Journal of Thermal Analysis, Vol. 33 (1988) 559–565

THERMAL ANALYSIS – A GUIDE TO THE OPTIMIZATION OF SINTERING PROCESSES

B. F. Kieback, G. Leitner and *K. Pischang**

ACADEMY OF SCIENCES OF THE G. D. R., CENTRAL INSTITUTE
OF SOLID-STATE PHYSICS AND MATERIALS SCIENCE,
DRESDEN, 8027
*TECHNICAL UNIVERSITY, DRESDEN, 8027, G. D. R.

During the sintering of multicomponent disperse systems prepared from mixtures of the components, a variety of solid-state reactions, phase formation or dissolution, and the occurrence of a liquid phase determine the densification and the final microstructure of the material.

The results are presented of investigations on the systems WC—Co and Fe—Si, through the simultaneous application of dilatometry, differential thermal analysis and thermogravimetry, coupled with metallographic and microprobe analysis.

A great variety of the materials used in the automotive and machine-building industries, in electronics or as tools in mechanical machining today are produced by powder metallurgy. One of the basic technological steps of this technique is the sintering process. Packed powders bond together when heated to temperatures in excess of approximately half of the absolute melting temperature. In general, powder metallurgical materials are of the multicomponent type. Their processing can start from mixed powders of differing chemistries or from prealloyed powders. The chemical interaction between the powder particles has to be taken into account for an understanding of the process occurring during sintering. Other factors influencing the behaviour during the thermal treatment result from the technology. Organic lubricants added to the powder mixture must evaporize completely at low temperatures, without cracking. Oxidizing or reducing processes occur, due to the interaction with the gaseous atmosphere in the furnace. Extensive experimental studies are necessary to optimize the sintering process and to define the conditions for processing a material with the desired microstructure and properties.

The application of thermoanalytical methods to study sintering can give valuable information about chemical, microstructural and dimensional changes. In this study, dilatometry, thermogravimetry and differential thermal analysis are used to

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

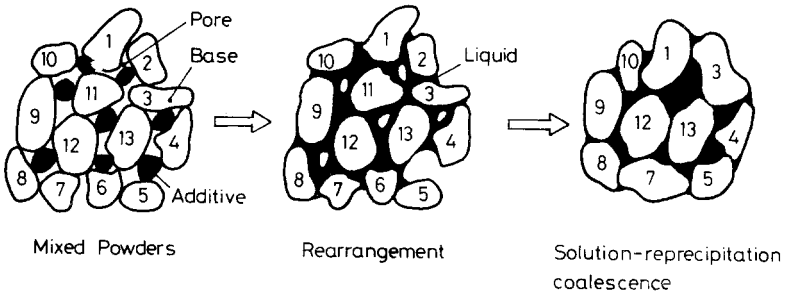

Fig. 1 Stages of liquid phase sintering involving mixed powders [1]

investigate sintering in iron-silicon alloys (soft magnetic materials) and WC–Co cemented carbides (cutting tool materials). Both of them are processed by liquid-phase sintering, starting from powder mixtures (Fig. 1).

The liquid phases in these systems result from the formation of eutectics. In the case of iron-silicon alloys (Si content 6 wt.%) the liquid is transient during sintering, while WC–Co alloys are treated in the presence of the liquid phase throughout the whole isothermal period.

Experimental

The samples for the thermoanalytical investigations were made by compacting the powder mixtures, i.e. WC and cobalt powders in the case of cemented carbides, and water atomized iron powder with silicon or ferrosilicon powder prepared by milling. An organic lubricant was added to the WC–Co powder mixture to permit compaction in a mould. For the thermoanalytical studies, a Netzsch 402 E Dilatometer and a Netzsch STA 429 Thermoanalysator were used. In the experiments the samples were heated to the sintering temperature at a constant heating rate. The atmosphere was argon (3 l/h) with a dew point of $-50°$.

Results and discussion

Cemented carbides

This group of materials is a typical example of compounds which can only be produced by powder metallurgical techniques.

During the heating period, diffusional processes lead to the formation of a eutectic of Co and WC [3]. Above the eutectic temperature, persistent liquid-phase

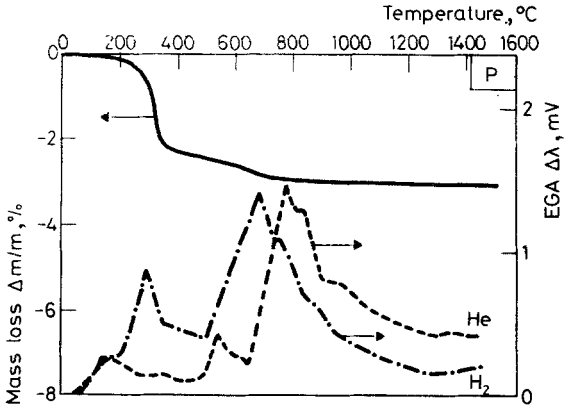

Fig. 2 Mass loss and degassing behaviour of Wc—Co

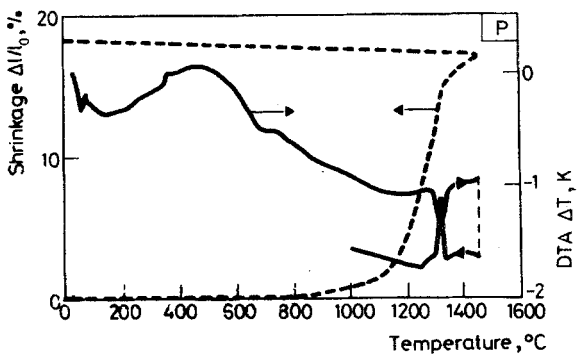

Fig. 3 Shrinkage behaviour and thermal effects of WC—Co

sintering takes place, and the compaction of the material is enhanced. WC–6 wt.% Co as a representative hard-metal was investigated by means of dilatometry, thermogravimetry and DTA (heating rate 10 deg min^{-1}, argon). The results are given in Figs 2–4. During the heating period several characteristic effects are found, which can be ascribed to mechanisms of material transport or the sintering process in general (Table 1).

Iron-silicon alloys

Powder mixtures of iron and silicon or ferrosilicon (FeSi) with a Si content of 6 wt.% undergo transient liquid-phase sintering at temperatures of about 1250°. The liquid enhances the homogenization of the alloying element. The results of the differential thermoanalytical investigations are shown in Fig. 5.

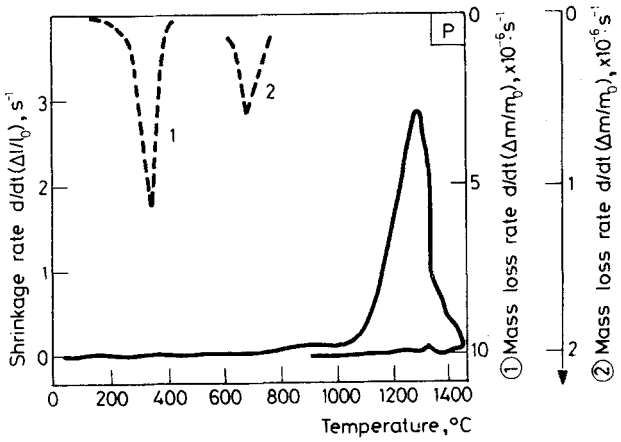

Fig. 4 Shrinkage rate and mass loss rate of WC—Co

Table 1 Characteristic effects during the heating of WC–Co hardmetals

Temperature range, °C	Effects—Mechanisms
100...500	delubrication loss of water degassing (reduction of cobalt oxide)
600...900	degassing (reduction of tungsten oxide)—maximum mass loss rate beginning of sintering in the binder (diffusion processes)
1200...1350	shrinkage (rearrangement of particles in the solid and the liquid state)—maximum shrinkage rate formation of a liquid phase
1350...1450	solution—reprecipitation (Ostwald ripening), residual shrinkage

Comparison of the characteristic temperature found by thermal analysis with the phase diagram [3] gives information on the actual constitution of the powder compact (Table 2). The formation of intermetallic compounds, indicated by the exothermic effects of the solid-state reactions, is the most important result. If FeSi additives are used, the powder particles are nearly completely transformed to Fe_2Si during heating, and congruent melting occurs at 1216°. Si addition leads to melting of the silicon-rich eutectic and to the transient formation of the intermetallic compounds FeSi, indicated by an exothermic effect at 1203°.

The transformation of the additive in the solid state explains the swelling effects observed in this temperature range [4]. Therefore, higher heating rates can prevent reactions before melting occurs and the swelling effects should be reduced.

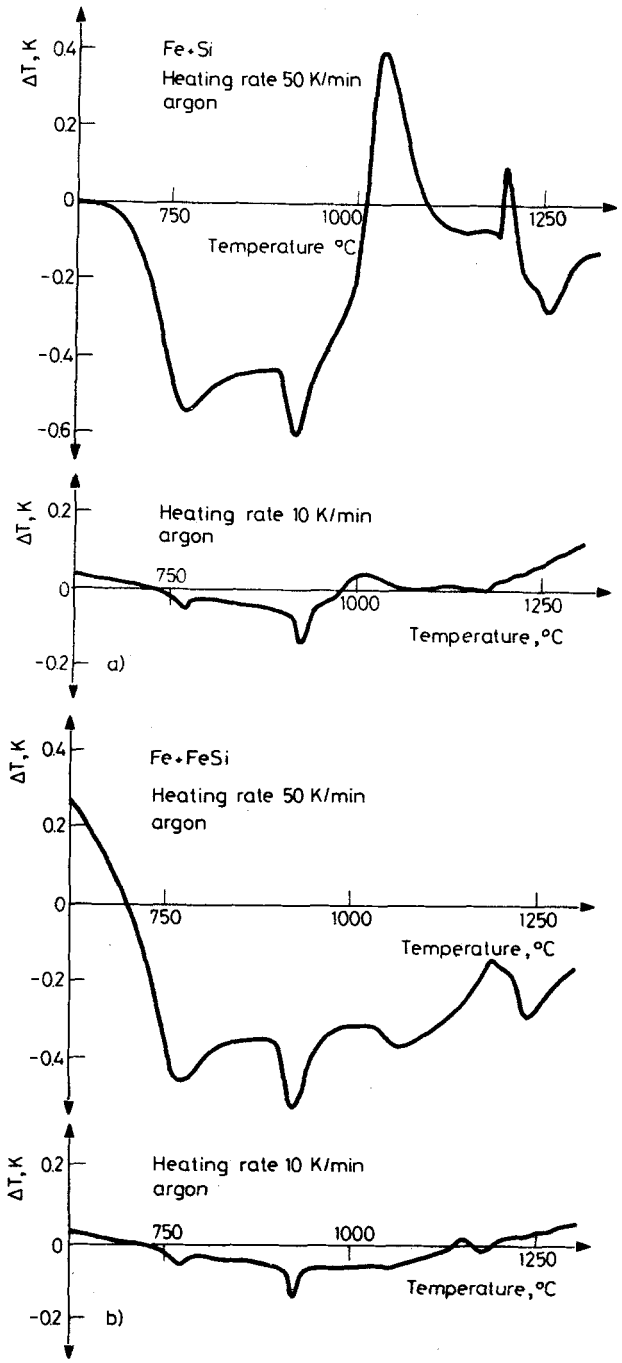

Fig. 5 Thermal effects during heating of Fe + Si (a) and Fe + FeSi (b) powder mixtures

Table 2 Temperatures of phase formation and dissolution in Fe + Si—and Fe + FeSi—powder compact during sintering (°C) (silicon content 6%)

	Fe + Si		Fe + FeSi	
Heating rate, deg/min	10	50	10	50
Magnetic transformation	758	768	760	768
$\alpha-\gamma$ transformation	910	903	909	904
Phase formation	970	985	—	—
$Si \rightarrow FeSi_2 \rightarrow FeSi$	1030	1060		
Dissolution of η-phase				
$Fe_5Si_3 \rightarrow Fe_2Si + FeSi$	1044	1041	—	—
Phase formation (diffusion induced) in the system				
Fe–FeSi	1175	1160	1125	1130
$FeSi \rightarrow Fe_2Si \rightarrow \alpha$-Fe	1190	1200	1150	1195
$Fe_2Si \rightarrow \alpha$-Fe				
Transient liquid phase	1203	1205	—	—
FeSi-formation				
Melting in the system Fe–FeSi				
(melting of the β-Fe_2Si-phase)	—	—	—	1216
Melting of α-Fe solid solution	—	1252	—	—

Conclusions

Thermoanalytical methods can be profitably used in the field of materials research, especially for the investigation of processes occuring during the sintering of powder metallurgically produced materials.

The results yielded by thermal analysis allow

— an interpretation of the dominating mechanism of the material transport within porous materials;

— optimization of the sintering process (e.g. temperature, duration, heating rate, atmosphere, etc.);

— optimization of the technological steps (e.g. delubrication, degassing, sintering, heat treatment, etc.).

References

1 R. M. German, Liquid Phase Sintering, Plenum Press, New York and London, 1985.
2 L. Suzuki and K. Kubota, Planseeber. Pulvermetall., 14 (1966) 96.
3 O. Kubaschewski, Binary Phase Diagrams, Springer Verlag, Berlin/Heidelberg/New York, 1982.
4 K. Pischang, Thesis, TU Dresden, 1986.

Zusammenfassung — Beim Sintern vielkomponentiger Systeme, die aus Gemischen der Komponenten hergestellt werden, bestimmt eine Vielzahl von Festkörperreaktionen, Neubildung und Auflösung von Phasen und das Auftreten von flüssigen Phasen die Verdichtung und die erreichbare Mikrostruktur des Materials.
Ergebnisse der Untersuchung in den Systemen WC—Co und Fe—Si durch kombinierten Einsatz von Dilatometrie, TG—DTA, metallographischen und Mikrosonden-Untersuchungen werden mitgeteilt.

Резюме — В процессе спекания многокомпонентных систем, полученных с помощью твердотельных реакций смеси компонентов, образование фазы или растворение, также как и наличие жидкой фазы определяют плотность и конечную микроструктуру материала. Представлены результаты исследований систем WC—Co и Fe—Si с использованием методов дилатометрии, дифференциального термического анализа и термогравиметрии, сопряженных с металлографическим анализом и анализом микропробы.