SINTERING OF HARDMETALS - THERMOANALYTICAL SIMULATION

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Dedicated to Dr. Andrej Šalak at the occasion of his 80th birthday.

Abstract

Current sintering technologies need a better and better knowledge on the processes taking place and advanced strategies for the optimization of the materials properties and the technologies for the production. The utilization of methods of thermal analysis for the experimental simulation of technological procedures under production-near conditions has been proved for some years. Debinding, outgassing and sintering are the basic processes during the heating of hardmetal mixtures. Results are given for WC-Co hardmetals, for doped hardmetals and for mixed carbide containing hardmetals. Methods of scale-up the results in the production area are discussed.

Keywords: debinding, outgassing and sintering, WC-Co hardmetals, simulation by thermal analysis, scaling-up, process knowledge, process optimization

INTRODUCTION

Use of thermal analysis methods has become well established in the development of powder metallurgy processes and materials, thanks to a series of successes achieved with them. Especially for the process steps of debinding, outgassing and sintering, experimental simulation is of particular importance, since an understanding of the processes occurring – process knowledge as a whole – is an important prerequisite for derivation of technologically relevant information that can be used for process control and optimization and for improvement of efficiency. Typically, techniques such as thermodilatometry (TD), differential thermal analysis/dynamic differential scanning calorimetry (DTA/DSC), thermogravimetry (TG) and evolved gas analysis (EGA) – especially in conjunction with mass spectrometry for gas detection – are used in investigations, often simultaneously or coupled using appropriate techniques [1-3]. Dilatometry yields information on the shrinkage or expansion behavior of a material during thermal treatment; even phase transformations can manifest themselves as changes in length. Thermogravimetric studies deliver information about mass changes, caused, for instance, by thermal decomposition of organic components or reduction of oxide impurities on powder surfaces. With coupled mass spectrometry, information about the composition of released gaseous species can be obtained. Calorimetry enables detection of caloric changes, caused by such effects as melting and evaporation of pressing aids or melting and solidification of eutectic mixtures.

Researchers at the Laboratory for Thermal Analysis at Fraunhofer IKTS in Dresden have worked extensively with a number of different material systems, especially hardmetals, steel powders (e.g., Cr and Mo steels), high-performance ceramics (e.g.,

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oxides, nitrides and carbides), functional ceramics (e.g., materials used in fuel cells and PZT ceramics) and intermetallics (e.g., titanium aluminide). In the present investigation, results on debinding, outgassing and sintering of typical hardmetals obtained by workers at IKTS or taken from the literature [4-16] are compiled and discussed.

Hardmetals are used as cutting or wear materials. They are manufactured using powder metallurgy methods: Powders of the hard material (e.g., WC) and the binder (e.g., Co) are milled (with simultaneous mixing), granulated and pressed. Organic aids (e.g., paraffin) added to improve pressing behavior are expelled from the green body (e.g., through heating) before the densification stage of sintering. Sintering proceeds with a liquid phase, an eutectic phase consisting of cobalt with dissolved tungsten and carbon. At the sintering temperature, the carbon balance, along with other factors, plays a decisive role in determining the properties of the sintered hardmetal. For example, the bending strength shows a strong maximum at a carbon concentration corresponding to the two-phase region consisting of WC and Co with W and C solved in it (see Fig.1). Knowledge of the process factors influencing the carbon balance is thus valuable for optimization of technological parameters (e.g., temperature-time-atmosphere profiles).
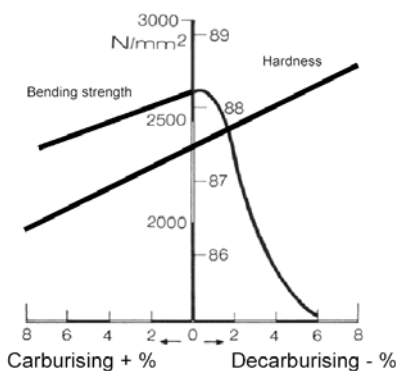

Fig.1. Bending strength and hardness of a WC-Co hardmetal in relation to carbon concentration [17].

METHODS AND MATERIALS USED IN THE INVESTIGATIONS

Equipment
For the experiments, the following analytical equipment was available:

Thermodilatometer	402E	Netzsch
Thermogravimeter	STA 429	Netzsch
Coupling system (skimmer)	403/4	Netzsch
Mass spectrometer	QMG 421	Balzers
Macro Thermobalance	TG 419	Netzsch
Calorimeter	DSC 404/DSC 7	Netzsch/Perkin Elmer
Laserflash apparatus	LFA 427	Netzsch

All of the measurements were made at a heating rate of 10 K/min in streaming helium (5l/h) with a quality designation of 5.0 under atmospheric pressure, unless otherwise noted.

Materials

Standard material:

- Hardmetal with medium grain size
    - WC-6 wt. %Co with 2 wt. % of paraffin (Type S14)
- Fine-grained hardmetal
    - WC-10 wt. %Co with 2 wt. % of paraffin (Type S14)
    - $d_{WC} = 1.3$ µm (H.C. Starck Type DS130)

Doped hardmetal:

- Ultrafine-grained hardmetal
    - WC-10 wt. %Co without or with paraffin (2 wt. %)
    - $d_{WC} = 0.6$ µm or 0.45 µm (H.C. Starck Type DS60 or DS40)

Hardmetal with varying C contents:

- Ultrafine-grained hardmetal
    - WC-10 wt. %Co with 2 wt.% of paraffin (Type S14)
    - $d_{WC} = 0.6$ µm (H.C. Starck Type DS60)

Mixed-carbide hardmetal:

- Hardmetal with medium grain sizes
    - WC-TaNbC-TiC-TiN-11 wt. % Co with 2 wt. % of paraffin

RESULTS

Standard Behavior – Overview

The standard behavior of a WC-Co hardmetal is described below. Figure 2 shows curves obtained for shrinkage (including shrinkage rate), mass change (including rate of change), caloric effects (e.g., formation of eutectic) and intensities of selected outgas products obtained by mass spectrometry for the hardmetal WC - 6 wt. % Co with medium grain size and 2 wt.% of paraffin (m28 for carbon monoxide, m44 for carbon dioxide, m29 and m43 for products of organic decomposition) as a function of temperature; y-axis labels are given in arbitrary units.
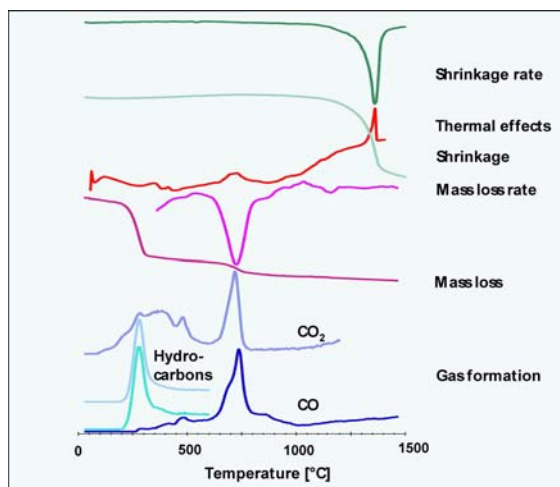

Fig.2. Debinding, outgassing and sintering curves for WC- 6wt. % Co with 2 wt. % of paraffin (medium grain sizes). Investigation parameters: 10 K/min, argon.

The following main effects are observed:

RT to 200°C
- Presence of moisture, organic impurities, plasticizers
- Melting of paraffin

200-600°C
- Decomposition of paraffin
- Reduction of oxide and hydroxide impurities (Co)

600-1150°C
- Start of shrinkage
- Further reduction of oxide impurities (WC)

1150-1450°C
- Pronounced shrinkage
- Formation and melting of eutectic

Individual effects are studied in more detail below.

Debinding – Standard Behavior

To illustrate standard behavior, the decomposition of paraffin in a hardmetal mixture is compared for use of vacuum or an inert/reducing atmosphere during the process; characteristic differences between these two alternatives are described in the literature [13].
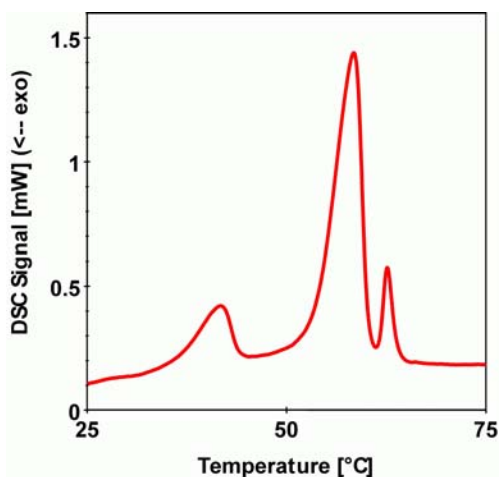

Fig.3. Melting of paraffin in the hardmetal WC – 6 wt. %Co with 2 wt. % of paraffin (medium grain sizes).

An endothermic peak indicates the occurrence of melting. However, the paraffin investigated in this study exhibited three peaks (see Fig.3), signifying that the paraffin either consisted of a mixture of different paraffin types with difference chain lengths or contained additional organic components.

The decomposition and outgassing behavior of a typical hardmetal is shown in more detail in Fig.4. In the curve depicting the mass change rate, two effects for decomposition of the paraffin can be seen: a relatively large one at ca. 280°C and a smaller one at ca. 370°C. The intensity curves obtained using mass spectrometry can be organized into groups whose maximums correspond to the two temperatures given above.

- C_nH_{2n+1} e.g., m43 (C_3H_7) m71 (C_5H_{11})
- C_nH_{2n-1} e.g., m27 (C_2H_3)
- C_nH_{2n-2} e.g., m26 (C_2H_2)
- C_nH_n e.g., m78 (C_6H_6)
- C_nH_{n-1} e.g., m51 (C_4H_3)

The first group is associated with the large jump in the mass change curve, and the third group with the smaller one at ca. 370°C. For the second group, the two effects are superimposed.

Outgassing 1 – Reduction Processes

At a temperature of around 370°C, maxima in intensity are also found in the curves for m18 (H_2O) and m44 (CO_2)/m28 (CO) (see Fig.4). The DSC curve in Fig.4 also exhibits a small effect at this temperature. Oxide impurities, hydroxyl groups or other functional groups bound to the surfaces of the metallic binder particles (Co) or the hard particles (WC) are reduced by carbon of the mixture. The carbon required for the desired reactions must be accounted for when the mixture is being prepared to ensure that optimum properties are achieved in the sintered hardmetal (see Fig.1).
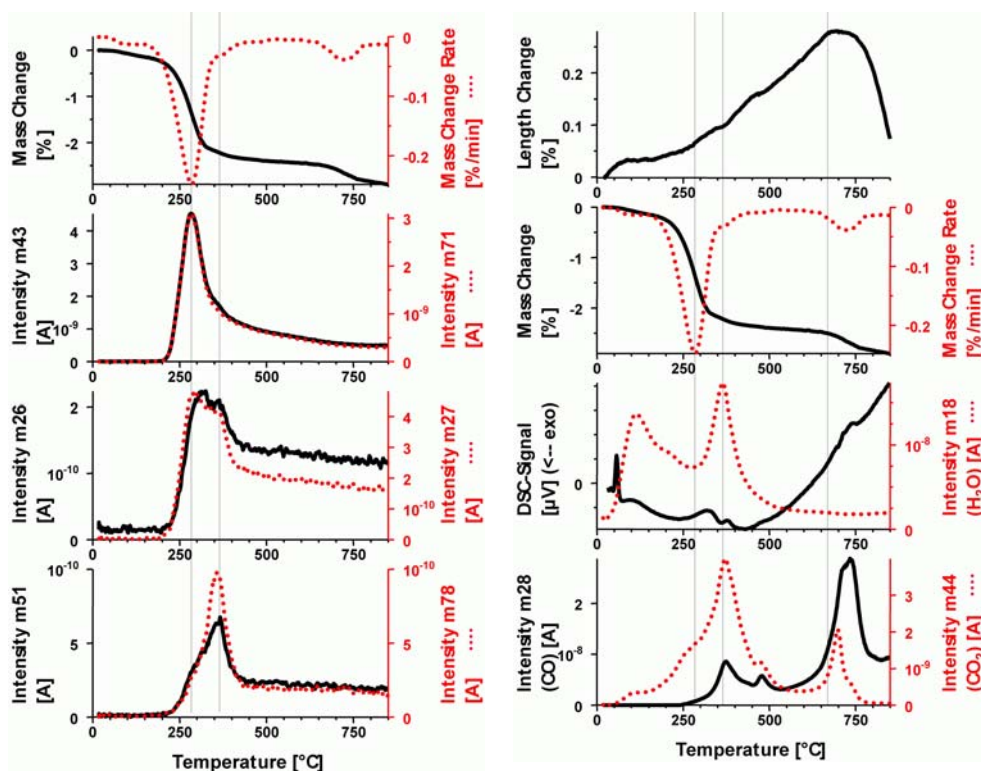

Fig.4. Debinding and outgassing curves for the ultrafine-grained hardmetal WC – 10 wt. % Co with 2 wt. % of paraffin (WC-DS60: 10 K/min, helium).

Outgassing 2 – Effect of Carbide Dopants

Hardmetal users are increasingly demanding fine-grained and ultrafine-grained hardmetals. To prevent grain coarsening during sintering, small amounts (ca. 1 percent by weight) of carbides (e.g., VC and/or Cr_2C_3) are added. These grain growth inhibitors effect a broadening of the temperature range in which oxide impurities are reduced to include significantly higher temperatures. Reduction products (CO) escape through the (still) open pores. When the liquid phase is formed, these pores close, thus preventing any gas that is later formed from being released. The technical process window between gas production and pore closure by melting becomes considerably smaller, the more so as the dopant components shift the melting temperature of the eutectic to lower temperatures.
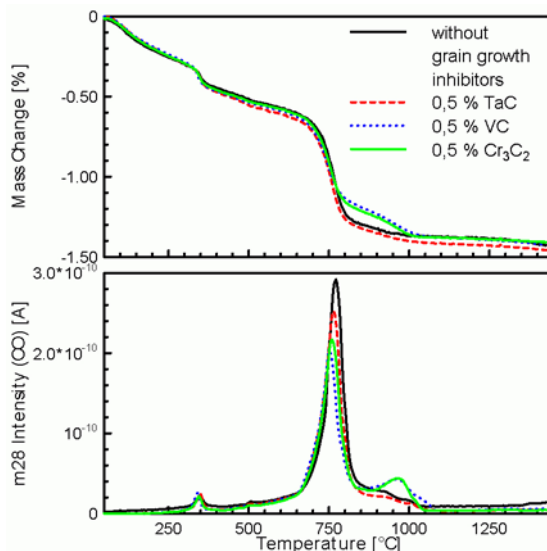

Fig.5. Effect of different grain growth inhibitors on mass change and formation of CO (m28) in the ultrafine-grained hardmetal WC-10wt.% Co without paraffin (WC-DS60).

In the curves shown in Figure 5, depicting mass change and CO formation as a function of use of different grain growth inhibitors, the outgassing effect shown by WC is not changed significantly through addition of tantalum carbide, whereas addition of VC or Cr_3C_2 shifts the outgassing process to much higher temperatures (1100°C and higher). These effects should be taken into account when determining the optimum process window (see "3.8 – Sintering 3").

Outgassing 3 – Mixed-Carbide Hardmetals

Hardmetals containing additional mixed carbides are needed for steel machining. Tantalum carbide, niobium carbide, titanium carbide and titanium nitride in amounts of up to 25 percent by weight can be added. The products of reduction (CO) of the oxide impurities in the carbides are formed at even higher temperatures; hence, the process window is even smaller. Moreover, titanium nitride becomes unstable and causes nitrogen to be released at higher temperatures. Release of nitrogen is halted on formation of the liquid phase.

The shrinkage (and shrinkage rate) and mass change (and mass change rate) curves are given in Fig.6 for the hardmetal WC-TaNbC-TiC-TiN-11 wt. % Co with 2 wt. % of paraffin and medium grain size.

After paraffin is evaporated, a continuous mass loss occurs until peak temperatures are reached, thus complicating the design of the optimum sintering profile. Comparison of the outgassing curves of this material with those of the undoped fine-grained hardmetal WC - 10 wt. % Co based on WC-DS130 (dashed curves in Fig.7) reveals a marked structuring of the curve for the mass change rate.
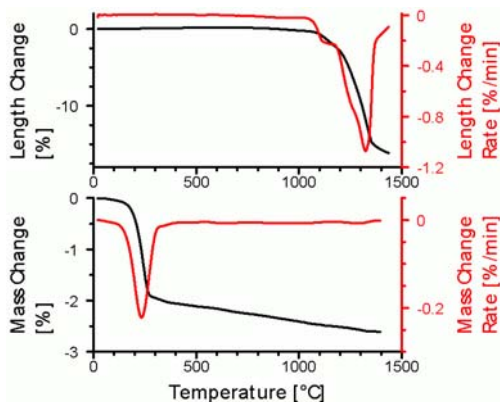

Fig.6. Length and mass changes in the mixed-carbide hardmetal WC-TaNbC-TiC-TiN-11 wt. % Co with 2 wt. % of paraffin and medium grain size.
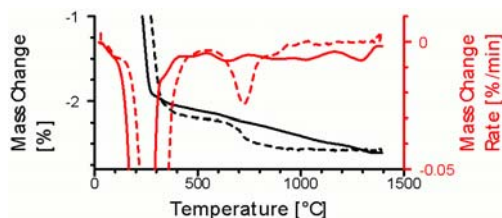

Fig.7. Comparison of mass changes in the mixed-carbide hardmetal WC-TaNbC-TiC-TiN-11 wt. % Co and the fine-grained hardmetal WC - 6 wt. % Co (WC-DS130 – dashed curves), both containing 2 wt. % of paraffin.
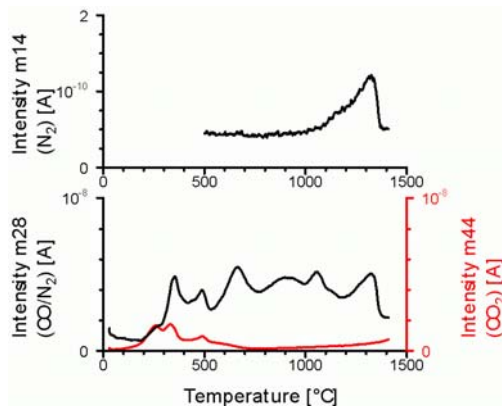

Fig.8. Formation of carbon monoxide and nitrogen in the mixed-carbide hardmetal WC-TaNbC-TiC-TiN-11 wt. % Co.

The continuous mass loss occurring until high temperatures are reached is mainly controlled by the release of CO during reduction (see Fig.8). The mass number m28 represents both carbon monoxide and nitrogen. If the mass number m14 is additionally measured, separate identification of both gases is possible. Already at temperatures above 1000°C, nitrogen is released due to the start of instability of TiN; as soon as the eutectic melt closes the pore space, this release of gas is no longer possible.

Sintering 1 – Start of Shrinkage

Densification (shrinkage) commences when reduction of impurities is completed and reactive surfaces have been created, thus resulting in accelerated diffusion and, consequently, growth of contact areas between particles.

As shown in Figure 9, for WC-Co hardmetals, the temperature range in which this occurs is 700-800°C. Mixed-carbide hardmetals, on the other hand, contain thermodynamically stable carbides, whose oxide impurities are reduced at higher temperatures. This leads to marked shrinkage at higher temperatures for these materials; additionally, the temperature range in which pronounced shrinkage occurs is much narrower than for WC-Co hardmetals.

In Figure 9, the shrinkage curve is expanded (the length change resulting from thermal expansion has been subtracted); shrinkage begins above 700°C. Also shown in this figure is the curve for thermal diffusivity (measured using the laserflash method). This curve also begins to exhibit a positive slope at ca. 700°C. The thermal diffusivity describes the rate at which a thermal field activated by an energy pulse moves through the sample; it is determined by the thermal resistance of the contacting surfaces of the particles. If the contact resistance is lowered by reduction of oxide layers or by an increase in contact surface area resulting from diffusion of cobalt atoms, the thermal diffusivity increases accordingly. The measurement results reflect the high level of sensitivity of this method for detecting changes in contact surfaces during sintering.

The shrinkage and thermal diffusivity curves for a Ti(C,N)-(Co,Ni) cermet are also given in Fig.9. Like mixed-carbide hardmetals, this material exhibits reduction of oxide impurities at much high temperatures. Shrinkage is correspondingly measured at temperatures of around 1000°C (determined for three different heating rates), and particle-particle contact surface area and thermal diffusivity (heat transport through the specimen) already increase measurably at lower temperatures.
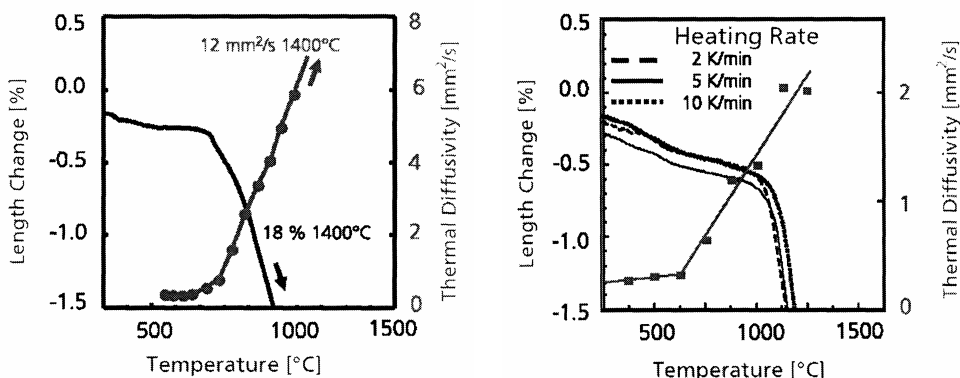

Fig.9. Start of shrinkage and thermal diffusivity of green body during heating for the fine-grained hardmetal WC-10 wt. % Co (WC-DS130) and a Ti(C,N)-(Co,Ni) cermet.

In the measurement of thermal diffusivity, it must be considered that the thermophysical properties are themselves temperature-dependent. Figure 10 illustrates this for the sintered sample. The curve measured for the green body during heating is thus mainly controlled by effects occurring during sintering.
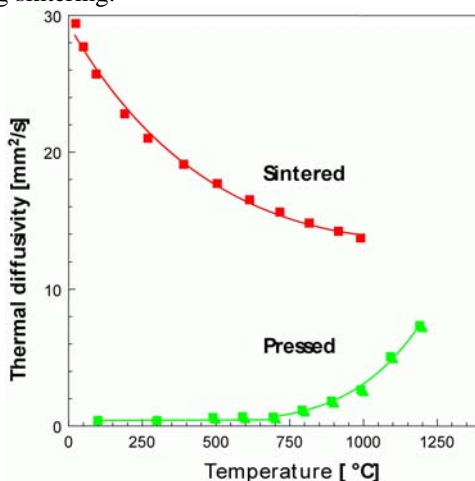

Fig.10. Thermal diffusivity for the ultrafine-grained hardmetal WC-10 wt. % Co with 2 wt. % of paraffin (WC-DS60) - Difference between the green body during heating and the sintered specimen.
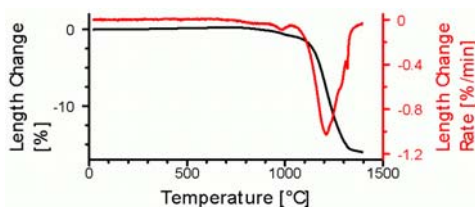

Fig.11. Shrinkage and shrinkage rate for the ultrafine-grained hardmetal WC-10 wt. % Co with 2 wt. % of paraffin (WC-DS60).

Sintering 2 – Pronounced Shrinkage

For hardmetals, shrinkage occurs mainly in the solid-phase region, as shown in Fig.11 (also see Figs.6 and 12). The large amounts of shrinkage can be accounted for by particle rearrangement.

Sintering 3 – Effect of Carbide Dopants

For doped hardmetals, the curves for shrinkage rate exhibit significant structuring. In connection with the curves for melting of the eutectics, they deliver important information about the critical process windows.

Doping with carbides significantly affects length changes (shrinkage) and length change rates. Figure 12 shows the changes in the curves for shrinkage rate resulting from doping with carbides. Particularly evident are the subpeak found for the VC-doped material at ca. 1000°C and the shift in the region in which pronounced shrinkage occurs to higher temperatures for doped material in comparison with the undoped material. Also of importance

are the small peaks in the shrinkage rate curves at temperatures of around 1350°C; these peaks can be correlated with melting of the eutectic for the various dopant carbides.
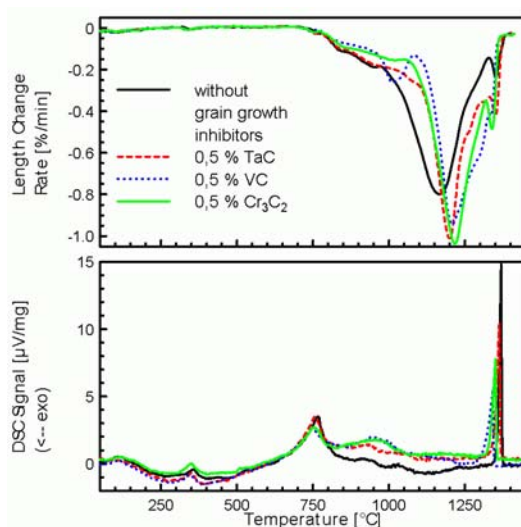

Fig.12. Effect of different grain growth inhibitors on length change rate and caloric effects for the ultrafine-grained hardmetal WC-10 wt. % Co without paraffin (WC-DS60).

This effect is shown in more detail in Fig.13. For the undoped hardmetal, the peak corresponding to melting occurs at a relatively high temperature (at the peak temperature, the entire eutectic phase is melted), in this case at 1374°C, and the peak width is ca. 20 K (melting commences at the temperature at which the DSC curve rises above the base line). For the doped materials, the peak temperature decreases in the order TaC < Cr_3C_2 < VC < VC/Cr_3C_2 (commercial composition) by ca. 50 K. However, the temperature at which melting commences sinks by even more, nearly 150 K. These two opposing effects resulting from doping – gas formation shifted to considerably higher temperatures and pore closure by formation of a liquid phase shifted to considerably lower temperatures – deliver information crucial for specification of optimum sintering conditions; the process window becomes smaller and smaller.
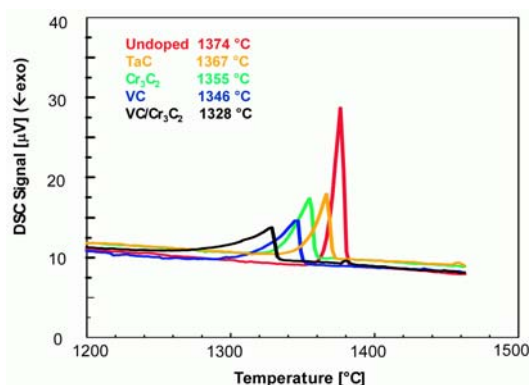

Fig.13. Effect of dopant on eutectic formation in the ultrafine-grained hardmetal WC-10 wt. % Co without paraffin (WC-DS40).

Sintering 4 – Effect of Carbon Content on Shrinkage and Eutectic Formation

The carbon balance in the hardmetal mixture influences shrinkage behavior. Even small changes in the carbon content lead to characteristic changes in the curves for shrinkage and shrinkage rate as well as in the correlated melting of the eutectics.

In Figure 14, the shrinkage rate curves are given for four different carbon concentrations in the temperature range in which pronounced shrinkage occurs and in which the maximum shrinkage rate is found. In the subpeak region, the temperature of the subpeak and the subpeak intensity decrease with increasing carbon content. In addition, the maximum shrinkage rate is shifted to lower temperatures, its magnitude thereby increasing. Hardmetals with relatively high carbon contents thus sinter at somewhat lower temperatures than carbon-poor hardmetals do.
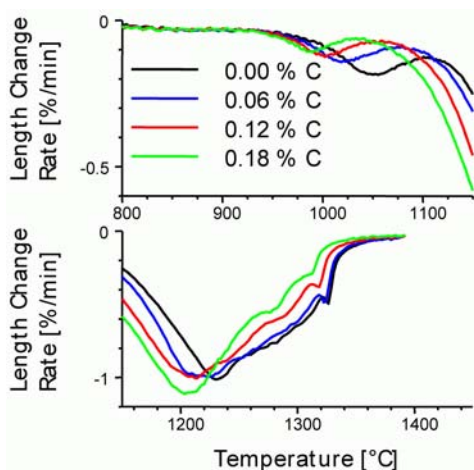

Fig.14. Effect of carbon content on shrinkage rate for the ultrafine-grained hardmetal WC-10 wt. % Co with 2 wt. % of paraffin (WC-DS60).
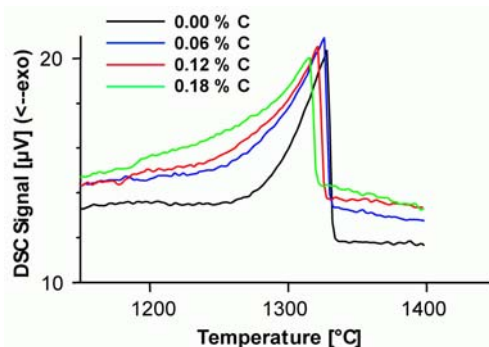

Fig.15. Effect of carbon content on eutectic melting in the ultrafine-grained hardmetal WC-10 wt. % Co with 2 wt. % of paraffin (WC-DS60).

The melting behavior of the eutectic is known to be affected considerably by the carbon content in the mixture. It can be seen from Fig.15 that the main effect is not the slight shift in peak temperature to lower temperatures, but rather the dramatic broadening of the temperature interval in which melt formation occurs. The temperature at which melting

commences shifts downward by ca. 100 K when the carbon content is changed by a mere 0.18 wt. %. Here, too, the consequences of this in terms of the critical process window should be considered (all of the gas formed must escape from the sample before the remaining pore space is filled by the liquid phase).

Sintering 5 – Solidification of Eutectic

During cooling from the sintering temperature, the sample passes through a temperature region in which the liquid phase solidifies. This solidification process is accompanied by a change in volume. A technically important question to be asked is whether or not this effect changes the internal compressive stresses in the material in dependence on the conditions of the temperature profile (cooling rate). This could directly influence the properties of the final hardmetal.

Scale-Up

There are a number of possibilities for transferring thermoanalytical results to the technical realm (scale-up).

Scale-up 1: FEM calculations (e.g., continuum mechanics approaches) using experimental results (e.g., shrinkage curves).

Scale-up 2: (Formal) Kinetic analysis of time-dependent processes using TA equipment and subsequent extrapolation of results to larger specimens.

Scale-up 3: Utilization of macroscopic thermal analysis equipment for direct investigation of real components, e.g., in a macro thermal balance.

Scale-up 4: Integration of sensors into technical systems (e.g., process dilatometer or mass spectrometer) and utilization of process knowledge gained from experiments.

It should also be noted that investigation of thermophysical properties (coefficient of thermal expansion, density, specific heat capacity, heat of transformation, thermal diffusivity and heat conductivity) also provides important information about processes occurring during sample heating and can be useful for optimization of these processes.

CONCLUSIONS AND FUTURE PROSPECTS

Investigation of debinding, outgassing and sintering of hardmetals using thermoanalytical methods leads to a better understanding of the processes occurring. Improved knowledge and simulation of processes are basic requirements for improvement of current materials and manufacturing technologies, as well as for development of new materials and technologies for the powder metallurgy and ceramics industries. Application of the results in the area of production (e.g., optimized temperature-time-atmosphere profiles) is aimed at reducing costs, improving properties and stabilizing the technology – It's not the destination that's important, it's the journey!

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