STUDY CONCERNING THE INFLUENCE OF ANNEALING TREATMENT ON THE PROPRIETIES OF WATER ATOMIZED CAST IRON POWDER

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ABSTRACT: The influence of the parameters of annealing process: temperature, time, nature of the protective atmosphere s.o, on the chemical, physical, mechanical, technological and structural properties of atomized cast iron powders. The research aims to improve the properties of sintered carbon steel obteining by blending iron and cast iron powder.

KEYWORDS: cast iron powder, reducing, annealing, nodular cast iron

1 INTRODUCTION

As known from the literature, there are anyway methods in order to produce cast iron powders: (i) the mechanical grinding of metallic swarfs resulted after mechanical producing of different parts [1] and (ii) atomizing of syntetical cast iron are the best known [2, 3, 4].

Because of the difficulty of choosing the cast iron swarfs with knows chemical composition, their shape and structure not quiet adequate, the time altering of the chemical composition of collected swarfs, the important content of abrasive impurities, the reduced plasticity of the particles due of strain hardening advanced state, as well as their reduced engineering properties, this type of cast iron powder can't be used as raw state.But subjected to a conditioning treatment by grinding, sifting and magnetic separation, it looses some of the carbon content.

The plasticity of the powder may be improved by an annealing treatment. But even in such of conditions due to the remanent abrasive impurities (SiO_2, silicates, sulfides, etc.) it can be used only for the production of sintered friction materials.

The atomized cast iron powder produced from syntetical cast iron (without Mn and Si) represents an intermediate product in the technological process of producing iron powders in the procedures RZ and IPM (Kiev) [2, 3, 4, 5, 12, 13]. The researches realized about cast iron powder produced by atomization were subjected to its transformation in an iron powder with low carbon and oxygen content.

De-carburation and de-oxydation processes of the cast iron powder is realized in this case by a means of a heat treatment called, self reduction. This treatment consists in oxidizing the carbon by using the oxygen from the iron oxydes. These iron oxydes may come from the superficial oxidation of cast iron particles during the atomization process, or from an external source as e.q. mille scale or pure iron one. The de-carburation reactions of free carbon, (graphite) of carbon soluted in the iron (Fe_γ) and the bounded carbon as cementite Fe_3C, are the following:

$$(a+b)\ C_{garphite} + Fe_xO_y = xFe + aCO + bCO_2 \qquad y=a+2b \quad a+b<y \qquad (1)$$

$$(a+b)[C]_{Fe} + Fe_xO_y = xFe + aCO + bCO_2 \qquad y=a+2b \quad a+b<y \qquad (2)$$

$$Fe_3C + Fe_xO_y = (x+3)Fe + aCO + bCO_2 \qquad y=a+2b \quad a+b<y \qquad (3)$$

No one of theese de-carburation posibilities above mentioned can produce an iron powder having both low carbon content and low oxygen content which reflect the actuall quality necesities; that's why it is preferably to obtain a powder with low carbon content (C<0.1%) but with an oxygen rezidual content higher (1.5-2%). This high oxygen content will be eliminate by a subsequent annealing treatment in a H_2 or H_2+N_2 athmosphere, but unforturatelly this process has a negative effect or the producing costs [6, 8]. More, the de-carburation - de-oxidation reaction is endothermic and occurs with acceptable technically speeds only at a temperature higher than 1050°C.

Recent researches accomplished in the field of sintered carbon steels and a sintered alloyed low carbon steels, in order to find an alternate way of introducing the carbon in the material have bing again in font the producing of a cast iron powder wich will play the role of bringing supplemental carbon.

The cast iron powder used with the purpose of producing sintered steel must have a carbon content between 3.5 and 4.3% and a small content of oxygene (for the high quality iron powders). Also, it is desirabile that the powder should have a plasticity highest possible. We mention that the last two analysis are overcame for the raw cast iron powder (as it results from atomisation).

This is the frame where belong this research which aims to solve a cast iron powder proper for producing sintered steel products.

The scientific literature about the annealing of cast iron products is very rich [8 - 16] and its effects on the structure and properties of these cast iron are also well known, but the obtained results can be used only qualitatively in the case of annealing of atomized cast iron powders. The reason for this is the important difference between the behavior at a foundry products during the treatment and the one of a powder obtained by means of atomization. As a compared with the foundry cast iron, the atomised cast iron powder has the following peculiarities:

- reduced size, less than 0.200 mm of the powder particle subjected to the annealing process;
- the specifical surface is much bigger compared wich annealed product (some order bigger);
- the particle surface resulted in a air or water atomization process is usually oxided;
- specific powder microstructure (martensite+carbides) is of the same type with the one obtained by a rapid solidification of cast iron.

Also, the are important differences concerning the aim of the annealing process. Thus, in the case of the powdered material, together with the modiffication of the microstructure other aims are:

- advanced de-oxydation of powder together with preventing de-carburation, which impose the using of a reducing atmosphere, with a high carbon potential;
- limiting the sintering of powder particles during the annealing process, in such a way that the resulting reduced sponge might be easy crushed in particles.

Additionaly, there are an important difference between the structure of foundry and powdered annealed materials: the first one being compact, while the last one is porous (consists of particles). The above mentioned difference reflects in the different value of the thermal conductivity of both materials which influences the extent and the heating and cooling conditions of materials.

The aim of this paper is to obtaining, by means of annealing treatment of the nodular cast iron powder, different microstructures of the bulk metallic as well as of the graphite separations.

2 MATERIALS AND METOD

For experimental measurement, a cast iron powder obtained by means of water atomization of a nodular cast iron was used. For the melt atomization an 10 kg metal induction furnance are used.

The atomizing parameteres were the following: the metallic melt temperature 1360°C, the metal stream diameter ϕ=6 mm; the atomization nozzle type: conical annular; the pressure of the water used as atomization agent = 5 MPa; the fly distance to the cooling medium (water) = 2000 mm.

After the atomization, the powder followed the following procedures: collecting, filtration, drying, sifting with a 0.200 mm sieve size and characterization. The properties of the obtained cast iron powder are shown in Table 1, Table 2 and Table 3 and its characteristic microstructure in Figure 2 and Figure 3.

Table 1. Chemical composition of as-atomized cast iron powder

Chemical composition, wt. %						
C	Si	Mn	S	P	Hydrogen loos	Fe
3.30	1.87	0.7	0.086	0.095	4.42	balance

Table 2. Grain size distribution of as-atomized cast iron powder

Particle size distribution, wt. %							
200-250 μm	160-200 μm	125-160 μm	100-125 μm	80-100 μm	63-80 μm	40-63 μm	<40 μm
10.2	11.53	5.24	9.56	15.7	17.6	7.64	22.5

Table 3. Engineering properties of as-atomized cast iron powder

Apparent density [g/cm^3]	Flowability s/50g	Compacting pressure, /Green density, g/cm^3				
		300	400	500	600	700
2.66	50/63	4.754	5.191	5.380	5.820	6.180

The annealing treatment of the powder was made in a laboratory muffle furnance. The 5g powder sample was introduced in porcelain cups and those in a metallic tray. The limits of the parameters token into acount were: working temperature: 650-1050°C; maintaining time in the hot zone: 20-120 min. The protecting atmosphere was hydrogen, with a gas flow - 0.5 l/h and with a dew point = - 65°C.

3 RESULTS AND DISCUSSION

The properties of cast iron powder obtained by means of a reducing annealing treatment depend on the properties of the atomized cast iron powder as well as on the treatment's parameters. From the large number of properties of an annealed powder, the authors focused on the chemical composition (C and O) and on the microstructure of powder particles. The powder microstructure determining the plasticity (compressibility) of the powder. Between the reducing annealing process parameters there were selected the following ones: the maintaining temperature, the maintaining time, the nature of reducing atmosphere, and the cooling rate. A suggesting schema concerning the influence of annealing process parameters on the cast iron powder properties is shown in Figure 1.

The main results of the study of the influence of the working parameters corresponding to reducing annealing process on the chemical, physical, mechanical and technological properties of annealed cast iron powder as compared with in as-atomized powder are presented in the Table 4, Table 5, Table 6, Table 7; those concerning at the modification of the particles microstructure in Figure 2, Figure 3 and those concerning the aspect of particles surface in Figure 4.

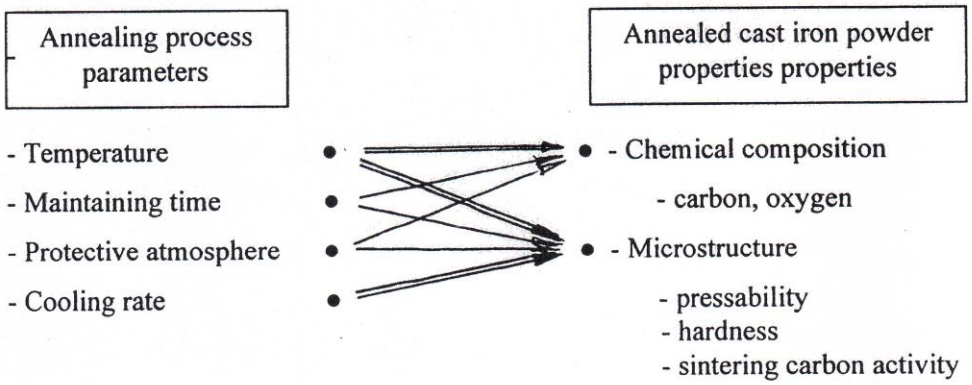


Fig. 1. The influence of annealing process parameters on the cast iron powder properties.

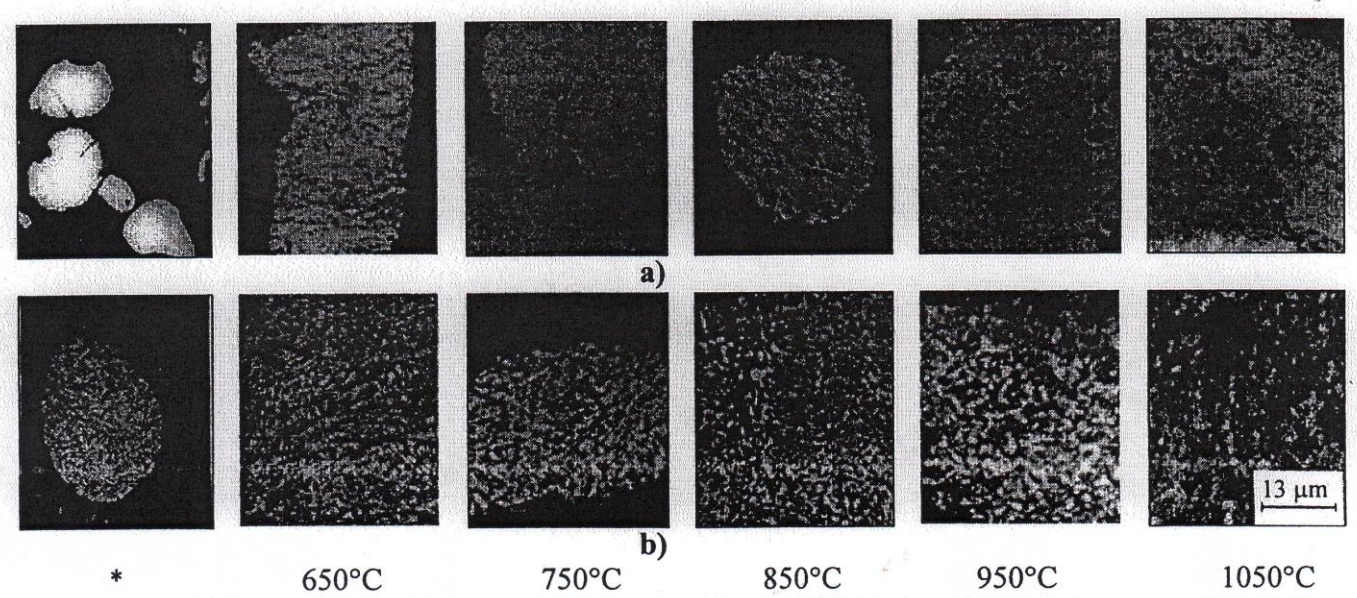


Fig.2. The influence of annealing temperature on the modification of microstructure of cast iron powder particles; the maintaining time 120 min, the cast iron particles size < 0.200 mm. a) not etched; b) etched with 4% Nital (as-atomized powder).

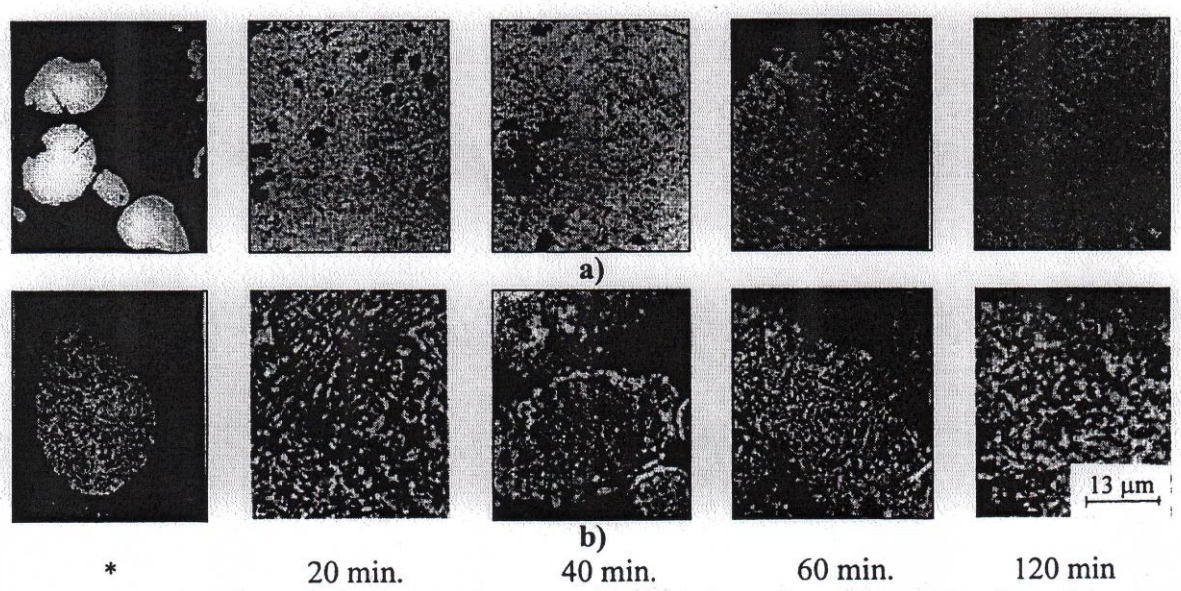


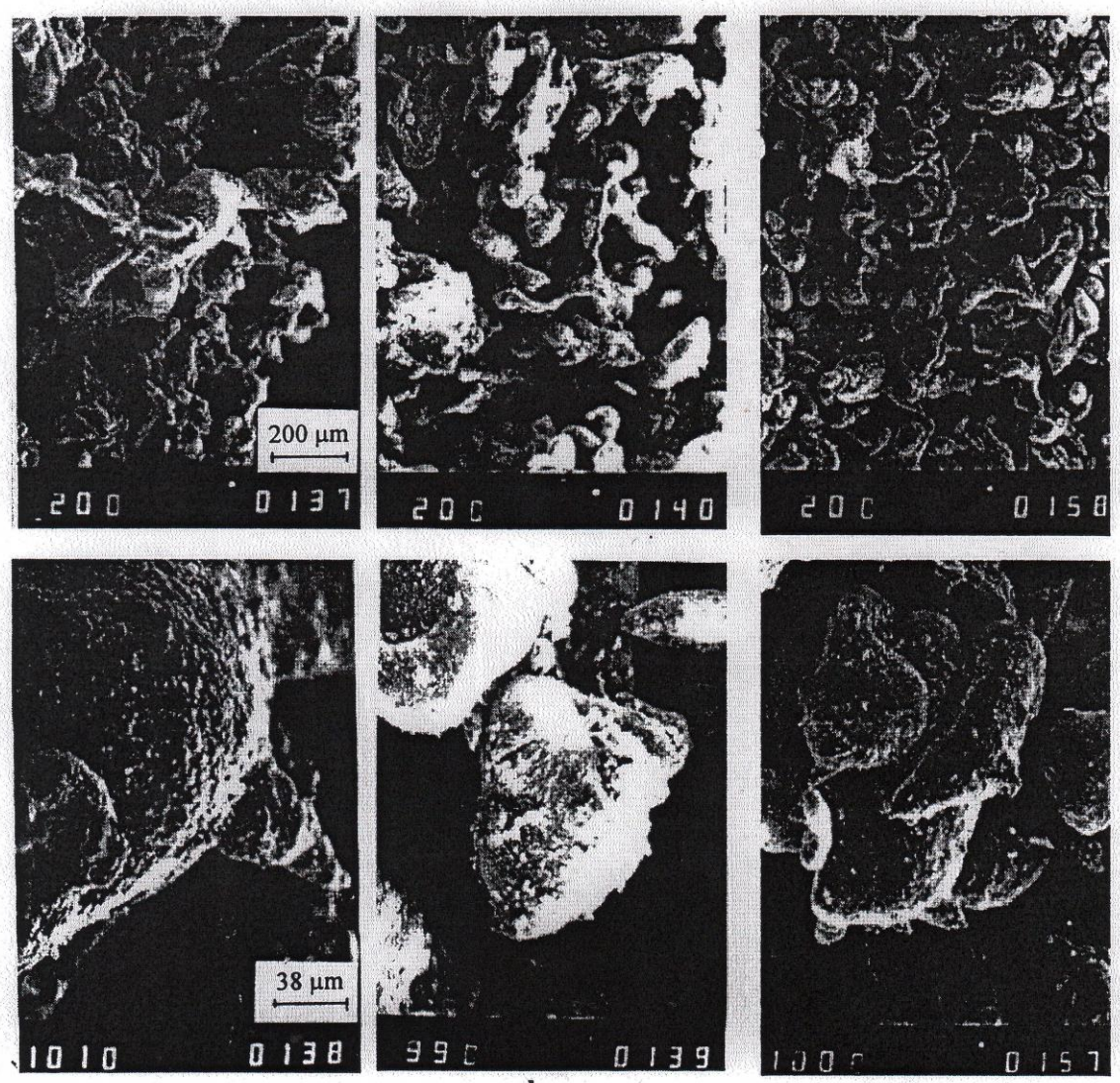
Fig. 3. The influence of maintaining time on the modification of cast iron powder microstructure, the annealing temperature 950°C; the size of cast iron particles < 0.200 mm; a. non etched; b. etched with 4% Nital, (* as-atomized powder).

Table 4. The influence of annealing temperature on the chemical composition of the cast iron powder for 120 min maintaining time, (*as-atomized powder)

Chemical composition, wt. %	Annealing temperature, °C					
	20°	650°	750°	850°	950°	1050°
Carbon	3.30	3.11	2.76	2.51	2.30	2.26
Hydrogen loos	4.42	1.22	0.78	0.51	0.38	0.29

Table 5. The influence of maintaining time at the annealing temperature of 950°C on the chemical composition of cast iron powder

Chemical composition, wt. %	Annealing time, min.					
	0*	20	40	60	90	120
Carbon	3.30	3.05	2.88	2.78	2.45	2.30
Hydrogen loos	4.40	3.42	1.55	0.64	0.49	0.38



a. b. c.

Fig.4. The aspect of cast iron particles surface shown by means of SEM: a – as-atomized; b – annealed for 120 min at 650°C; c – annealed for 120 min at 950°C.

Table 6. The influence of the annealing temperature on the green density (g/cm^3) of cast iron powder'compacts; the maintaining time at annealing temperature 120 min; the compacting presure 600 MPa

Annealing temperature, °C/ Green density, g/cm^3					
20*	650	750	850	950	1050
4.55	5.60	5.62	5.61	5.65	5.50

Table 7. The influence of maintaining time at the temperature of 950°C and of the compacting pressure 600 Mpa on the green density

Annealing time, °C/ Green density, g/cm^3					
0	20	40	60	90	120
4.55	5.08	5.35	5.53	5.65	5.50

The influence of the temperature and the time of reducing annealing on chemical composition of the powder

By the study of the influence of the temperature and time of reducing annealing on the chemical composition of the cast iron powder, Table 4 and Table 5, most take into account the following processes occurring concomitant:

(i) the structural modifications occurring in solid phase due to of the maintaining of the samples at the annealing temperature consists in transformation of a non-equilibrium structure (martensite+carbides) in a equilibrium one (ferite+perlite+graphite) accordingly with the annealing temperature. The critical interval of temperatures for the eutectoidal transformation of a nodular cast iron [11]:

$$A_{cinf} = 730 + 10[\%Si] = 730 + 10.1.87 = 788.8°C$$

$$A_{csup} = 750 + 28m[\%Si] - 25\ [\%Mn] - 1.8\ [\%S] = 788.8°C$$

is beetween the experimental limits (650°-1050°C).

(ii) the chemical interaction decarburation and de-oxydation reactions depending of temperature, between the components of the solid phase (oxygen and carbon):

$Fe_xO_y + C = xFe + yCO$ (1)
$Fe_xO_y + [C]_{Fe} = xFe + yCO$ (2) t>710°C, with acceptable rate t>950°C
$Fe_xO_y + y\ Fe_3C = (x+3y)Fe + yCO$ (3)

(iii) the chemical interaction, depending on the temperature, between the solid phase components (oxygen and carbon) and that of the gaseous phase (controlled atmosphere):

- reducing reactions: t>500°C

$Fe_xO_y + yH_2 = xFe + yH_2O$ (4)
$Fe_xO_y + yCO = xFe + yCO_2$ (5)

- de-carburation reactions: t>800°C

$C + CO_2 = 2CO$ (6)
$[C]_{Fe} + CO_2 = 2CO$ (7)
$Fe_3C + CO_2 = 2CO + 3Fe$ (8)

- de-carburation reactions: t>800°C

$C + H_2O = CO + H_2$ (9)
$[C]_{Fe} + H_2O = CO + H_2$ (10)
$Fe_3C + H_2O = CO + H_2 + 3Fe$ (11)

- de-carburation reactions: t<800°C

$C + 2H_2 = CH_4$ (12)
$[C]_{Fe} + 2H_2 = CH_4$ (13)
$Fe_3C + 2H_2 = CH_4 + 3Fe$ (14)

Consequently taking into account the facts mentioned above, as well as the experimental, results, it can be said that the significant demising of oxygen content together with the minimum demising of carbon may be ensure by:

- preventing the occurrence of (1) – (3) reactions, by limiting the annealing temperature between 900 – 950°C
- preventing the occurrence of (6) – (11) reactions by increasing the C potential of reducing atmosphere by inlet of CH_4, with the role of consuming CO_2 and H_2O resulted from (4) and (5) reactions: $H_2O + CH_4 = 3H_2 + CO$; $CO_2 + CH_4 = 2CO + 2H_2O$
- the production of a cast iron powder with a lowest oxygen content.

The influence on annealing temperature on the microstructure of the cast iron particles

The fact that the critical temperature interval of eutectoidal transformation of cast iron is inside of the temperature domain, where the reducing annealing may occur, allow the possibility of suitable chosen temperature such that it may be obtain powders with a different microstructure from the point of view of the structure components. Thus:

- the annealing temperature situated above the critical temperature of eutectoidal transformation determine the obtaining of microstructures type: ferite+perlite+graphite, Figure 2
- the annealing temperature situated bellow the critical temperature of eutectoidal transformation determine the obtaining of microstructures type: perlite + ferite+graphite, Figure 2
- the annealing in two temperature steps at $t>t_{cinf}$ and $t<t_{csup}$, outside of the experimental temperature (domain), determine the obtaining of microstructures type: ferite+graphite.

The influence of annealing temperature and the annealing time on the powder plasticity

The modification of the structure due to the annealing temperature and the annealing time influences too the plasticity of the powder. The plasticity of the powder expressed in this paper by the compact green density, is inffuenced not only by the powder structure type but also by the shape, the size and the distribution of microstructure components Table 6 and Table 7.

The results shown in Table 6 and Table 7 reflects that the microstructure type (ferite+perlite+graphite) has a better compactibility.

The influence of annealing temperature on the configuration of the surface of annealed powder

Because of the reducing, during the annealing process, of the iron oxides which forms the surface layer of powder particles, the surface of particles is porous. The size and configuration of pores depend on the annealing temperature, as can be seen in Figure 4.

4 CONCLUSIONS

The annealing treatment modifies the microstructure of the cast iron powder from martensite+carbides to ferite+perlite+graphite. The proportion of the annealled cast iron powder structural components ferite+perlite+graphite depends upon the annealing temperature. Thus at temperatures under the critical interval eutectoid transformation temperature 748.8 – 788.8°C perlite becomes the main structural component while at temperatures above the critical value, ferite dominates. Annealing improves powder plasticity. Higher annealling temperatures (ranging between 650 – 950°C) lead to higher green density

compacts. Plasticity and compact green density also go up wille annealling duration time, up to one hour, after which the increase diminishes.The carbon and oxygen content in the annealled powder decreases with increased annealling temperatures and longer treatment time.

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