

DEGASSING AND DEOXIDATION PROCESSES DURING SINTERING OF UNALLOYED AND ALLOYED PM STEELS

H. Danninger, C. Gierl, S. Kremel, G. Leitner, K. Jaenicke-Roessler, Y. Yu

Dedicated to Prof. Dr. Gerhard Jangg at the occasion of his 75th birthday

Abstract

For successful sintering of ferrous compacts, removal of the surface oxides is of critical importance. Within this work, the sintering and degassing behaviour of various PM steels was investigated by thermal analysis combined with mass spectrometry. It showed that with plain carbon steels or Mo alloyed ones, degassing and deoxidation, which are noticeable from mass loss and formation esp. of CO/CO₂, occur in 3 different temperature ranges, the most pronounced degassing peak being found at about 700°C. This degassing behaviour is not markedly affected by the carbon content while the starting powder size and also the morphology has some impact on the relative intensity of the degassing peaks; also with sponge iron most of the deoxidation occurs at T>900°C. With Cr prealloyed steels, deoxidation takes place predominantly at higher temperatures, at least 1000°C being necessary to remove the surface oxides and enable formation of metallic sintering contacts. Also here, however, the admixed carbon content is of minor importance. Among further alloying elements, esp. Mn retards the reduction process. In any case, sintering of Cr alloy steels should be done at temperatures above 1120°C, preferably 1250°C or higher, to ensure as complete oxygen removal as possible.

Keywords: *Sintered steels, degassing, deoxidation, thermal analysis, mass spectrometry*

INTRODUCTION

Virtually all technical metal powders are covered by layers of atmospheric constituents and/or of layers generated by reaction of these components with the base metal. The main impurity is of course oxygen, and oxide layers are known to prevent e.g. sintering of cemented carbides in which case the onset of shrinkage is linked to reduction of the WC surfaces [1].

For sintered steels, shrinkage is not a main target, due to the necessity of dimensional stability [2], but the formation of strong interparticle necks is an essential criterion [3]; also here, oxides are detrimental [4]. Surface reduction can be attained by sintering in suitable atmospheres, e.g. in such containing hydrogen. For carbon containing steels, also inert atmospheres are viable since the carbon acts as reducing agent. Carbon is less effective than hydrogen at low temperatures but becomes very much more so at

Herbert Danninger, Christian Gierl, Sabine Kremel, Vienna University of Technology, Institute for Chemical Technologies and Analytics, Vienna, Austria

Gert Leitner, Klaus Jaenicke-Roessler, Fraunhofer Institute for Ceramic Technologies and Sintered Materials, Dresden, Germany

Yang Yu, Höganäs AB, Höganäs, Sweden

$T > 1000^{\circ}\text{C}$ [5]. This can be made use of e.g. for PM steels covered with rather stable oxides such as Cr alloyed ones while the classical PM steels, either unalloyed ones or such containing Cu, Ni, and Mo as alloy elements, can be easily reduced also at low to moderate temperatures.

Chromium as an alloy element is widely used in structural and tool steels produced by ingot metallurgy. In powder metallurgy parts production, however, the high oxygen affinity of Cr results in very strict requirements towards atmosphere purity when sintering these materials [6]. Numerous approaches have been made to produce Cr alloy structural steel parts by pressing and sintering, both powder mixes and prealloyed powders have been used [6-10], but so far acceptance for industrial production has been fairly slow. Recently, new prealloyed PM steel powders have been developed based on Fe-Cr-Mo [5, 11] and Fe-Cr-Mo-V [12] that supplant the well known 4100 (Fe-Cr-Mn-Mo) type which has been available as water atomized [13] and for a short time also as oil atomized [14] grade.

The main surface related problems when sintering powder compacts are a) avoiding oxidation by interaction with the atmosphere and b) removal of the oxide layers covering each powder particle. The former problem can be solved by using sufficiently pure protective gases but the latter one is present also in very clean, i.e. non-oxidizing, environment. For proper sintering of these materials it is necessary to identify the temperature ranges within which the deoxidation preferentially takes place. It has been shown earlier [15-18] that the degassing behaviour of carbon containing steels can be studied by thermal analysis in inert atmospheres (vacuum or He). This method gives a quite reliable information about the critical temperature intervals. Within this work, the degassing and reduction behaviour of various unalloyed and alloyed carbon containing PM steels is described.

EXPERIMENTAL TECHNIQUE

The starting powders used are listed in Tab.1. All powder grades were mixed with 1.0 mass% natural graphite and were then uniaxially compacted under die wall lubrication at uniformly 600 MPa pressure. For dilatometric runs, pieces approx. 10 mm long were dry cut and inserted into a pushrod dilatometer Bähr 801, the dimensional change transverse to the pressing direction being recorded. The runs were performed at $10\text{ K}\cdot\text{min}^{-1}$ heating and cooling rates in rotary pump vacuum (cold: approx. $4\cdot 10^{-3}$ mbar). For studying the degassing behaviour, the pressure in the system was continuously recorded.

Tab.1. Nominal composition of the starting powders used (contents in mass%).

Designation	Cr	Mn	Mo	V	Fe
ASC 100.29	-	approx. 0.15	-	-	balance
SC 100.26	-	approx. 0.30	-	-	balance
MSP3.5Mo	-	0.12	3.92	-	balance
KIP 4100	1.0	0.62	0.27	-	balance
KIP 103V	1.0	0.08	0.32	0.29	balance
Astaloy CrM	3.0	-	0.50	-	balance

For DTA/TG/MS investigations, small pieces were cut from the compacts and carefully crushed to form a granulate of 0.5 ... 1 mm particle size. Approx. 400 mg of the granulates were placed into small alumina crucibles which were placed into a simultaneous thermal analyzer Netzsch STA 429 equipped with a quadrupol mass spectrometer Balzers QMG 421 via a two-stage pressure reduction system with alumina orifices. Before each test

run, the system was evacuated and flooded with high purity helium for 3 times. Then the runs were performed by heating at $10 \text{ K}\cdot\text{min}^{-1}$ up to 1400°C , soaking for 10 min and then cooling down at $10 \text{ K}\cdot\text{min}^{-1}$. DTA and thermobalance signals were continuously recorded as were the signals of various mass numbers on the mass spectrometer. The respective signals of an empty run were subtracted in order to eliminate the influence of apparatus characteristics. For the Cr alloyed steels the very high maximum temperature of 1400°C , well above the solidus, was selected in order to ensure maximum reduction effect. Furthermore, a second run was done each to check if complete de-gassing had been attained.

DEGASSING OF CARBON STEEL COMPACTS

Fe-1% C from atomized iron powder

With all the materials tested, pronounced degassing (pressure vs. time) curves were obtained in the dilatometer, and clearly defined TG/DTA/MS plots could be recorded; the second run did not reveal any marked pressure change in the dilatometer or mass loss in the STA. This indicates that deoxidation in the first run had been quite complete, which is not surprising with respect to the high maximum temperatures attained.

In Figures 1 and 2 the dilatometric and pressure graphs as well as TG/DTG/DTA curves are plotted for Fe-1.0% C prepared from water atomized iron powder. It is clearly evident that there is quite surprisingly good agreement between the two techniques. In both cases the trends are strikingly similar, and also the relevant temperatures are in good agreement, indicating that degassing and carbothermic reduction proceed in a virtually identical way in vacuum and flowing helium, respectively. At low temperatures some mass loss occurs over a rather broad temperature range, in agreement with a pressure increase in the dilatometer. Further on, there is a very pronounced mass loss rate/pressure peak within a small temperature interval at about 700°C , closely below the onset of the α - γ transition which is discernible from the DTA and to a small extent also the dilatometric (length) signals. A less pronounced, but in total larger, mass loss, coinciding with a broad pressure peak in the dilatometer, occurs between 950 and 1100°C . Typically the processes are strongly dependent on the temperature but are virtually independent of time, i.e. during isothermal soaking periods there is always a decrease of the pressure, and only after further heating the pressure rises again.

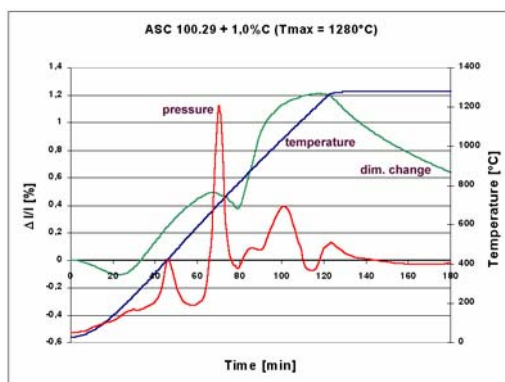


Fig. 1. Dilatometric and pressure graphs for Fe-1.0% C. $10 \text{ K}\cdot\text{min}^{-1}$, vacuum.

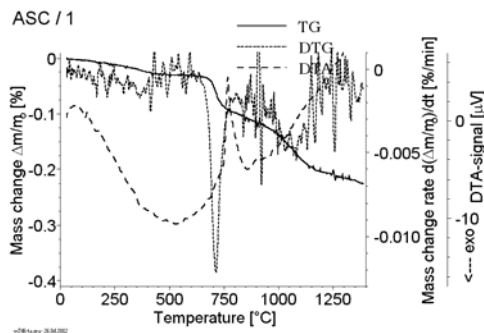


Fig.2. DTA/TG/DTG plot of Fe-1.0% C (ASC 100.29) vs. temperature.
Heating/cooling rate $10 \text{ K} \cdot \text{min}^{-1}$, helium.

In Figure 3, spectra for various masses are shown for Fe-C. Apparently the most pronounced signals are caused by mass 28 which in principle could be N_2 or CO. However, the virtually identical graph shown by mass 12 (carbon) indicates that mass 28 is CO here and not N_2 . Furthermore, also mass 44 (CO_2) shows a very similar behaviour in the medium temperature range, indicating that Boudouard's equilibrium is fulfilled here. The pronounced m44 peak in the range $300\text{--}400^\circ\text{C}$ without any m12 peak there is in agreement with Boudouard's equilibrium which strongly favors CO_2 at low temperatures and CO at higher ones. Finally, mass 18 is detected at $T < 500^\circ\text{C}$, in two temperature intervals, probably linked to desorption of H_2O and dissociation of hydroxides, respectively.

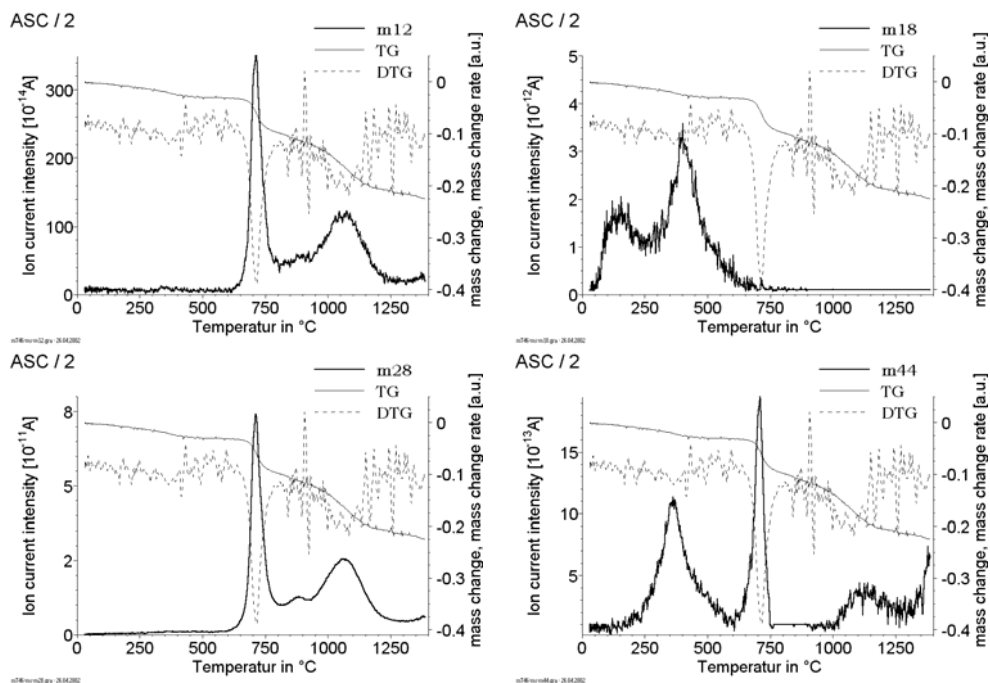


Fig.3. Mass spectra for m12, m18, m28, and m44 of Fe-1.0% C (ASC 100.29)

vs. temperature. Heating/cooling rate $10 \text{ K} \cdot \text{min}^{-1}$, helium.

It seems therefore that the de-gassing of Fe-C (but also with Mo, Cu and Ni, see below and [16]) occurs in three temperature intervals, i.e. $250 \dots 400^\circ\text{C}$, about 700°C , and $900 \dots 1050^\circ\text{C}$, the peak at 700°C being the most pronounced one. The gases formed are CO and, at lower temperatures, CO_2 and H_2O , i.e. the de-gassing process in fact indicates primarily the carbothermic reduction of the oxides contained by the powder particles. Furthermore, it can be concluded that the fairly simple technique of recording the pressure in the dilatometer gives a surprisingly good agreement with the very sophisticated STA/MS equipment.

Influence of the admixed carbon content

Since the reducing agent in the PM steels both in He and vacuum is exclusively carbon, the role of the carbon content can be regarded as critical. Higher carbon activity should enhance reduction, e.g. by shifting the reduction to lower temperatures.

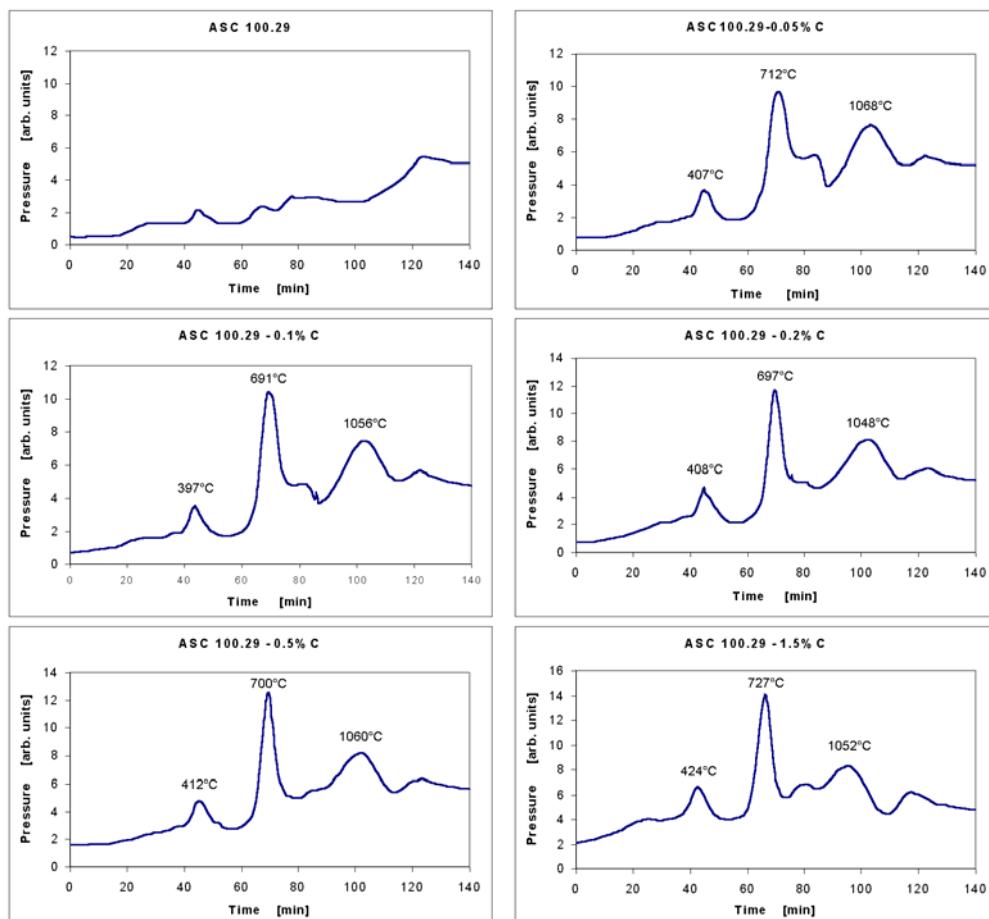


Fig.4. Degassing curves (dilatometric run) for Fe-x% C (ASC 100.29; x = 0.05...1.5% C).

In order to investigate the influence of the admixed carbon content, dilatometric runs were performed in vacuum using Fe-x% C compacts. The carbon content was varied between 0.05 and 1.5% admixed, with plain iron as reference. The resulting pressure graphs are given in Fig.4 Here it stands out clearly that while in the carbon-free reference material none of the pressure peaks is found and only the background pressure slightly increases during heating, even at 0.05% C the degassing behaviour is very similar to that found at higher carbon contents, and between 0.2% and 1.5% C the graphs are virtually identical. Also the temperatures of the degassing maxima are only marginally shifted. That the degassing peaks found at lower temperatures, i.e. up to 700°C, are hardly affected is not surprising since the chemical activity of carbon is unity for all compositions as long as carbon is not dissolved in the matrix. Since dissolution does not occur at temperatures below at least 800°C [19, 20] the degassing phenomena found at 250...400°C and at 700°C are surely caused by reaction with plain graphite, and therefore the thermodynamic conditions for reduction are the same for various carbon contents. At the third degassing maximum, however, there should be at least some influence of the concentration of – now dissolved – carbon. If the peak temperatures are compared there is however at best a marginal shift to higher temperatures in the case of low C contents.

The reason for this effect might be that for reduction of internal oxides, as is supposedly the process responsible for this third degassing maximum, the limiting process might be rather the diffusion of oxygen out of the particle cores. Under the conditions given here, carbothermic reduction of iron oxides is thermodynamically possible even at rather low carbon activities, and since the reduction can only take place at the surfaces (at least in the case of water atomized and therefore internally dense powders) the reduction (and CO formation) rate is controlled by the rate of oxygen diffusion in austenite. Even the comparatively low carbon activity present in the case of low carbon steels is sufficient to cause reduction as soon as the oxygen reaches the surface. On the other hand, the high carbon activity in the high carbon materials is of little use here since the equilibrium is strongly in favour of reduction anyhow.

Influence of the iron powder particle size

At first it was not quite comprehensible why carbothermic reduction of oxides occurs in two different temperature intervals (the low temperature peak being attributed to evaporation and decomposition processes). The only reasonable explanation was that the oxygen originated from different sources, i.e. the reduction at about 700°C involves the surface oxygen and the process at higher temperatures the oxygen present within the powder particles. In this case there should be a considerable effect of the starting powder size since the specific surface is larger for fine powders and on the other hand the diffusion paths for the oxygen from the interior should be shorter. I.e. the peak at 700°C should be more pronounced with compacts prepared from finer starting powders and the peak commonly found at about 950..1050°C should be probably smaller and at least slightly shifted to lower temperatures.

Dilatometric experiments were thus carried out with compacts prepared from various iron powder fractions. The pressure graphs are given in Fig.5. It is evident that in fact the degassing peak at 700°C is the more pronounced the finer the starting powder was, which is understandable due to the larger specific surface there and the resulting higher content of surface oxygen. On the other hand, the peak in the temperature range 900..1100°C is less pronounced for the finer material while it is significantly more pronounced in the case of coarse starting powders, and also the peak maximum is shifted to higher temperatures, the more, the coarser the starting powder was, which supports the

above hypothesis that the third degassing peak is caused by internal oxygen. If this internal oxygen is detrimental for the mechanical properties and if yes, to which extent, is difficult to assess; however, for Fe-C this question is not so relevant since the common sintering temperatures are well above the degassing temperatures even for internal oxygen. For Cr alloy steels things are different, as will be shown below.

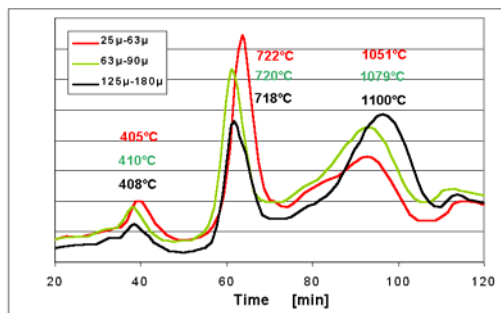


Fig.5. Degassing curves (dilatometric run) for Fe-0.5% C from different powder fractions. $10 \text{ K} \cdot \text{min}^{-1}$, vacuum.

Comparison of water atomized and sponge iron powder grades

It is well known that sponge iron powders contain internal porosity within the particles and that their oxygen content is significantly higher than that of the atomized powder grades. Therefore it could be assumed that for sponge iron the ratio between surface and internal oxygen would be shifted towards the latter, and this should result in more pronounced reduction at higher temperatures.

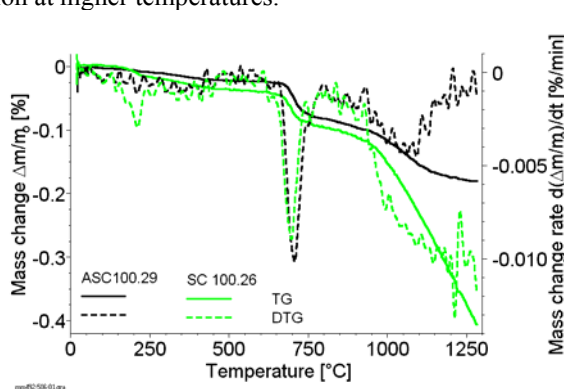


Fig.6. TG/DTG graphs for Fe-0.8% C prepared from water atomized and sponge iron powders, respectively. $10 \text{ K} \cdot \text{min}^{-1}$, flowing He.

Therefore, compacts Fe-0.8% C were prepared from atomized iron powder ASC 100.29 and sponge iron powder SC 100.26 and investigated in parallel in the dilatometer and the STA with mass spectrometry. Once more the pressure graphs from the dilatometer and the TG/DTG/MS graphs were in excellent agreement. Here, TG/DTG graphs are shown in Fig.6; it is clearly evident that at low to medium temperatures the degassing and reduction behaviour of both powder types is almost identical, with the characteristic mass loss rate peak at 700°C ; also the mass loss itself is the same, being 0.05% in both cases. At

higher temperatures, however, there are pronounced differences: while for the compact from atomized powder the mass loss rate shows the third maximum at about 1050°C and then rapidly diminishes, in the case of sponge iron powder the mass loss continues at a significant rate up to the maximum temperature of 1300°C, and even in the second run the heating TG graph shows slight mass loss at higher temperatures. The mass loss in the temperature range >900°C is 0.07% for the atomized material but 0.30% for the sponge grade.

This indicates that in fact the amount of oxygen present in the interior of the powder particles is removed drastically more slowly than the surface oxygen covering the powder particles. From the appearance of the starting powder it might be assumed that the oxygen present within the sponge iron particles is also surface oxygen since it covers the internal pores which are at least to some extent open to the surface. Here however it must be kept in mind that this holds for the starting bulk powder but not at all for the powder particles after compaction. Although it is well established that sponge iron powders are slightly less compactible than atomized ones and that this difference is at least partly due to the internal pores, the difference in green density is only about 0.2-0.3 g.cm⁻³, and this indicates that the internal pores are mostly eliminated, but at least completely closed during pressing, and therefore removal of the internal oxygen has to occur through diffusion processes, quite similar to the case of atomized powders, with the difference that sponge iron particles contain much more internal oxygen, in part from the larger internal surface, and in part from slag impurities.

DEGASSING BEHAVIOUR OF ALLOYED STEELS

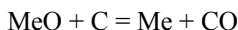
Cr-Mo prealloyed steel containing 1.0% C

Cr prealloyed steel powders are manufactured by water atomisation followed by a reduction process to remove the thick oxide layers generated during atomisation. This reduction is done either in vacuum, carbon contained by the powders being used as reducing agent [13] or in H₂ containing atmosphere [11]. In both cases, the oxide layers are effectively reduced but some reoxidation occurs during cooling and handling of the powders. Typical oxide contents are in the range of 0.15 mass% as compared to 0.08% for plain iron powder, i.e. not drastically more. However it is of course not only the amount of oxygen present but also the stability of the respective oxide(s) that controls the degassing/reduction behaviour, Cr oxides being significantly more stable than those of Fe, Mo, Ni, or Cu.

Therefore, carbothermic reduction of Cr containing steels can be regarded to be markedly more difficult than that of unalloyed or e.g. Mo alloyed ones due to the higher thermodynamic stability of the Cr oxides, and only at higher temperatures the stability e.g. of Cr₂O₃ is low enough and on the other hand the reducing power of CO is high enough to result in sufficient reduction of the Cr oxides. Here, it has to be kept in mind that for CO its free energy of formation becomes more negative at higher temperatures [5] (due to the increase in entropy when forming 2 moles of CO from one g-atom of O₂) while with virtually all other oxides, also H₂O, ΔG_r becomes less negative, i.e. the oxides are less stable thermodynamically. Therefore, carbon is less effective a reducing agent than H₂ at lower temperatures but becomes more effective at higher ones.

This also has significant implications on the practice of sintering: If the respective thermodynamic stability of the oxides is taken from the literature as the Gibbs free energy of formation (e.g. [5, 21]), and the activity coefficients are taken e.g. from [22] the

reduction of the (surface) oxides can be calculated, at least at higher temperatures following the basic equations:



and for the equilibrium constant $K_p = a_{\text{Me}} \cdot p_{\text{CO}} / a_{\text{MeO}} \cdot a_{\text{C}}$

For a given composition (i.e. activity of Fe or Cr and of C) the critical parameter is the CO partial pressure; it controls if reduction or oxidation takes place. If $p_{\text{CO}} < P_{\text{CO,eq.}}$, carbothermic reduction occurs, otherwise the atmosphere oxidizes the metal.

This partial pressure has been calculated for Fe-C and Fe-3% Cr-C with varying C contents using the literature data cited above; the graphs $p_{\text{CO, eq.}}$ vs. temperature are given in Fig.7. From this graph can be clearly derived that at the standard sintering temperatures of 1000...1250°C unalloyed carbon steels can be sintered even in plain CO atmosphere. For the Cr containing steel, on the other hand, the critical CO partial pressure is much lower, and even at the highest sintering temperatures that are technically feasible the commonly used atmosphere endogas, which contains about 20% CO, is in fact an oxidizing atmosphere for this sintered steel. It is also evident that the influence of the carbon content – i.e. the carbon activity – is comparatively small compared to the effect of Cr addition.

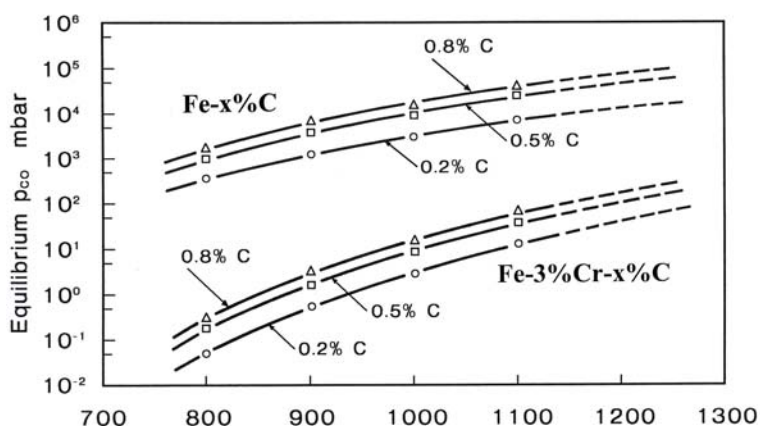


Fig.7. Equilibrium CO partial pressure as a function of the temperature for the carbothermic reduction of oxide in Fe-C and Fe-3% Cr-C, respectively.

The DTA/TG/DTG graph for a Cr-Mo alloyed powder compact, prepared from the prealloyed powder Astaloy CrM, is shown in Fig.8a. It is clearly evident that compared to Fe-C the Cr alloy steel exhibits the maximum of mass loss rate at significantly higher temperatures, the de-gassing peak at about 700°C being marginal. This confirms the prediction from Fig.7 that indicates that the reduction of the oxides present in Cr alloy powders is shifted to higher temperatures.

Typically, however, also here two de-gassing maxima are observed (in addition of that at 250...400°C) as with Fe-C, but the temperatures are shifted to considerably higher ranges. For Astaloy CrM the mass loss rate maxima are found at 1000°C and 1200-1250°C, respectively, and are similar in intensity. In order to illustrate the effect of Cr compared to other, more conventional alloy elements in PM steels, another steel containing the same mass% of alloy metal but as Mo exclusively was also investigated (see Fig.8b), and the TG/DTG graphs for this MSP3.5Mo steel closely resemble those for unalloyed Fe-C, with

the typical sharp mass loss rate peak at about 750°C (slightly shifted compared to Fe-C, see [16]) and a broader peak at about 1000 to 1100°C.

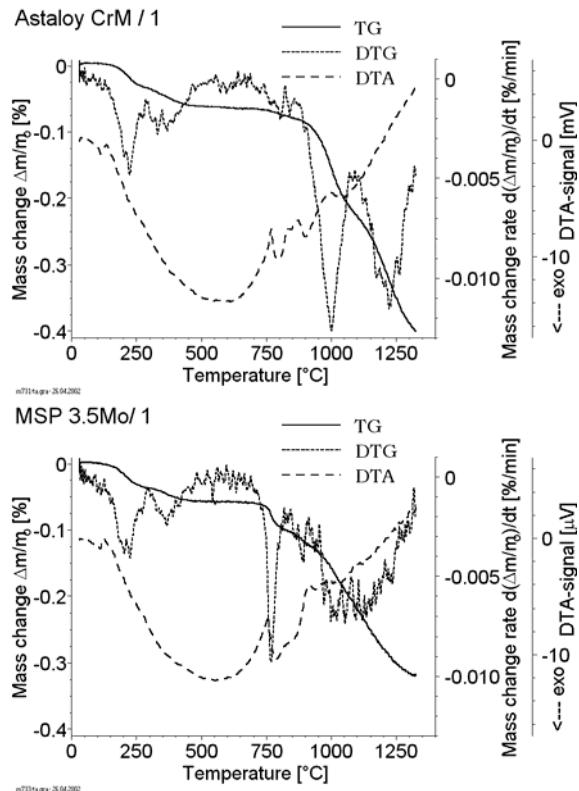


Fig.8. DTA/TG/DTG plot of Astaloy CrM-1.0% C and MSP3.5Mo-1.0% C, resp., vs. temperature. Heating/cooling rate 10 K.min⁻¹, helium.

Astaloy CrM, in contrast, requires 1000°C minimum to attain at least some carbothermic reduction, once more the first mass loss rate maximum being attributed to removal of the surface oxides. In [4] it has been shown that 1000°C also the minimum sintering temperature necessary for formation of metallic contacts since the oxide layers covering the powder particles inhibit formation of sintering bridges and also retard dissolution of carbon in the matrix; only after their removal the usual sintering processes taking place. It is difficult to assess if it is sufficient to exceed the temperature of the first maximum, i.e. to remove the surface oxygen, and leave the internal one in place, which is the case when sintering at the standard temperature of 1120°C. However, systematic investigations with Astaloy CrM with varying C contents [23, 24] have shown that this material is very much improved by increasing the sintering temperature, much higher impact toughness levels being attained without loss in hardness and strength. This can be taken as an indicator that also the internal oxygen has some detrimental effect on the properties of the Cr-Mo alloyed steels.

If the various mass spectra for Astaloy CrM are taken as a function of the temperature (Fig.9), the typical reduction behaviour of this steel stands out quite clearly, and the mass loss rate maxima are in excellent agreement with the signals for the reduction

products. Once more, the degassing is predominantly caused by formation of CO (corroborated by the virtually parallel graph for m12) and at lower temperatures some CO₂, following Boudouard's equilibrium. Generally the natural carbon loss in the Cr alloy steels should be slightly higher than with Fe-C or Fe-Mo-C since the reduction occurs at temperatures at which the formation of CO₂ is negligible and therefore more carbon is consumed per mass% O removed.

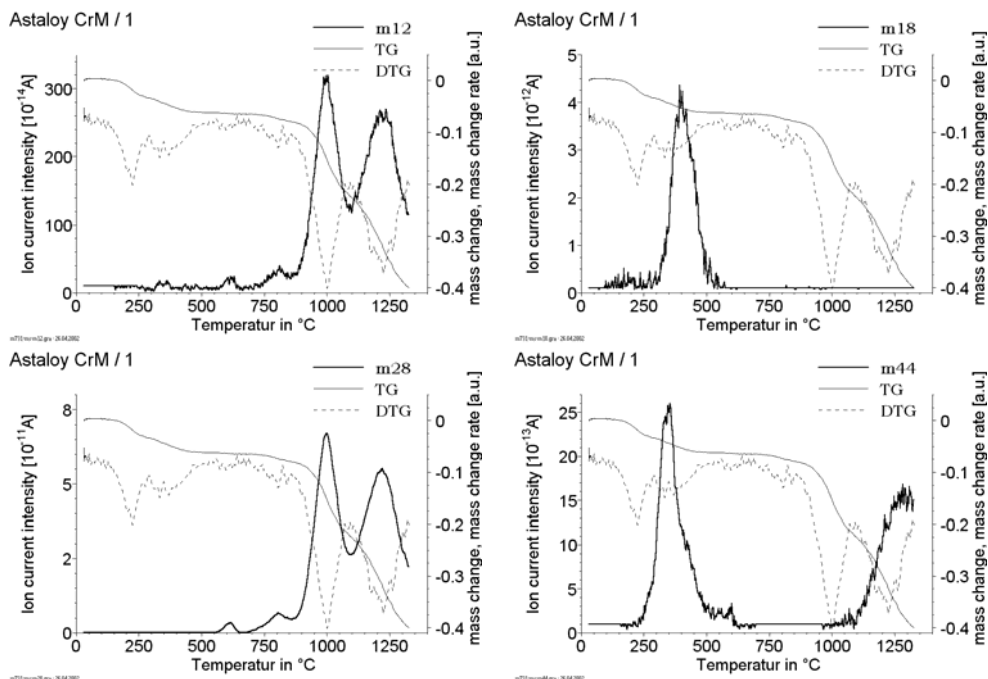


Fig.9. Mass spectra for m12, m18, m28, and m44 of Astaloy CrM-1.0% C vs. temperature. Heating/cooling rate 10 K.min⁻¹, helium.

Removal of water (m18) is discernible only in the low temperature range, i.e. dissociation and desorption are of minor relevance compared to reduction; the comparatively high temperature of the m18 peak can be taken as an indicator that dissociation of hydroxides dominates compared to desorption of physically bonded water.

Cr-Mo steels with varying carbon content

For unalloyed steels the carbon content was found to be of marginal importance for the degassing behaviour; as soon as some carbon is present the typical gas peaks typical for reduction appear. From the calculations given e.g. in Fig.7, similar results were expected also for Cr alloyed steels. Nevertheless, due to the critical importance of the reduction esp. for these materials, experimental verification was regarded essential, the more, since for attractive applications as. E.g. for case hardened gears low admixed carbon contents can be expected that nevertheless also have to afford sufficient reduction.

Therefore, thermal analysis was performed on Astaloy CrM compacts with carbon levels varying between 0.2% and 1.0%. The TG and DTG graphs are shown in Fig.10. Here it is clearly visible that the graphs are in fact rather similar for all carbon levels which indicates that the effect of the carbon content on the degassing/reduction behaviour is

comparatively small also for the Cr alloyed steels. One exception is of course the carbon-free material which exhibits a virtually horizontal TG graph with a hardly discernible mass loss in the range 200–300°C. This is however not surprising since in this case there is no reducing agent – carbon or hydrogen – present in or around the material. The results also indicate that the amount of volatile (e.g. adsorbed H_2O) and dissociating (e.g. hydroxides) compounds is too low to have any marked impact on the specimen mass; otherwise at least some significant mass loss would have been observed. (The fact that there is no increase in mass either indicates that the testing atmosphere was really oxygen-free and the equipment was airtight).

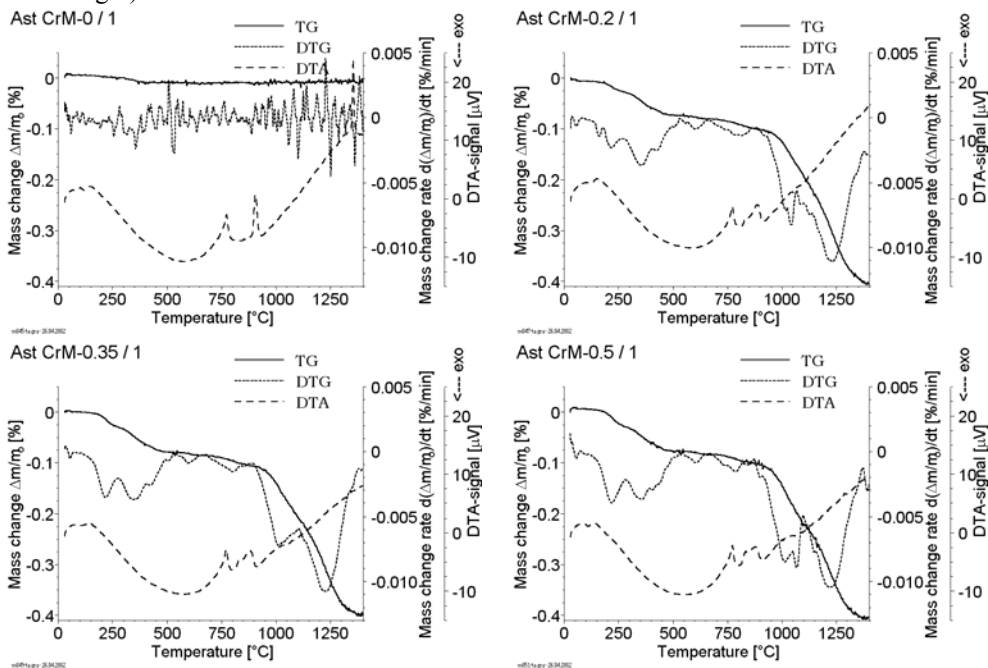


Fig.10. TG/DTG/DTA graphs for Astaloy CrM-x% C vs. temperature.

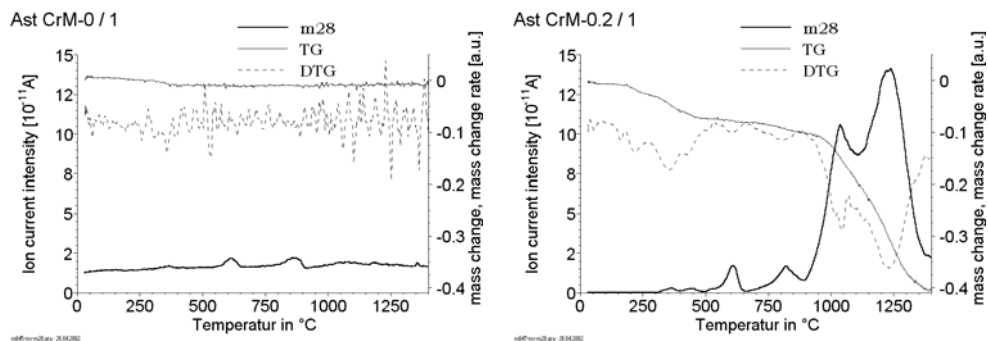


Fig.11. Mass spectra for m28 (CO) of Astaloy CrM-x% C.

In Figure 11 the graphs for m28 are given for the carbon-free material and for 0.2% C, respectively. In the latter case the m28 graph is virtually a reverse plot of the DTG graph, confirming that the mass loss observed, at least at $T > 500^\circ\text{C}$, is primarily due to the formation of CO. The fairly small influence of the carbon content is once more visible if comparing the graph with that obtained for 1.0% C (see Fig.9); the only visible effect is a markedly smaller first peak (at 1000°C) compared to the second one at 1250°C for the low carbon variants while for those with higher C level the first peak is even slightly higher. The carbon-free material exhibits only very small m28 signal variations from the base line, typically at 600°C – where also the C containing materials have a small peak – indicating some reaction within the base powder, without any effect of admixed graphite.

All other signals are less pronounced. That one for m44 shows a pronounced peak at about 350°C that is virtually identical for all carbon levels. Only in the carbon-free material this peak is markedly lower but still clearly discernible, indicating that also the small amount of C present in the atomized powder can have some effect. Apparently this peak indicates the first carbothermic reduction step that forms CO_2 and not CO, following Boudouard's equilibrium. The graph for m12 (carbon) once more is almost identical to the m28 signal, but of course at lower intensity. Only at low temperature, at about 350°C , an additional signal is discernible that however coincides with the m44 signal found there since the signal for C must follow not only CO but also CO_2 .

The signal for water, m18, finally shows a pronounced and relatively broad peak in the temperature range $300 \dots 500^\circ\text{C}$ (Fig.12). Somewhat surprisingly, also this signal is more pronounced with the graphite containing materials than with plain Astalloy CrM, which can be taken as an indicator that at least part of the water set free in fact also originates from the admixed fine graphite. The remaining H_2O seems to originate rather from hydroxides at the surfaces of the metal powder than from adsorbed water at the steel powder since in the latter case a more pronounced signal at $T < 200^\circ\text{C}$ would have been expected.

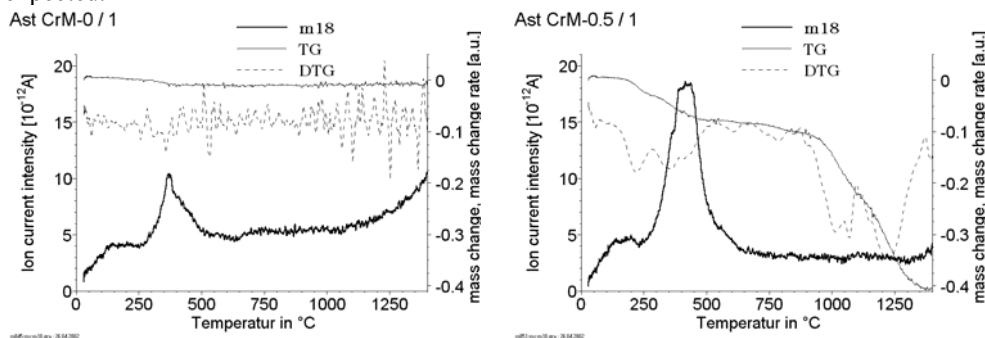


Fig.12. Mass spectra for m18 (H_2O) of Astalloy CrM-x% C.

Cr-Mo-X prealloyed steels

In addition to the Cr-Mo steel powders, also more complex powder systems containing Cr-Mn-Mo and Cr-Mo-V are available, manufactured through water atomisation with subsequent vacuum anneal. The former composition, designated KIP4100, is the typical AISI 4100 material well known in its ingot metallurgy variants; the latter, KIP103V, is a newer development aiming at improved as-sintered microstructure, i.e. very fine pearlite in place of the coarse upper bainite found in the Cr-Mn-Mo material [12].

Form both powder grades compacts containing 1.0% C were prepared and investigated in the STA 409. DTA/TG/DTG graphs are depicted in Fig.13 and 14.

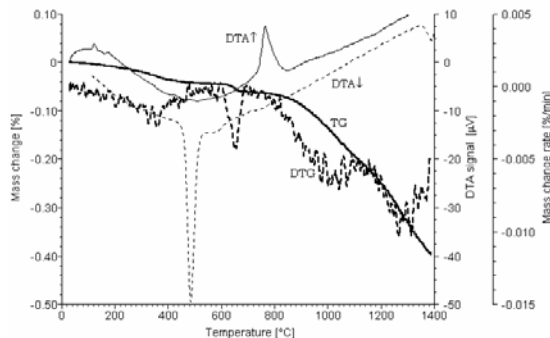


Fig.13. DTA/TG/DTG plot of KIP 4100-1.0% C vs. temperature.
Heating/cooling rate $10 \text{ K} \cdot \text{min}^{-1}$, helium.

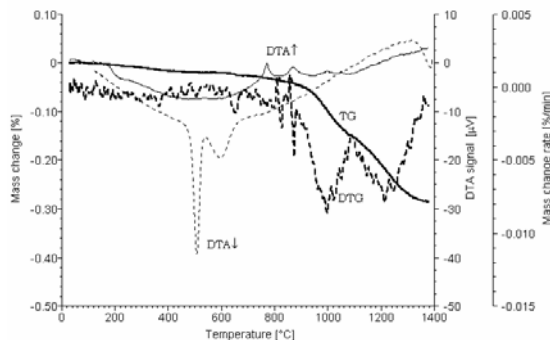


Fig.14. DTA/TG/DTG plot of KIP 103V-1.0% C vs. temperature.
Heating/cooling rate $10 \text{ K} \cdot \text{min}^{-1}$, helium.

As clearly visible there are significant differences between the powder grades: KIP 4100 (Fig.13) shows a small but well defined DTG peak at about 650°C , i.e. even below that found with Fe-C, but most of the mass loss occurs above 850°C more or less continuously – similar to the effect with sponge iron powder – , some maxima being found at about 1000°C and, slightly more pronounced, at 1300°C . With KIP 103V, on the other hand (Fig.14), the peak at 650°C is hardly noticeable, but in the higher temperature range the mass loss rate peaks are much more clearly defined than with 4100, with maxima at 1000°C and 1200°C , respectively, and above 1350°C hardly any mass loss is found at all. In that respect the Cr-Mo-V material is fairly similar to Astaloy CrM, i.e. the – rather small – V content does not affect the carbothermic reduction too much. Mn addition in contrast seems to retard the degassing process; maybe the oxides, esp. the internal ones, are more strongly bonded due to the higher stability of MnO compared to Cr_2O_3 [21] and also due to the sequence of Mn oxides with increasing thermodynamic stability, i.e. $\text{MnO}_2 - \text{Mn}_2\text{O}_3 - \text{Mn}_3\text{O}_4 - \text{MnO}$, which results in a more complicated and probably also slower reduction process.

CONCLUSIONS

- The reduction/degassing behaviour of sintered steels can be studied by DTA/TG/MS measurements in He atmosphere, but also recording the pressure in dilatometric runs done in vacuum gives at least qualitatively a realistic image that agrees well with that obtained by the more sophisticated and more expensive thermoanalytical methods.
- For Fe-C - and for Fe-Mo-C - , mass loss during heating occurs predominantly in the range 700°C and 950 ... 1100°C, the former peak being more pronounced but the latter bringing the larger total mass loss. Both peaks are caused by formation of CO and some CO₂, following Boudouard's equilibrium. At low temperatures – 250...400°C – some less pronounced degassing is observed that is caused by formation of some CO₂ but predominantly H₂O. The sequence and intensity of the peaks is only slightly affected by the admixed carbon content, 0.05% C being already sufficient to generate the typical degassing pattern.
- The gas formation processes are strongly dependent on the temperature but virtually independent of time
- The two CO/CO₂ peaks can be attributed to removal of oxygen present at the surface and the interior of the powder particles, respectively. This is corroborated by the fact that with finer starting powder the peak at 700°C is more pronounced while that at 950..1100°C is stronger in the case of coarse ones and is also shifted to higher temperatures.
- Sponge iron powders, which initially contain more oxygen, exhibit a much more pronounced mass loss in the high temperature range >900°C that continues at least up to 1300°C. This can be attributed at least in part to the oxygen from the internal pores in the powder particles which are closed during compaction, thus preventing easy oxygen removal.
- With Cr containing steels prepared from prealloyed powders, the mass loss at the lower temperature is insignificant, most of the de-gassing occurring at temperatures >1000°C due to the higher thermodynamic stability of the oxides. 3Cr-Mo steels exhibit two pronounced degassing maxima at 1000 and 1250°C, respectively, the former being linked to reduction of surface oxides which process is essential for formation of metallic sintering contacts.
- Cr-Mn-Mo alloyed steels exhibit fairly continuous de-gassing up to about 1400°C while Cr-Mo-V variants are similar to Cr-Mo ones, showing two distinct mass loss rate maxima at 1000 and 1200°C, respectively,
- For sintering of Cr containing steels made of prealloyed powders, sufficiently high sintering temperatures should be selected to ensure as complete reduction of the oxides as possible to ensure excellent mechanical properties.

Acknowledgement

This work was in part carried out within the project “Höganäs Chair”. The authors wish to thank Höganäs AB, Sweden, QMP Metal Powders GmbH, Germany, and Kawasaki Steel, Japan, for supplying the starting powders used.

REFERENCES

- [1] Gille, G., Leitner, G., Roebuck, B. In: Proc. Europ. Conf. Adv. Hard Metals Prod., Stockholm, Shrewsbury : EPMA, 1996, p.195
- [2] Salak, A.: Ferrous Powder Metallurgy. Cambridge : Cambridge Int. Sci. Publ., 1995
- [3] Slesar, M., Dudrova, E., Parilak, L., Bersterci, M., Rudnayova, E.: Sci. Sintering,

- vol.19, 1987, p.17
- [4] Kremel, S., Raab, C., Danninger, H. In: Proc. EuroPM2001, vol. 1, Nice. Shrewsbury : EPMA, 2001, p.52
 - [5] Froberg, MG.: Thermodynamik für Metallurgen und Werkstofftechniker. Leipzig : Dt.Verlag für Grundstoffind., 1980
 - [6] Lindqvist, B. In: Proc. EuroPM2001, vol. 1, Nice. Shrewsbury : EPMA, 2001, p.13
 - [7] Tengzelius, J., Grek, SE., Blände, CA.: Modern Dev. in Powder Met., vol. 13, 1981, p.159
 - [8] Sanderow, HI., Rodriguez, HA., Ruhkamp, JD.: Progr. Powder Met., vol. 41, 1985, p.283
 - [9] Danninger, H. In: Proc. Int. Conf. on P/M in CSFR, Piestany, 1992, vol.1, p. 81
 - [10] Salak A., Danninger, H., Selecka, M., Unami, S. In: Proc. Int. Conf. Deform. & Fract. Struct. PM Mater., vol. 1, Piestany. Ed. L.Parilak, H.Danninger. Kosice : IMR-SAS, 1999, p. 167
 - [11] Hull, M.: Powder Metall., vol. 41, 1998, no.4, p. 232
 - [12] Unami, S., Ogura, K., Uemono, S. In: Proc. 1998 Powder Metall. World Congress, Granada, vol. 3. Shrewsbury : EPMA, 1998, p. 173
 - [13] Ogura, K.: Metal Powder Rep., vol. 42, 1987, p. 292
 - [14] Karasuno, I., Koshiro, K., Umino, M., Ishidate, M. In: Proc. PM'86, vol. 1, Düsseldorf, 1986, p. 53
 - [15] Danninger, H., Leitner, G. In: Sintering Technology. Ed. R.M.German, G.L.Messing, R.G.Cornwall. Marcel Dekker, 1996, p. 165
 - [16] Danninger, H., Wolfgruber, E., Ratzi, R. In: Proc. Euro PM'97, Munich. Shrewsbury : EPMA, 1997, p. 99
 - [17] Danninger, H., Gierl, C., Leitner, G., Jaenicke-Rößler, K. In: Proc. 1998 Powder Metall. World Congress, vol. 2, Granada. Shrewsbury : EPMA, 1998, p. 342
 - [18] Danninger, H., Gierl, C., Leitner, G., Jaenicke-Rößler, K., Unami, S. In: Sintering Science & Technology. Proc. Int. Conf. Sintering '99. Ed. R.M.German, G.L.Messing, R.G.Cornwall. State College : Pennsylvania State Univ., 2000, p. 9
 - [19] Danninger, H., Gierl, C.: Mater. Chem. & Physics, vol. 67, 2001, p. 49
 - [20] Danninger, H., Frauendienst, G., Streb, K.-D., Ratzi, R.: Mater. Chem. & Physics, vol. 67, 2001, p.72
 - [21] Glassner, A.R.: The thermochemical properties of the oxides, fluorides, and chlorides to 1500°K. U.S. Atomic Energy Comm. Rep. ANL-5750, 1957
 - [22] Lundberg, R., Waldenström, M., Uhrenius, B.: CALPHAD, vol. 1, 1977, no. 2, p. 159
 - [23] Campos, M., Kremel, S., Marcu Puscas, T. In: Proc, EuroPM2000 Conf. on Materials and Processing Trends for PM Components in Transportation, Munich. Shrewsbury : EPMA, 2000, p. 47
 - [24] Danninger, H., Kremel, S., Altena, H., Yu, Y. In: Proc. PM Auto'02. 3rd Int. Conf. on Powder Metall. for Automotive Parts, Isfahan. Ed. H.Danninger, A.Arvand. Tehran : MPM Co., 2002, p. 26-1