information found from the application of dilatometry DILA (length change), thermogravimetry TG (mass change), differential scanning calorimetry DSC (thermal

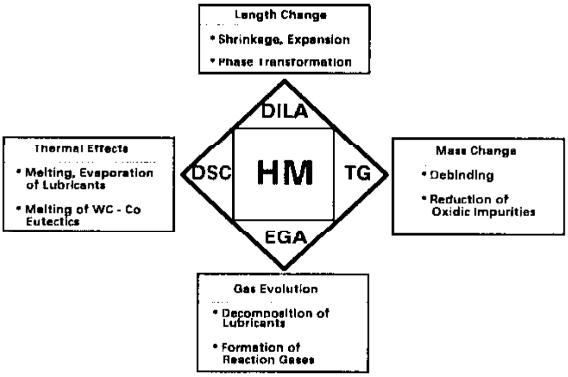


Fig. 4 Thermal analysis of hardmetals

effects), and evolved gas analysis EGA (gas evolution) is shown for the investigation of outgassing and sintering of hardmetals.

Thermal behaviour of hardmetals

Technological approach

First we look for shrinkage and liquid phase formation (Fig. 5). The material is a normal-grained WC-Co hardmetal with 10 wt% Co and WC with a mean grain size of 1.3 μm (WC DS130 from H. C. Starck/Germany). All investigations were carried out under argon with a heating rate of 10 K min^{-1}.

The black curve is the DSC curve. It shows the formation of the liquid phase – an exothermic effect – at about 1350°C. If we look for the grey curve – the shrinkage

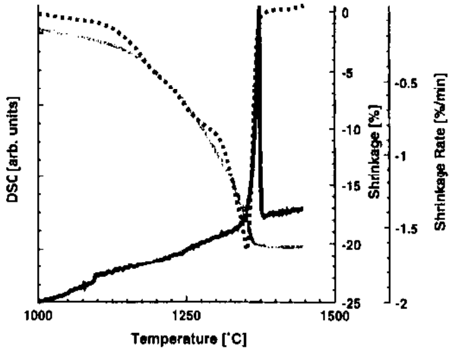


Fig. 5 Shinkage and liquid phase formation for a normal grained hardmetal WC-10 wt% Co (DS 130)

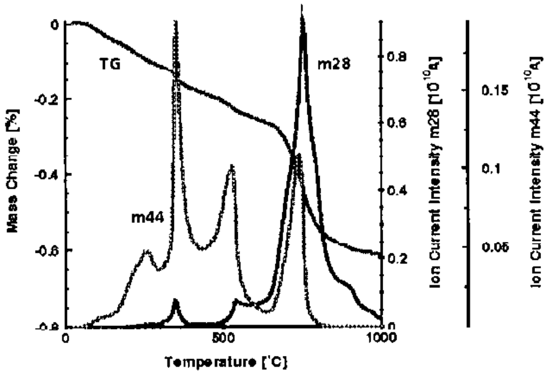


Fig. 6 Mass loss and evolution of CO and CO_2 for a normal grained hardmetal WC-10 wt% Co (DS 130)

curve – we see that the greater part of the shrinkage takes place in the solid state before melting of the eutectic. The shrinkage rate curve (dotted curve) shows a close relation to the DSC curve (caused by corresponding mechanisms).

Let us look for the outgassing behaviour at lower temperatures (Fig. 6). The TG curve shows the mass loss during heating of the pressed sample to 1000°C. For a better interpretation of the effects this sample was pressed without any organics. We find several steps in the mass loss curve which can be correlated with mass spectrometric curves of the evolved gas analysis. The evolution of CO and CO_2 is shown in

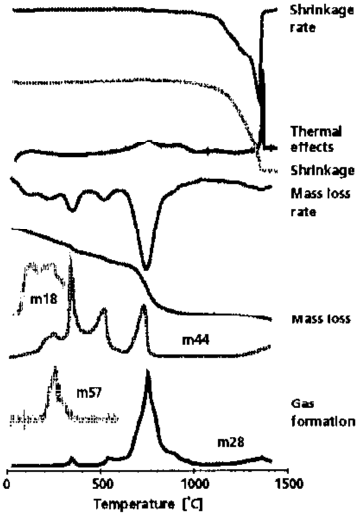


Fig. 7 Outgassing and sintering of a normal grained hardmetal WC-10 wt% Co (DS 130)

the curves of ion current intensities for mass numbers m28 and m44. The effects at about 350 and 520°C result from the reduction of oxidic impurities of the cobalt powder by the carbon in the mixture. In the same way the larger effect at about 750°C results from the reduction of the oxygen content of the hard material WC. Most of the oxygen comes from the technological pre-treatment of the mixture, especially from milling of the components.

For technical purposes it is important to realize that the carbon balance is responsible for the quality of properties in the final hardmetal. Technologists have to take care to minimize disturbances of the carbon balance in the production cycle.

Figure 7 shows an overview of the results of a complex thermal analysis of this material. For comparison the ordinate is given in arbitrary units.

Shrinkage, thermal effects, mass loss and gas formation show characteristic effects which may be better understood by synergetic interpretation of all curves.

Materials development

Fine-grained hardmetals are produced by doping the mixture with additional carbides such as vanadium carbide (VC) or chromium carbide (Cr_3C_2), which prevent grain growth during sintering. Figure 8 shows the influence of doping on the liquid phase formation. Small contents of less than 1 wt% change the eutectic temperatures and the widths of the temperature range of liquid phase formation.

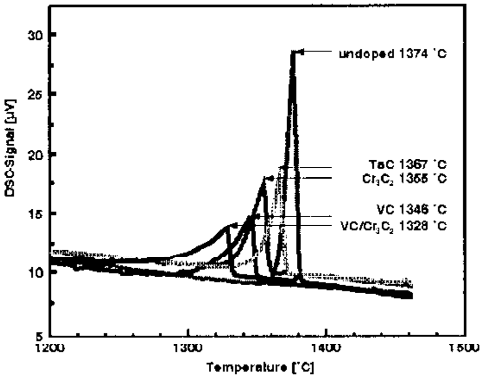


Fig. 8 Influence of doping on liquid phase formation of fine-grained hardmetals WC-10 wt% Co (DS 60 base)

The correlation of these results with the corresponding influence on shrinkage and shrinkage rate – which cannot be discussed here – gives very important information about the efficiency of the doping procedure.

Basic mechanisms

For some reasons, especially for modelling of sintering, one must know the temperature at which sintering begins.

At first we look at the shrinkage experiment. Enlarging the scale and correcting for the thermal expansion, the shrinkage curve shows a relatively sharp bend above 700°C (Fig. 9), characterizing the beginning of sintering.

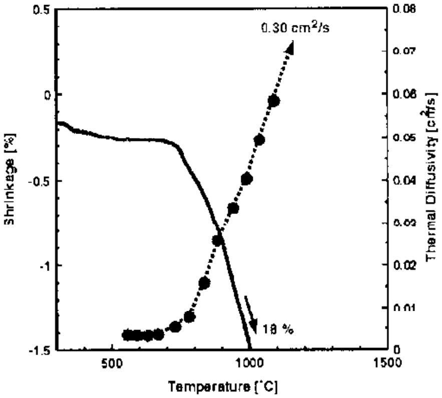


Fig. 9 Beginning of sintering (thermal diffusivity, shrinkage) of a normal grained hardmetal WC-10 wt% Co (DS 130)

But there is another possibility for identifying the change in the contact area between the particles. A very sensitive method for the investigation is the determination of the thermal diffusivity measured by the laser flash technique [6]. If the contact area between the particles is enlarged by diffusion-controlled processes we measure an increase in the thermal diffusivity. The measuring curve shows a real increase in the contact area. At first particle approach takes place. At higher temperatures particle rearrangement is relevant. A theoretical description is given in Ref. [3].

Shrinkage and increase in thermal diffusivity begin at the same temperature, about 700 to 750°C. Both effects are based on the same mechanisms. The beginning of shrinkage is made possible by the fact that at this temperature particle surfaces are

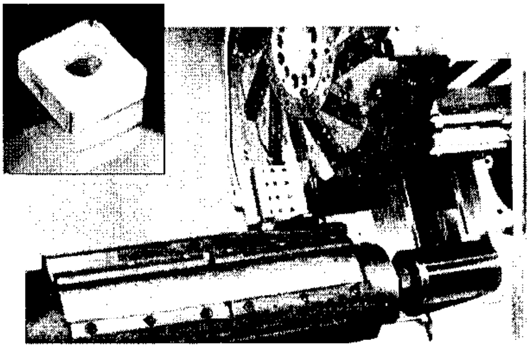
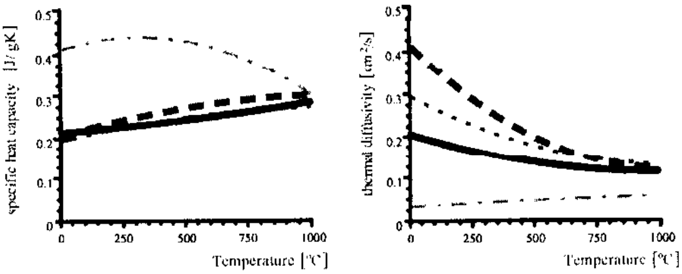


Fig. 10 Application of hardmetals – cutting

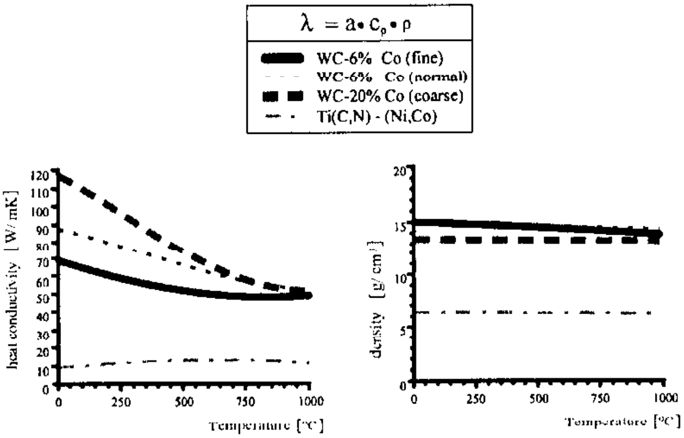
cleaned by reduction processes determined by evolution of CO and CO_2. On these activated and reactive surfaces diffusion processes are now enhanced and lead to mass transport, particle approach, shrinkage, reduction of porosity, and finally to sintering.

Data bases

If we consider the application of hardmetals in cutting, we know that the temperature at the edge of a cutting tip reaches values of about 800 to 900°C (Fig. 10). For describing this process it is necessary to know the heat conductivity of such materials not only at room temperature but also at the temperature of the application. A normal hardmetal (discussed previously) shows a heat conductivity of about 80 W m^{-1} K^{-1} at room temperature; the value at the edge of the cutting tip is reduced during cutting by 40% (Fig. 11). The tool designer must consider this change in order to optimize tool geometry and cutting conditions.



Specific heat capacity c_p Thermal diffusivity a



Heat conductivity λ Density ρ

Fig. 11 Thermal properties of hardmetals and cermets

Up-scaling and outlook

Many valuable results can be achieved by using methods of thermal analysis for characterization of materials and technological procedures. Our main aim is the description of outgassing and sintering of high-temperature materials. In our case, *in situ* sintering means the modelling of sintering using methods of thermal analysis. However, samples in thermal analysis are very small (on the order of 100 mg or smaller). If we want to transfer the results to a production scale we have to develop methods of up-scaling (which are also extremely necessary for successful partnership with industrial colleagues).

An example of up-scaling experiments is given in Fig. 12. In a macro thermobalance (sample mass<450 g) the mass loss by outgassing is shown for a ceramic tile. The results can be used in the development of improved temperature-time-atmosphere cycles on a production scale.

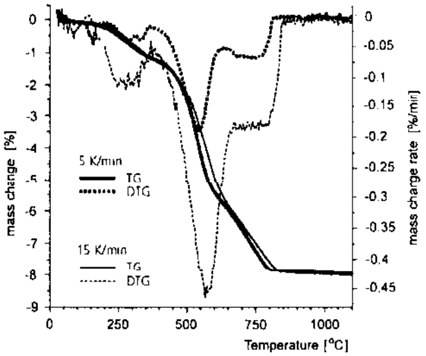


Fig. 12 Up-scaling with a macro thermobalance. Initial mass: 21 g; atmosphere: dynamic air

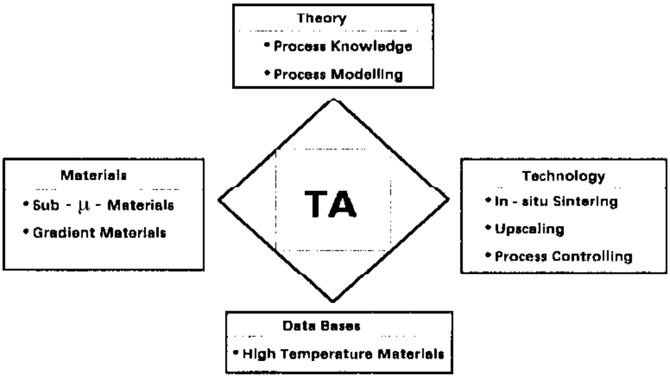


Fig. 13 Outlook – Application of TA

In Fig. 13 important future fields of application of thermoanalytical investigations are summarized. Development of new materials and improvements in production technology are the main aims of TA modelling. Results for hardmetals given in this paper seem to be a suitable example for demonstrating the potential of TA methods for solving materials problems.

* * *

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References

1 G. Leitner, K. Jaenicke-Rößler, T. Gestrich and T. Breuning, Metal Powder Report, 52 (1997) 32.
2 G. Leitner, K. Jaenicke-Rößler, T. Gestrich and T. Breuning, 'Entbindern und Sintern von Keramik – Optimierung durch thermoanalytische Simulation', cfi/Ber. DKG 76 (1999), in press.
3 G. Gille, G. Leitner and W. Hermel, Z. Metallkd., 89 (1998) 73.
4 G. Leitner, G. Gille and T. Gestrich, 'Shrinkage, liquid phase formation and gaseous reactions during sintering of WC-Co hard metals and correlation to the WC grain size', in: Proc. 14th Plansee Seminar, ed. by G. Kneringer, P. Rödhammer, P. Wilhartitz, Metallwerk Plansee, Reutte, Vol. 2, 1997, p. 86-99.
5 W. Schedler, 'Hartmetall – Aufbau, Herstellung, Eigenschaften und industrielle Anwendung einer modernen Werkstoffgruppe', VDI-Verlag, Düsseldorf 1988, p. 125.
6 M. Perl and G. Leitner, J. Thermal Anal., 47 (1996) 643.

Presentation of NETZSCH-GEFTA Award

The recipient was Dr. G. Leitner. The award was presented by Professor E. Gmelin.

Congratulations!

Let me first thank the board of GEFTA for nominating me for this year's NETZSCH-GEFTA Award. It is an extraordinary honour for me to receive this prize.

The probability of being awarded with this prize is approximately zero for a member of the thermoanalytical community. But there are many reasons and preconditions for which this probability should be different from zero which must be considered.

Let me emphasize explicitly that I see three very dominant preconditions for being awarded with this prize.

There must be

- an outstanding scientific and technical team which produces excellent results,
- efficient equipment which allows experiments to be carried out even under unconventional conditions, and
- an exceptional social and human background which facilitates an aim-oriented and engaged working atmosphere.

So, I want to express my warm thanks

- to the team of my lab for excellent cooperation,
- to the German Fraunhofer Society – a society for applied research – for giving us excellent facilities,
- and last but not least to my wife and my family for their abundance of help and for their understanding that my working day is normally much longer than eight hours.

This award encourages me to continue working with my team on the borderline of basic science and applied technology.

Thank you.