DILATOMETRY COUPLED WITH MS AS INSTRUMENT FOR PROCESS CONTROL IN SINTERING OF POWDER METALLURGY STEELS

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Abstract

The production of ferrous powder metallurgical parts by the press-and-sinter route becomes more and more attractive. Today, parts are produced for loading requirements that until now only could be fulfilled by conventional produced steel components. The high mechanical properties that must be attained require the use of alloying elements so far not common in powder metallurgy because of their high affinity for oxygen. The sintering of chromium containing steels is a challenge for the whole production process, because the reduction of the surface oxides is critical for successful sintering.

Dilatometry can be a useful instrument to control the sintering behaviour of the materials, especially the combination with mass spectroscopy allows analysing the very complex sintering process and simultaneously monitoring the solid-gas reactions. This work shows that the sintering atmosphere plays a major role in the whole process. Degassing and desoxidation processes during sintering are demonstrated for different alloying systems (Fe, Fe-C, Fe-Mo-C, Fe-Cr-Mo-C). Dilatometry coupled with MS is shown to be a very good instrument for process control of the sintering process. The generated analytical data can be related to the mechanical properties of the sintered steels if the size of the specimen is large enough.

Keywords: sintered steels, thermal analysis, sintering behavior

INTRODUCTION

In the production of iron based structural powder metallurgical (PM) parts, the sintering process is a critical step to fulfil the requirements concerning mechanical and dimensional properties. In the last 50 years the sintering of the parts usually was no problem from the chemical viewpoint because the alloying elements used are easy to reduce and their oxides are less stable than iron oxides, as in the case of Ni, Cu and Mo. This means that the removal of the surface oxides becomes possible at low temperatures and in atmospheres of low purity. This deoxidation process is critical for successful sintering because otherwise no metal-metal contact is possible to allow forming sintering bridges by diffusion processes. The parts thus produced were of complex shape, but the mechanical properties were rather low [1,2].

Nowadays the aim to produce parts which can be more highly mechanically loaded leads to several techniques. Some of them are designed to eliminate porosity, such as powder forging for the whole part or rolling techniques for surface densification which strengthen the gears wherever the rest of the part stays porous. The second approach is to

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introduce alloying elements as Cr, Mn, Si or V [3-5] which are the main work horses for ingot metallurgy to produce heat treatable steels. These alloying elements have very positive impact on the hardenability of steels, and their second advantage is that they are much cheaper than the conventional alloying elements used in PM. The reason why their use is still not very common in PM is that the stability of their oxides is much higher. This implies that very much attention has to be paid on the processing conditions of these alloys. In neutral atmospheres the deoxidation process of PM steels alloyed with e.g. Cr is dominated by Cr-oxides and not by Fe-oxides any more [6], and further implies for the sintering process that higher temperatures and atmospheres with higher purity are required to reduce these oxides [7]. In reducing atmospheres the surface condition of the powder is even more important. As shown e.g. in [8-11] the surface of these powders are mainly covered up to 90-95% by an iron oxide layer which constitutes about 50% of the total oxygen amount of the powder. The rest of the surface is decorated by particular features consisting of oxides of the more stable alloying elements – here Cr-oxides or Cr-Fe-oxides. Successful sintering is now a question of processing parameters to reduce the iron-oxide layer with hydrogen before an oxygen transfer from the iron oxide to the more stable ones can happen.

To study the sintering process, dilatometry is commonly used, but it gives no information about the degassing process, except in vacuum where significant degassing peaks can be observed simply by recording the pressure in the system [12]. TG/DTA combined with mass spectroscopy is a well established technology for monitoring the degassing processes [12-15], but it has 3 main disadvantages: the samples have to be crushed, and therefore no mechanical properties or microstructures can be studied after the measurement. The method is also limited to inert gases such as nitrogen, helium or argon because hydrogen containing gases will destroy the standard thermocouples made of Pt/Pt10Rh (type S), and can only be overcome by replacing the standard thermocouple by a W/WRe type, which can be operated in reducing atmospheres (H_2 or mixes of H_2 with Ar or N_2). The third disadvantage is that these methods do not provide any information about the sintering behaviour regarding dimensions.

Therefore here it was decided to use dilatometry with coupled MS to monitor the sintering process, which allows to combine the analysis of sintering with regard to dimensional behaviour (by recording the dilatation), the degassing (by MS) and correlate the results to the mechanical behaviour after the sintering process and the resulting microstructure as well.

EXPERIMENTAL PART

The dilatometer used for this study was a Netzsch DIL 402C in which a thermocouple type S was encapsulated in an alumina tube for protection against hydrogen containing gases. The dilatometer was coupled with Netzsch QMS Aeolos, the coupling devices like quartz capillary and coupling heads being heated to 300°C to prevent condensation of any material.

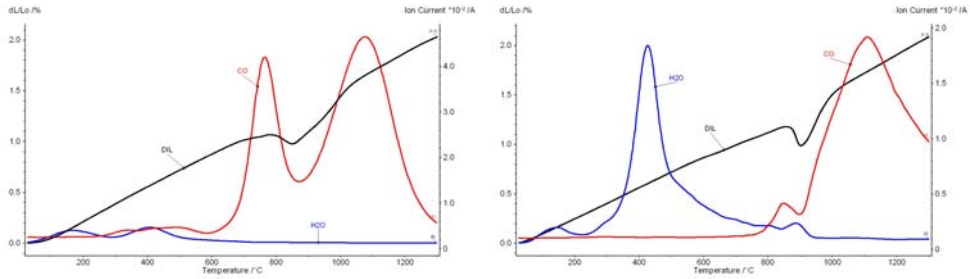
The specimens investigated were prepared from mixed powders (metal + natural graphite) by pressing at 600 MPa pressure in a floating die with die wall lubrication to the approximate size of 55 x 10 x 8 mm^3.

The time-temperature profile used was consistently heating at 10 K/min to the maximum temperature of 1300°C, 60 min isothermal sintering and cooling at 10 K/min to room temperature.

All gases used were of high purity (99.999%, i.e.5.0 quality). The starting metal powders were supplied by Höganäs AB, Sweden, the graphite used was Kropfmühl grade UF4.

The influence of reducing atmosphere on Fe-C

To analyse the difference in degassing behaviour between neutral atmosphere (Argon) and reducing atmosphere (Hydrogen) the system Fe-C was investigated. High purity iron powder (ASC 100.29) was mixed with 0.5w% graphite.



a) Argon b) Hydrogen

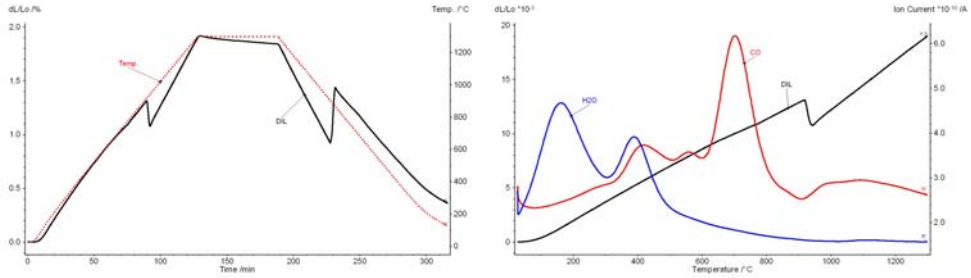
Fig.1. Dilatometry runs of Fe-0.5C coupled with MS. 10 K/min, 1300°C 60 min isothermal, 10 K/min, atmosphere as indicated.

The measurements show clearly that in inert atmosphere (argon) two reduction peaks appear. One rather narrow peak is visible closely before the α–γ transition of the system Fe-C starts, peak maximum at 766°C, indicating the reduction of the surface oxides. The second peak is markedly broader, indicating the reduction of the internal oxides with maximum at 1079°C. For both reduction processes, the main product is CO as indicated by mass 28. The absence of peaks 14 and the presence of mass 12 prove that mass 28 is evidently CO (and not e.g. N_2). In hydrogen the reduction mechanism is slightly different. The surface oxides are reduced at markedly lower temperatures (maximum at 426°C) by hydrogen, generating water as product (mass 18), but the internal oxides are reduced by carbon just as in inert atmosphere at slightly higher temperatures (1107°C), and no water is generated at higher temperatures any more.

The reason for this phenomenon is that by thermodynamical reasons the reducing power of hydrogen is lowered by higher temperatures, but is high at low temperatures, which explains the reduction of the surface oxides in presence of hydrogen. The reducing power of carbon is rather low at low temperatures but rises significantly by shifting to higher temperatures, which means that internal oxides, which are more stable than surface oxides, will be reduced by carbon even in the presence of hydrogen. This knowledge is of extreme importance also because the mechanical properties of the steel are very much influenced by the combined carbon. If some carbon is lost by reducing the oxides, the remaining carbon content in the alloy is markedly lower than the admixed one, which must be considered for the alloy design. It is also interesting to mention, that the α–γ transition in hydrogen starts at higher temperatures although the surfaces are already reduced and there is no interface hindering the carbon to be dissolved. The dissolution of the carbon in the austenite then happens much faster compared to argon atmosphere indicated by the increase of the CTE in the range of 900-1000°C.

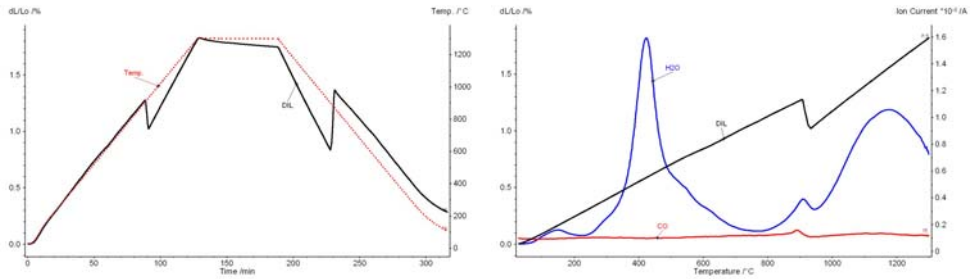
The influence of the atmosphere on carbon free alloys

It was shown above that carbon is one of the most important factors in reducing oxides. Even in pure hydrogen carbon is the reducing agent for the more stable internal oxides. To analyse the behaviour of the carbon free alloys experiments with different alloying systems (Fe, Fe1.5Mo, Fe1.5Cr-0.2Mo, Fe-3Cr-0.5Mo) are performed. The most important questions are: What are the desoxidation processes for carbon-free alloys? Do they contain enough C as impurity to reduce at least the surface oxides sufficiently to enable successful sintering? Do the sintering atmospheres affect the resulting mechanical properties?



a) time vs. Dil b) heating ramp; dil. + MS

Fig.2. Dilatometry runs coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min Argon atmosphere; dil. and temp. vs. time (a) and heating ramp (b).



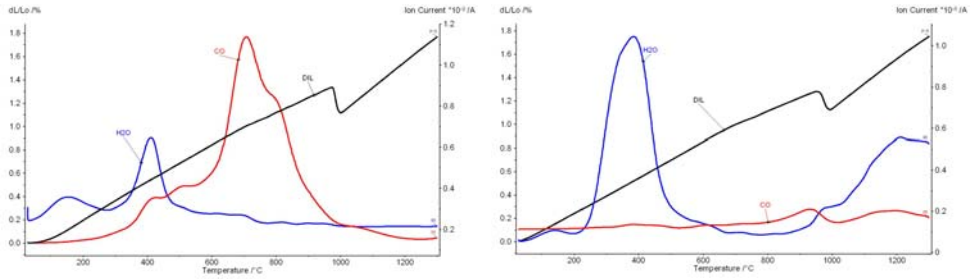
a) time vs. Dil b) heating ramp; dil. + MS

Fig.3. Dilatometry runs of Fe coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min hydrogen atmosphere; dil. and temp. vs. time (a) and heating ramp (b).

The first effect shown in Fig.2a) is the extremely unsymmetrical phase transition behaviour of the pure iron sample. The back transition from γ-iron to α-iron is much more pronounced than the α–γ transition, which effect causes unexpected growth of the sample, as already reported in [16-18]. The MS graphs show that enough carbon as impurity is available in the iron powder to reduce partly the surface and allow successful sintering, although the reduction is obviously not complete and usually leads to very poor mechanical properties (here impact energy is 2.3 J/cm²). Compared to the system containing admixed carbon (Fig.1a) the CO peak is much lower (ion current for mass 28 $6x10^{-10}$ compared to $4.5x10^{-9}$ for carbon containing system).

The analysis in pure hydrogen reveals that anisotropic transition occurs also here and the sample is growing. The main difference to the inert system is that the reduction of the oxides is done by hydrogen generating water (mass 18) for the surface oxides and for

the internal oxides as well. This reduction results in very high impact energies, measured by charpy test of 71.3 J/cm² compared to the extremely low ones in inert atmosphere of 2.3 J/cm². All other properties are comparable (see Tab.1.).



a) Argon b) Hydrogen

Fig.4. Dilatometry runs of Fe-1.5Mo coupled with MS 10K/min, 1300°C 60 min isothermal, -10K/min, atmosphere as indicated.

The addition of 1.5% molybdenum causes a slight stabilisation of the α-phase indicated by a higher onset of the α–γ transition (+5°C) compared to pure iron (873.3°C), and the transition is symmetrical in both atmospheres [17]. The deoxidation of the surface oxides take place at 5°C higher temperatures compared to pure iron. The internal oxides are not reduced which, together with the very low ion current, indicates that the reduction of the surface oxides is incomplete. The little peak of water at about 400°C can be explained by adsorbed water.

In hydrogen the onset temperature of the α–γ transition is a little lower than in Ar, maybe caused by the carbon still present as impurity which stabilizes the γ-phase. The deoxidation of the surface oxides occurs at fairly low temperatures. The internal oxides are reduced at slightly higher temperatures.

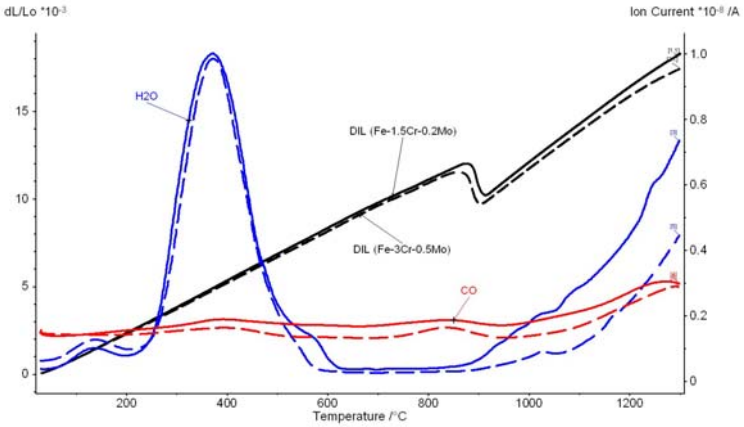
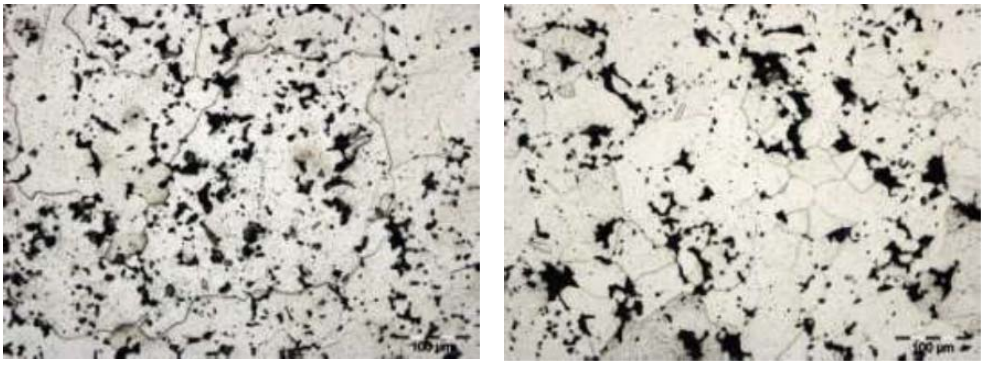


Fig.5. Dilatometry runs of Fe-1.5Cr-0.5C (continuous lines) and Fe-3Cr-0.5Mo (dotted lines) coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min, hydrogen; heating ramp.

The effect of prealloyed Cr (present in the starting powder in solid solution) can be described as follows: the α-phase is stabilized by Cr and Mo as well, therefore the onset temperature of the α–γ-transition is 20°C higher compared to pure iron, and as for molybdenum the transformation is symmetrical. The very stable Cr-oxides allow only a slight reduction of Fe-oxides on the surface at very low temperatures. Internal oxides and all Cr-oxides are not (or not completely) reduced at the sintering temperature of 1300°C in H_2 atmosphere. Both systems show very similar behaviour, only the reduction of the Cr-oxides starts at slightly lower temperatures for the alloy containing less Cr (900°C compared to 1100°C). It is very interesting that the reduction of the iron oxides of the surface starts even at lower temperatures than for pure iron and is completely unaffected by the rising Cr-content. This confirms the findings of Chasoglou, Nyborg et al. [8,9], that the surface of these Cr-Mo-prealloyed powders are covered by a thin layer of iron oxides and the more stable oxides are located internally or on the surface as fine particulate compounds of nano-metric size. This may even lead to much cleaner iron oxide surface which is easier to reduce compared to pure iron powders, as the impurities are entrapped within these particulate compounds.

Tab.1. Mechanical properties of investigated samples sintered in dilatometer 10K/min, 60 min 1300°C isothermal sintering, -10K/min cooling; in hydrogen and argon.

	Green density [g/cm^3]	Sintered density [g/cm^3]	Dimensional change [%]	Impact energy [J/cm^2]	Hardness [HV10]
Fe in H_2	7.12	7.21	0.07	71.3	44
Fe in Ar	7.14	7.20	0.09	2.3	54
Fe1.5Mo in H_2	7.04	7.16	-0.29	70.2	59
Fe1.5Mo in Ar	7.04	7.16	-0.33	>40	58
Fe1.5Cr0.2Mo in H_2	6.94	7.09	-0.33	50	58
Fe1.5Cr0.2Mo in Ar	6.94	6.99	0.07	35	56
Fe3Cr0.2Mo in H_2	6.89	7.01	-0.82	73.8	57
Fe3Cr0.2Mo in Ar	6.89	6.96	-0.18	50.9	60



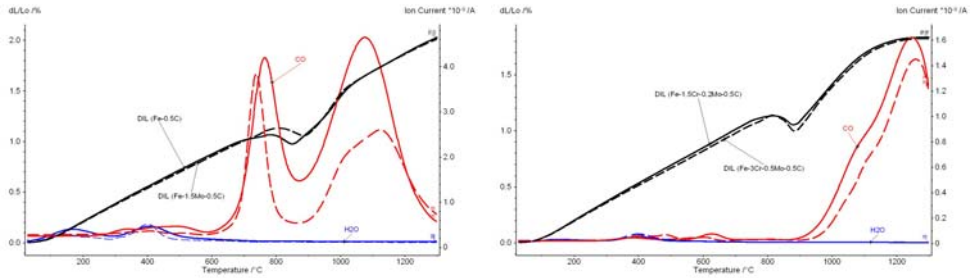
a) Fe b) Fe-1.5Mo

Fig.6. Micrograph of Fe and Fe-1.5Mosintered in dilatometer 10K/min. 60 min 1300°C isothermal -10K/min cooling, in argon, etched with nital.

The mechanical properties measured on the samples of the dilatometry run show that after sintering in hydrogen the impact energy – which is extremely sensitive to the quality of the sintering contacts - is very high for all materials. It shows also that plain iron sintered in argon has extremely low impact energy compared to all other materials, which is caused by excessive grain growth during the γ–α-transition and apparently of oxygen enrichment on the grain boundaries (see Fig.6). The second effect that is of technical interest is the high shrinkage of the Fe-3Cr-0.5Mo system in hydrogen.

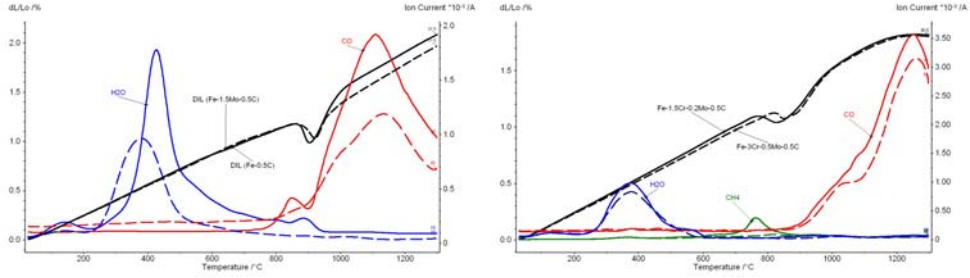
Addition of carbon

As shown before for the system Fe-C the addition of carbon influences deoxidation behaviour a lot. Now the influence of alloying elements, especially the more oxygen sensitive element chromium should be investigated. In order not to demonstrate that molybdenum which is often combined in chromium alloys does not affect the deoxidation behaviour also a Fe-Mo alloy is investigated.



a) Fe-0.5C and Fe-1.5Mo-0.5C b) Fe-1.5Cr-0.2Mo-0.5C and Fe-3Cr-0.5Mo-0.5C

Fig.7. Dilatometry runs of different PM steels coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min. Argon; heating ramp.



a) Fe-0.5C and Fe-1.5Mo-0.5C b) Fe-1.5Cr-0.2Mo-0.5C and Fe-3Cr-0.5Mo-0.5C

Fig.8. Dilatometry runs of different PM steels coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min. Hydrogen; heating ramp.

The main difference of the oxides is that Cr-oxides are much more difficult to reduce than Fe- or Mo-oxides, which causes a shift of the deoxidation to very much higher temperatures with chromium. The shift is so pronounced that the usual separation between surface oxides and internal oxides is not visible any more. Only for small samples (10x10x8

mm³) the differentiation becomes possible (see Fig.9). The use of hydrogen containing atmosphere again shows that only the surface oxides are reduced by hydrogen but the internal oxides by the added carbon as in inert atmospheres. For the chromium containing materials only the Fe/Mo-oxides are reduced by hydrogen as shown for the carbon-free material. An interesting effect can also be observed close to the transition temperature: The reaction $C + 2H_2 \rightarrow CH_4$ does only occur in Cr containing material, in a very narrow temperature range, and was never observed in all the Fe-C systems. This reaction is an unlike side reaction which can cause carbon loss, but the measurements indicate, that the reaction happens only in Cr-containing materials and to a very low amount which will in practice cause hardly any problem.

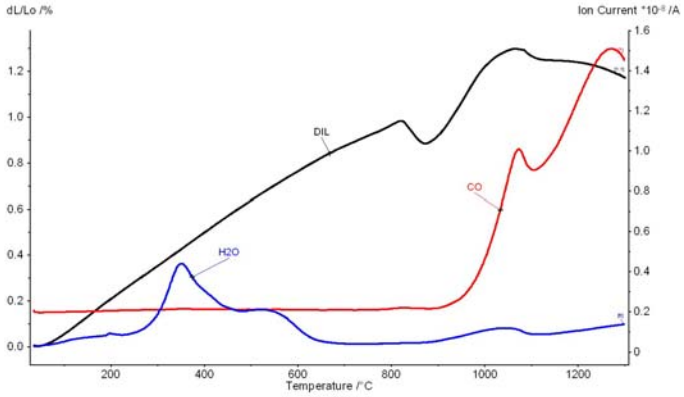


Fig.9. Dilatometry run of Fe-3Cr-0.5Mo-0,5C coupled with MS.
10K/min, 1300°C 60 min isothermal, -10K/min. Hydrogen;
heating ramp for small sample (10x10x8 mm³)

Another interesting effect can be observed when masteralloys of oxygen sensitive elements like manganese and silicon are admixed to the iron carbon system. In neutral atmospheres the deoxidation peak of the surface oxides becomes much lower compared to the unalloyed system Fe-C. But it cannot be expected, that the surface of the iron particles was changed during the process therefore it must be something like a metallothermic reaction transferring the formed CO from the surface of the iron particles to the more stable oxides of the master alloy where it is strongly oxidising for manganese and silicon. This means that the master alloy performs in neutral atmospheres as an “internal getter” which is oxidised by the desoxidation products of the iron which is of course the biggest source of oxygen in the mix. Therefore it is not so much of importance to produce master alloys with extreme low oxygen content as the danger of being oxidises during the process through oxygen transfer reactions is much higher.

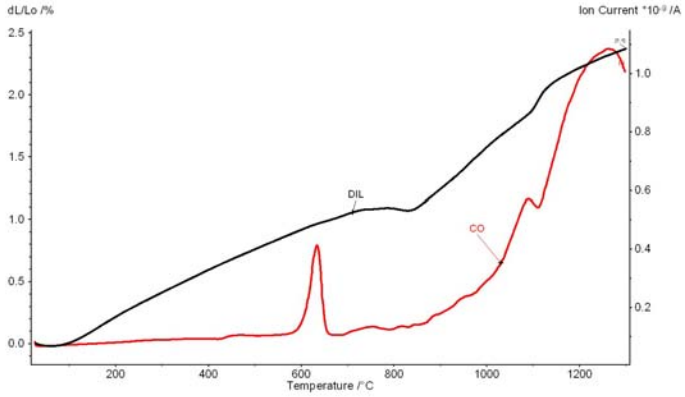


Fig.10. Dilatometry run of Fe-0,6C-4MA coupled with MS. 10K/min, 1300°C 60 min isothermal, -10K/min. Argon; heating ramp.

CONCLUSIONS

The experiments performed in the dilatometer coupled with MS show that the information provided by this thermoanalytical method is very well suitable for process control of sintering iron and steel structural alloys. It is possible to analyse the degassing processes in virtually all atmospheres except vacuum and this provides useful information about the behaviour of the investigated materials. The reduction processes of surface and internal oxides can be distinguishes. If the peaks are overlapping then the use of smaller samples is useful. The size of the samples – standard impact test bars - enables mechanical testing and the generation of micrographs after the sintering run and allows the correlation between sintering behaviour and the resulting mechanical properties. The effect of additions – here master alloy – can be studied to understand the behaviour especially during the heating period.

Acknowledgement

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