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# STUDY OF THE SINTERING PROCESS OF IRON POWDERS COATED WITH NANO-HYDROCARBON AND THE RESULTING MICROSTRUCTURE AT TEMPERATURES UP TO 1200°C

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## ABSTRACT

*The objective of the research is development and study of a new ecologically friendly and technologically advanced method for introduction of carbon during sintering of low alloyed iron powders ASC 100.29. The method is based on using hydrocarbon coating of the green powder, which transforms into carbon nano-layers between the powder particles, during the sintering process. The method avoids the use of graphite as alloying element and reductant, and allows for a much better homogenization, less porosity and overall increase of the quality of the final sintered product.*

*The research presented is focused on the processes related to apparent density, fluidity and compressibility of the coated powder and resulting porosity after pressing and sintering. The aim is to determine the optimal coating conditions, and to acquire experimental data concerning key processes during the sintering and the originated microstructure. The sintering process was monitored in situ through DTA measurements and measurement of the exhaust gases pressure. Results obtained so far show better handling conditions for the green coated powders, compared to those using classical approach and higher homogeneity of the sintered specimens.*

KEYWORDS: powder metallurgy, coating, hydrocarbon, densification, sintering, microstructure

## 1. Introduction

In many cases, conventional materials do not posses required specific properties required by the modern technologies. Thus, development of new advanced materials and technologies is in high demand. Powder metallurgy (PM) technologies have lucrative position since they enable efficient energy and raw material saving production, combined with an extremely high productivity rate. The main group of parts produced by powder metallurgy, is based mostly on ferrous and, to a less extent, on nonferrous metals. PM produced materials and parts are mostly intended to replace the ones produced by conventional technologies, e.g. by machining, forging and/or casting. In any case saving of large amounts of material, energy and reduced production costs is achieved. The main differences between PM produced parts and their wrought counterparts is the porosity generated from the particles boundaries and the oxide inclusions introduced through the green powder. These microstructural features considerably deteriorate the mechanical, especially dynamic properties of the parts produced. Obviously, a combination of highly cohesive green particles boundaries and high density is essential for better dynamic properties. It was found that problems above could be solved, to some extend and better mechanical properties achieved, by adding graphite powder into the green powder mixture. In PM the role of carbon is threefold, reduction of the internal and surface oxides introduced powder particles, thus improving the mechanical properties, alloying and densification of the sintered parts. Regretfully, the introduction of carbon is not cost free. The considerable difference between the specific weights of graphite and metal powders, leads to segregation of graphite during handling of the powder mixture at compaction. As a result, the produced parts have inhomogeneous microstructure, which again leads to low densities and inferior mechanical properties. Even worse, it is impossible to avoid the pollution of the working premises with carbon dust, which leads to increased health hazards. Recently, a new technology was developed, which eliminates direct addition of graphite into the green powder mixture. Instead, graphite is added indirectly via coating of the powder particles with certain organic polymers. Thus varying the thickness of the coating a controlled addition of carbon could be achieved. The aim of the present research is the improvement of the powder coating technology that we developed and study of some technological aspects of the sintering process: determination of the coating thickness; achieved surface density of the coating; microstructure development and some calorimetric and thermochemical effects during processing.

## 2. Experimental procedure

In previous papers [1-3] we discussed some results obtained when using polyvinylchloride as coating. Although polyvinylchloride was a successful coater and led to the results that we desired by us results, it was noted that its use is hazardous from the ecological point of view, because of the vinyl chloride gas released in the process. That is why in the present research a new, less hazardous, polymer was used, namely, polyvinyl alcohol (PVA). The coating method developed is as follows: Firstly, the PVA is thermally decomposed at 663 K (in pure Ar or $N_2$). In the specific case here, the thermal regime was: Heating with 5 K/min. up to 663 K, isothermal hold at this temperature for ~35 min and cooling in oven at temperature room. Secondly, the obtained residual, a brown powder, is milled and dissolved into xylene ($C_6H_4(CH_3)_2$). After filtering, which removes coarse particles, the concentration of the dissolved into the hydrocarbons solution ($\mathbf{C_nH_m}$) is determined. The coating procedure itself is simple. The powder, in our case ASC 100.29 is mixed with the hydrocarbon solution and the xylene is evaporated. During this part of the coating process, the mixture powder+xylene+hydrocarbons ($\mathbf{C_nH_m}$) is vigorously stirred, resulting in an even coating of all powder particles with hydrocarbons.

In the case studied, the hydrocarbons $\mathbf{C_nH_m}$ concentration in the solution was selected to be around 52.5 g/l. To determine the amount of carbon produced from this hydrocarbon solution a calibration procedure was carried. Fixed volumes of the solution were evaporated and the obtained residue was heated in vacuum, ~ $10^{-2}$ mmHg, up to 1000ºC. The obtained carbon was weighed with high precision balance (**METTLER AE200**) and the results were plotted in $\mathbf{C_nH_m(g)}$ vs. **C(g)** (see Fig.1).

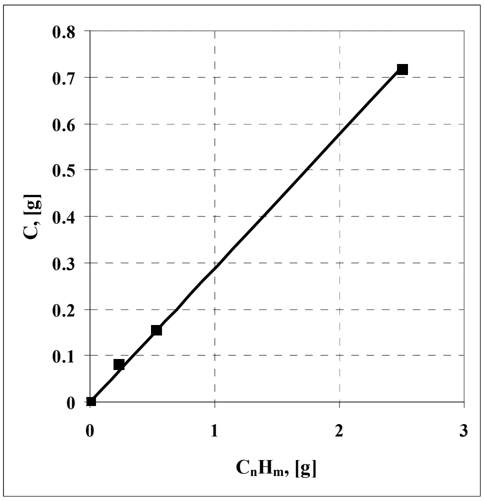

***Fig.1.*** *The experimentally obtained calibration dependence* **C(g)** vs. $\mathbf{C_nH_m(g)}$**.**

The dependence obtained allows selecting the correct volume of $\mathbf{C_nH_m}$ solution for obtaining the desired coating thickness (in other words the amount of carbon introduced into the powder mixture).

For the specific research carried here, 700 g of ASC 100.29 iron powder were coated using 147 ml solution, which according to our calibration equation is equal to introduction of 0.8% wt. carbon into the green powder mix.

The results of the coating procedure were controlled using TEM. Figure 2 shows a TEM micrograph where the coating is clearly visible as a pale halo around the powder particle.

***Fig.2.*** *TEM (**JEM 1011 / JEOL** microscope) micrograph of: uncoated (**a**) and coated with hydrocarbon (**b**) powder particles. The coating is seen as a pale halo, with several nanometers thickness, around the particles.*

## 3. Results and discussion

The coated particles obtained thus were tested for apparent density and fluidity. The results obtained are summarized in Table 1. The carbon content introduced through the coatings into the green powder was also studied using **Leco Determinator CS**244. The results obtained coincide with the ones obtained using the calibration dependence above. The specifics of the sintering process of coated powders was studied on six specimens, compacted in cylindrical die at different pressures (between 200 and 800 MPa, measuring 8 mm (diameter) x 12 mm). Fig.3 shows plot of the green density of the compacts vs. the applied pressure (solid line).

The porosity of the compacts, was determined by the Parilák's equation [4, 5]:

$$P=P_o.\exp(-K.p^n) \qquad (1)$$

where **P=1-D** is the porosity in %, **D** is the relative density, **K** is particles' geometry factor and **n** is a parameter accounting for the plasticity of the powder material. The results obtained are shown in Fig.3 with dashed line. The parameters **K** and **n** obtained with the Parilák's equation together with the correlation coefficient **r$^2$** are shown in Table 1.

***Table 1.** Apparent density and fluidity of coated powder.*

| Material studied | Apparent density [g/cm$^3$] | Fluidity [sec] | K | n | Correlation coefficient, r$^2$ |
|---|---|---|---|---|---|
| ASC 100.29 | 2.7 | 31 | 0.124 | 0.439 | 0.9992 |

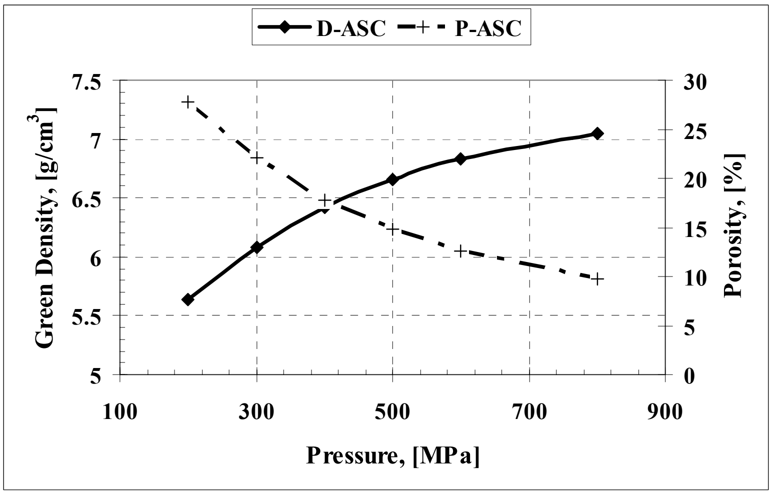

***Fig.3.** Compressibility of ASC powder coated with hydrocarbons.*

The influence of the hydrocarbon coating on the compaction and the quality of the compacts was studied using SEM (**JOEL- SUPERPROBE 733**). For this purpose two series of compacts, with and without coatings (compacted at 200, 400 and 800 MPa), were prepared. The results obtained are shown in Figs.4 and 5. Both series show similar response to the applied pressure, namely, decrease of the "free surface" between the compacted particles leading to better contacts between them.

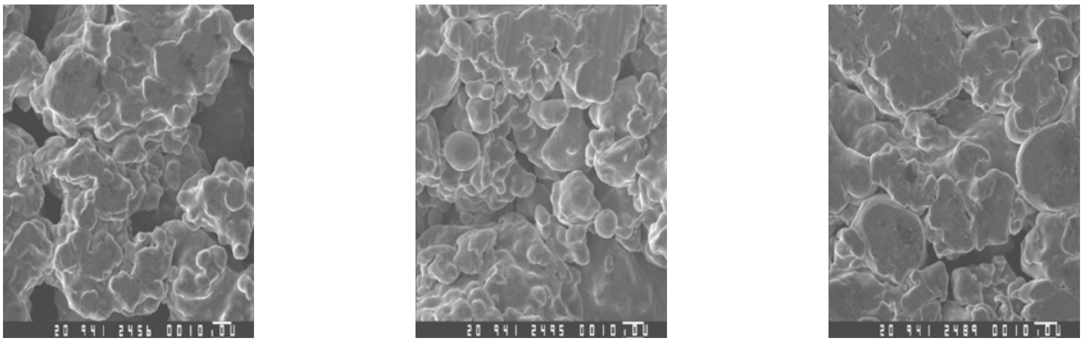

***Fig.4.** SEM micrographs of iron powder compacted at: a) - 200, b) -400 and c) -800 MPa.*

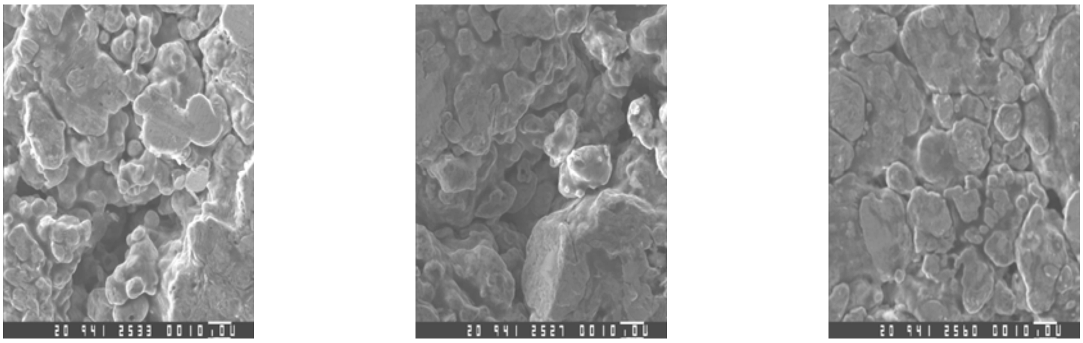

***Fig.5.*** *SEM micrographs of hydrocarbon coated iron powders compacted at: a) - 200, b) -400 and c) -800 MPa.*

Remember, that higher "free surface", leads to higher porosity in the final product. The coated particles, however, show finer structure of the compact and decreased tendency to form conglomerates, compared to the uncoated particles, which leads to a better contact between the particles, higher fluidity, better compaction and higher homogeneity of the compact.

The specimens prepared thus, are referred below as (A1,…A5 and A6, and compacted, respectively, at 200, 300, 400, 500, 600 and 800 MPa) were, prior to sintering, heat treated at 873 K for 30 min. in inert atmosphere to remove the volatile components of the coating.

The sintering process was carried out at 1480 K for 60 min. in vacuum ~ $10^{-5}$ mm Hg. During the heating, cooling and the sintering of the specimens the overall pressure of the emitted gases and the calorimetric effects due to the reactions taking place during sintering (DTA) were monitored.

The DTA curves obtained are shown in Fig.6, specimens A1 and A2 and in Fig.7 specimen A6.

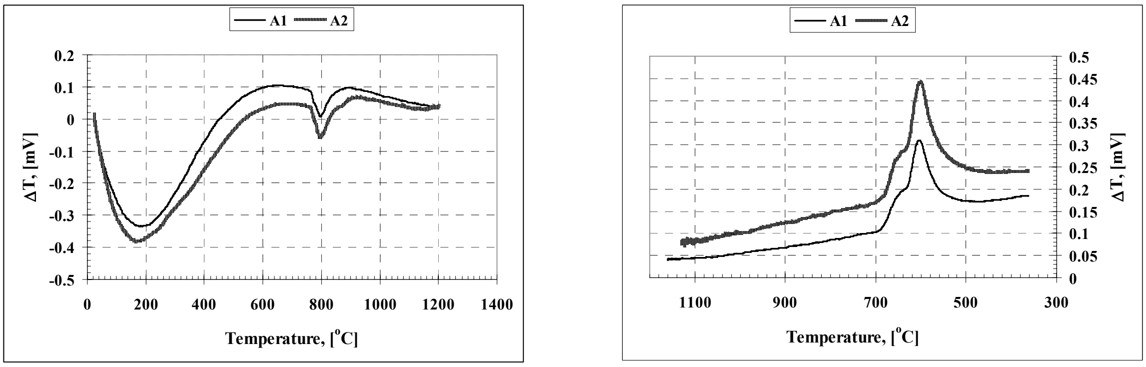

***Fig.6. a, b.*** *DTA curves obtained at heating and cooling rates of 9 K/min. of the specimens A1 and A2 compacted at 200 and 300 MPa, respectively.*

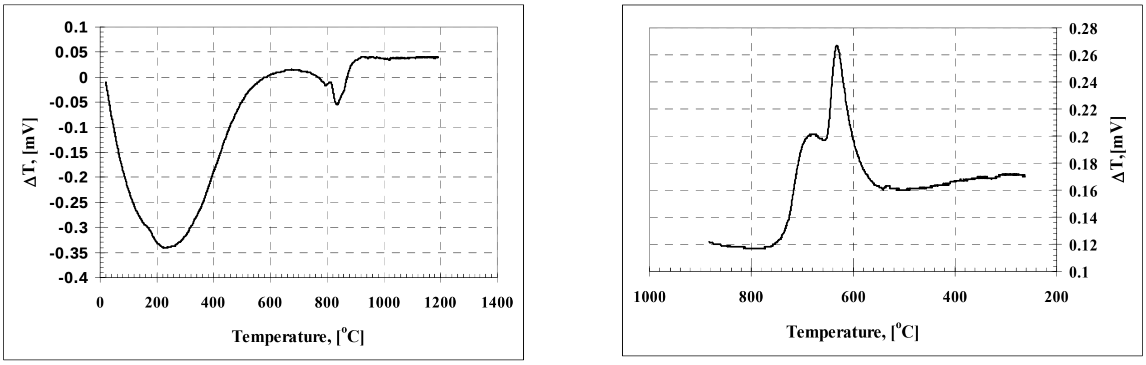

***Fig.7. a, b.*** *DTA curves obtained at a heating rate of 10 K/min and "free fall" cooling of the specimen A6, 800 MPa.*

The analysis of the obtained curves shows that the endothermic process, observed between room temperature and lasting up to 600ºC, is due to the decomposition of the coating polymer and its transition into nano-layers of carbon on the particles' surfaces. This conclusion is confirmed by the peaks of the total gas pressure of the emitted gases, presented in Fig.8.

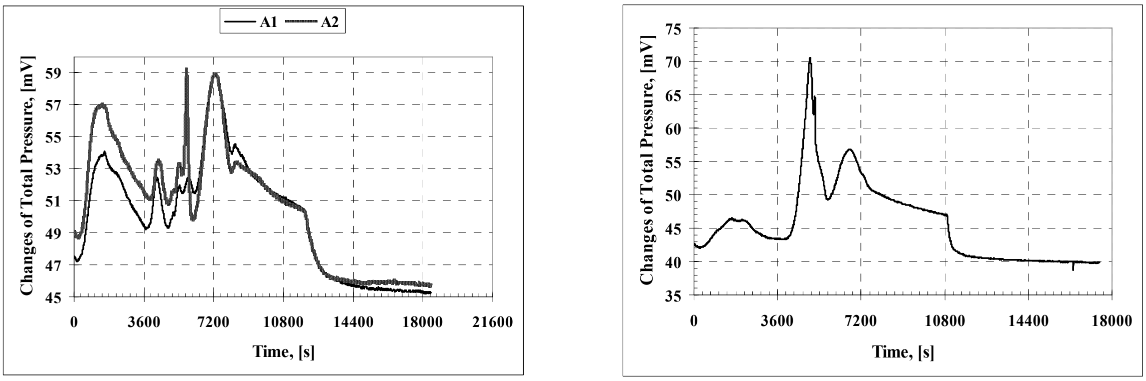

***Fig.8. a, b.*** *Dependencies of the overall gas pressure vs. time of the emitted during the sintering process gases*
*a) specimens A1 and A2, b) specimen A6.*

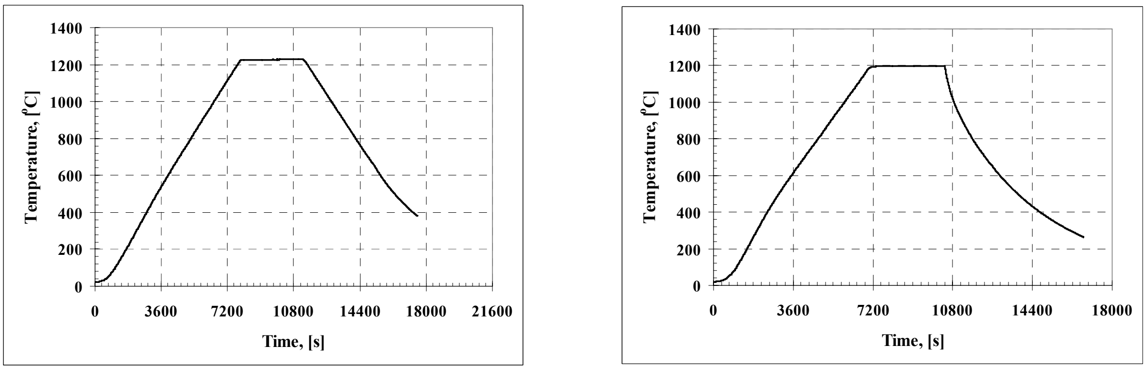

***Fig 8. c, d.*** *Temperature regimes used.*

Low temperature peaks observed are probably due to the cracking and decomposition of the polymers. The peaks above 600ºC, however, are formed due to the surface and volume oxides reduction. It was believed that because of the relatively high heating rate, the diffusion of the carbon into the iron could be neglected. Based on the experimental evidence, however, this assumption was not confirmed. Note that the $\alpha$–$\gamma$ transition takes place at ~800ºC, i.e. well below the ferrite-austenite transition of pure iron (912ºC). Obviously, the carbon dissolution takes place before the $\alpha-\gamma$ transition temperature in pure iron and is extenuated by the highly active interstitial nano-carbon formed. The cooling DTA curves show the typical pattern of precipitation of two different phases from austenite, in our case incipient ferrite (the small peaks on Figs.6b and 7b) and ferrite+cementite (the large peaks).

Figure 9 shows micrographs of the sintered specimens A1, A2 and A6. One notes the homogeneous microstructure of fine pearlite and ferrite.

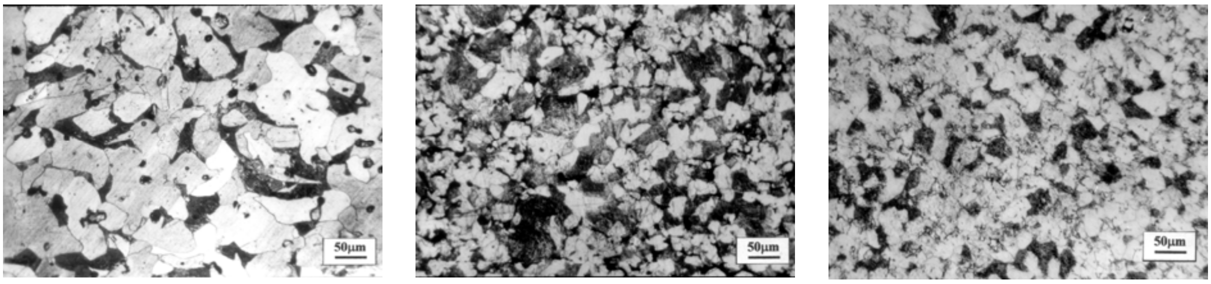

***Fig.9. a, b, c.*** *Microstructure of the a) A1, b) A2, c) A6 specimens after sintering.*

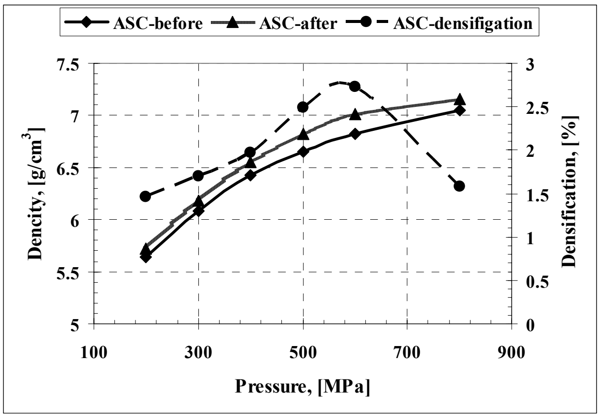

***Fig.10.*** *Measured ASC 100.29 specimen's density before and after sintering vs. the compaction pressure.*

The decrease of porosity with the increase of the compaction pressure is also clearly seen. The density measurements (see Fig.10) of the same specimens, however, show that the maximal densification is achieved at compaction pressure of 600 MPa. Obviously, additional experiments are needed to explain this result. Finally, the concentration of the carbon into the sintered specimens was measured (**Leco Determinator CS244**). It was found that the leftover carbon concentration is 0.35- 0.45 % by mass. What remains is that the initial concentration was 0.8 wt.%.

## 4. Conclusions

Based on the results obtained, the following conclusions could be drawn:

A new, less hazardous from the ecological point of view, polymer coating method for iron based powders is developed.

The method yields finer structure of the compacts and decreases tendency of conglomerates formation. The produced by the method coated particles, posses higher fluidity of the green powder at die loading and higher homogeneity of the compact.

The sintered compacts show homogeneous microstructure and decreased porosity. For the specific case studied, ASC 100.29 iron powder, the maximum densification was achieved for the compacts compacted at 600 MPa.

The analysis of the gas pressure curves obtained shows that the low temperature peaks, observed below 600ºC, are formed due to the cracking and decomposition of the coating polymers. The peaks above 600ºC are formed due to the surface and volume oxides reduction.

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