DETERMINATION OF PHASE TRANSFORMATION TEMPERATURES DURING SINTERING OF FEROUS POROUS ALLOYS BY THERMAL ANALYSIS METHODS

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Abstract: In the present article the sintering behaviour of the Fe+C+Cu PM samples has been investigated by thermal analysis methods. Sponge SC100.26 iron powder, 2% natural graphite and 2% electrolytic Cu powder as a starting materials have been used. Sintering process (heating 10^{o}C/min, holding 60min, cooling 20^{o}C/min, Ar protective gas atmosphere) has been experimentally followed in simultaneous thermal analyser STA (DTA+TG). Critical temperatures of ferrite-austenite transformation, carbothermic reduction of surface oxides, Fe-matrix carburisation, and Cu melting during heating have been obtained. Carburisation has started at 840^{o}C when thermodynamic conditions become favourable, and has not been arrested by surface oxides reduction (700-750^{o}C). During cooling STA has shown that carbon content is not homogeneous, and Cu alters austenite-pearlite transformation.

Key words: *iron powder, thermal analysis, DTA, TG, sintering*

1. Introduction

Sintering is the most important operation in powder metallurgy (PM) technology. It is a complex thermal process in controlled atmosphere where different chemical reactions and structure changes take place. The increasing demands on the PM components require the development of cost effective materials with high performance.[1] Better understanding of the basic reactions during sintering will help this. Widely used methods for thermal analysis (TA). [2],[3] are dilatometry, differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TG). The modern experimental equipment allows comprehensive studies by TG and DTA or DSC methods in the same experimental set to be carried out.[4],[5] For this purpose a sample of the studied system is subjected to controlled heat effect in a dynamic or a static mode, or in a combination of the both. In the dynamic mode the sample is subjected to heating or cooling, and in the static mode – it is subjected to retention at a constant temperature (isothermal process). The experimental data accumulated in the thermal analyses TA are used to describe the thermodynamic behaviour of the studied systems. The results from the TA are usually presented in a graphic form (the so-called thermal analysis curves), that represent the quantity measured as a function of the temperature or the time.

In this study, experiments to determine the physical and chemical properties of systems (pure substances, mixtures and/or reacting mixtures) as a function of temperature or time, simulation thermal analysis (DTA+TG) will be presented. The behavior of the samples in the process of sintering upon heating and cooling in inert gas environment argon (Ar) is examined. The selected parameters are consistent with those, used in the sintering practice of these alloys.

2. Experimental

The object of this study is sponge iron powder SC100.26, produced by "Hoganas-AB" Sweden. As alloying materials natural graphite and electrolytic Cu powders have been used. Premixes with composition given in tabl.1 have been compacted at 600MRa to rectangular compacts (5x5x15mm^3).

Tabl.1 Samples composition

Code	Composition
SC	100% SC powder
SC02C	SC+0.2%C
SC02C2Cu	SC+0.2%C+2%Cu

With the purpose to be studied (sintered) in a thermal analyzer NETZSCH STA 409 C/CD, small pieces 0.3-0.5g have been crushed from

the compacted samples. The sintering of PM components in the analyzer runs under the following conditions: temperature of isothermal sintering 1120°C with holding time 60 min, heating rate 10°C/min; cooling rate 20°C/min. Empty container as a reference has been used.
Phase transition during heating (α Fe → γ Fe + Δ H) takes place with absorption of heat. In this case, the thermal effect is negative (-Q) and downwards endothermic peak on the DTA curve forms. Opposite phase transition (γ Fe → α Fe - Δ H) takes place during cooling of the samples. In this reaction the thermal effect is positive (+Q) and forms upwards DTA exothermic peak. When the thermal effect of the reaction is positive, the total energy of the system decreases. The products of the exothermic reactions have less energy than the initial substances, and therefore they are more stable.

3. Results and Discussion

On Fig.1 the experimental DTA and TG curves during heating period, are shown (part of Fe-C diagram is also incorporated). Determined temperatures of phase transformations are summarised in tabl.2.

Tabl.2 Temperatures of phase transformations during heating

Types of powder mixtures	Phase transf.	The heating T°C	
		Beginning	End
SC100.26	αFe → γFe	887	929
+0.2%C	αFe → austenite	840	910
+0.2%C +2.0%Cu	αFe → austenite	839	906
	Melting of Cu	-	-

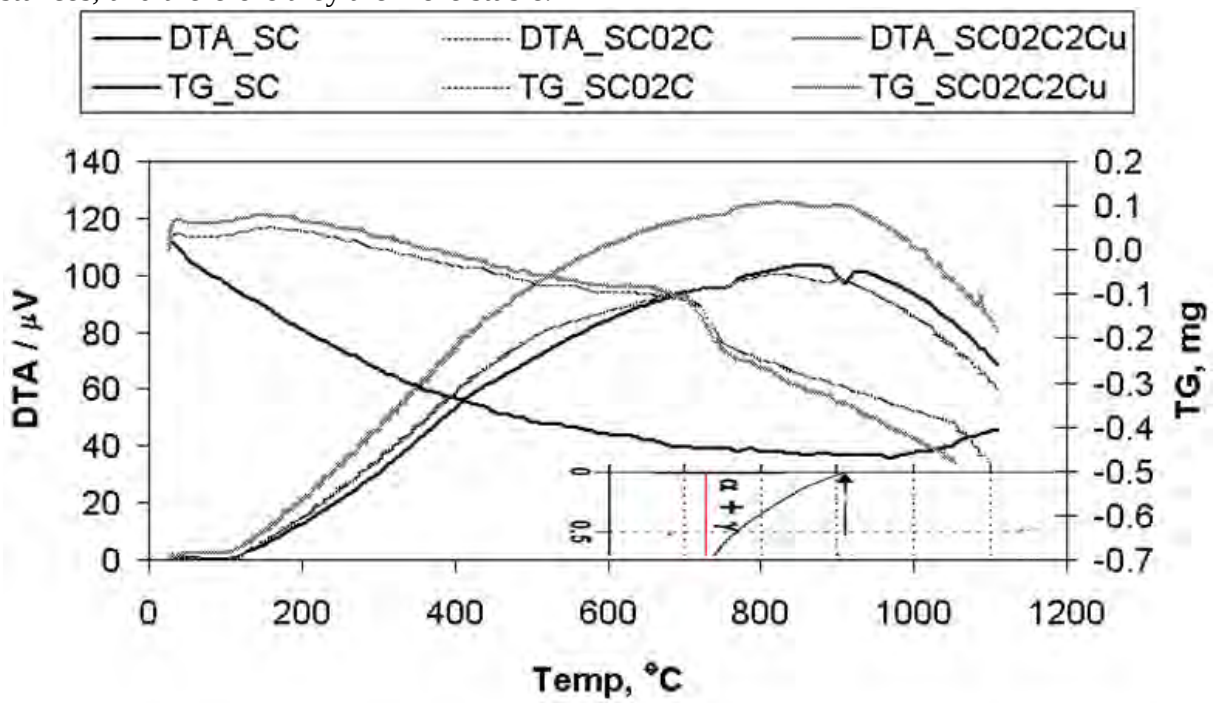

Fig.1 Recorded DTA, TG curves during heating step. (rate 10°C/min; Ar-atm.)

On the carbon containing samples TG curves sudden mass loss in the temperature interval 700-750°C, is clearly seen. This is due to carbothermic reduction of the surface oxides covering powder particles. [5] Small peaks on DTA curves at these temperatures are not connected with the phase transition, but Curie transformation of iron (Cp changes). Pure SC sample DTA curve shows that the phase transformation α→γ starts at temperature 887°C which is below 911°C in Fe-C diagram. We suppose that, because of its nature, powder have small carbon content. Phase transformations in graphite containing samples detected by DTA curves start at 840°C. Peaks are board and not so clear, indicating simultaneous processes of carburisation and austenite transition of ferrite matrix. This temperature is higher than the Ac_1 temperature (727°C), showing delayed carburisation of iron matrix. It can be stated that one of the carbon diffusion limiting factors is the presence of surface oxides. Their reduction

finishes at about 750°C but carburisation is still arrested. As the local carbon potential is controlled from Boudouard equilibrium ($2CO \rightarrow C(s)+CO_2$), it is evident that thermodynamic conditions in this case don't favour carburisation below 840°C.[6] On the Cu-containing sample DTA curve also sharp endothermic peak at 1086°C, indicating Cu melting is found.

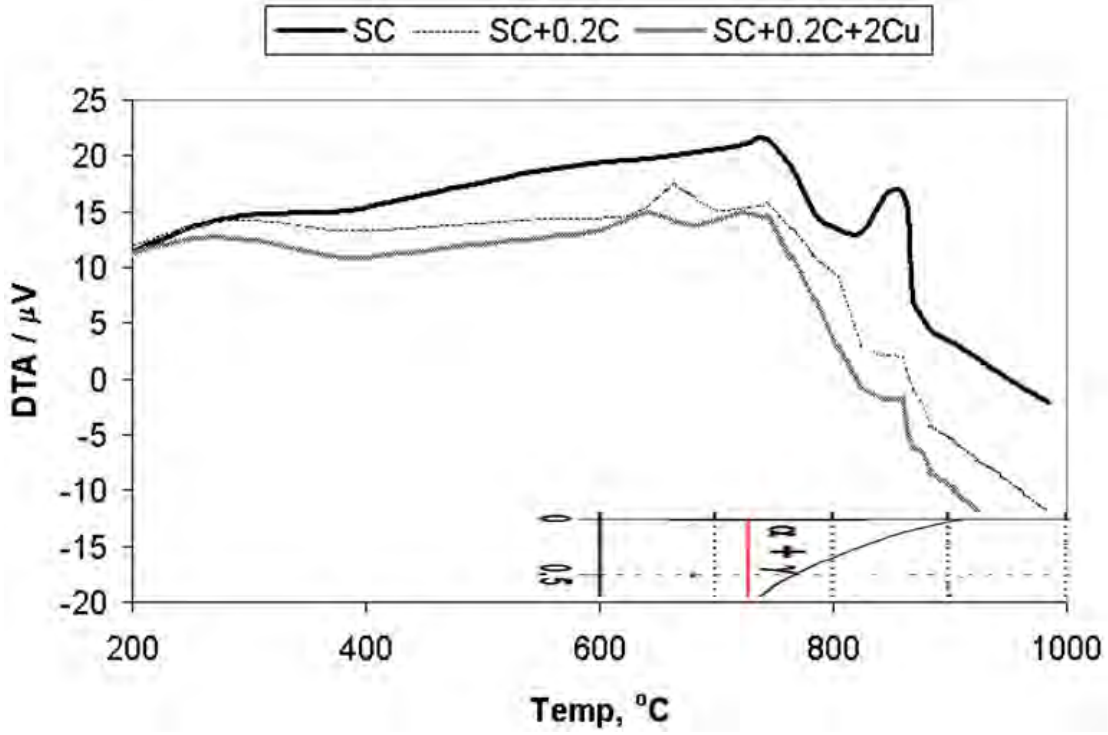

Fig.2 Recorded DTA curves during cooling step. (rate 20°C/min; Ar-atm.)

Holding time at 1120°C is needed for diffusion processes like homogenisation of alloying elements and austenite selfdiffusion.

Tabl.3 Temperatures of phase transformation during cooling

Types of powder mixtures	Phase transf.	The cooling T°C	
		Beginning	End
SC100.26	γFe→αFe	890	809
+0.2%C	γFe→αFe	883	835
	γFe→pearlite	699	651
+0.2%C +2%Cu	γFe→αFe	881	832
	γFe→pearlite	683	623

Cooling rate has been chosen 20°C/min to follow the industrial sintering conditions (for closed pusher type sintering furnaces). Cooling DTA data curves are shown on Fig.2. Part of Fe-C diagram is incorporated at the bottom of the figure to illustrate the peaks origin. Determined temperatures of phase transformations are summarised in tabl.3. The opposite phase transition in SC sample is seen as a clear exothermic peak in the temperature interval 890-809°C. Similar peaks are found out on the other two curves at the same temperatures. According to Fe-C diagram in carbon containing samples proeutectoide ferrite continuously have to precipitate before the pearlitic transition at 723°C, so these peaks indicate that carbon in austenite phase is not uniformly distributed. There are free of carbon areas which transform earlier. Austenite-pearlite transition peaks in the temperature interval 600-700°C on the carbon containing samples curves can be seen. It is known that Cu alters the carbide precipitation from austenite, so as expected in these samples pearlitic transformation starts at lower temperature (688°C, tabl.3)

4. Conclusions

As a result from the above made experimental studies the thermal effects, resulting from the phase transformations, occurring in Fe+C+Cu powder mixtures during heating and cooling (when the sample is already sintered and its operating properties are formed), have been

analyzed. The behaviour of the studied PM samples during sintering in Ar protective gas atmosphere and influence on the temperatures of the phase conversions and the change of their mass, has been experimentally followed. The experimental studies prove that:

- carburisation of ferrite matrix during sintering begins at higher than possible temperatures;
- holding time 60min is not enough to carbon homogenisation;
-with the addition of Cu to carbon containing samples the temperature of the beginning of the pearlite transformation during cooling decreases.

As a result of the studies made, it can also be added that the carbon in the process of sintering is an important reduction agent.

5. References

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