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DIMENSION CHANGES OF IRON POWDER MATERIALS ALLOY WITH PHOSPHORUS DEPENDING ON THE PROCESS PARAMETERS DURING SINTERING

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Abstract*: As a result of sintering the powder workpieces large part of the separated free energy leads to higher density of sintered body. This in turn is accompanied by a change in linear dimensions of workpieces. These linear changes in addition to the alloying elements in iron matrices largely depend on the technological parameters of the sintering process - temperature, duration, protective atmosphere and others. This study monitored the impact of the type of protective atmosphere and duration of sintering on the size change of powder workpieces of iron powder ASC 100.29 alloyed 0,15 ÷ 0,60% P. Sintering is conducted at 1150ºC a duration of 15 ÷ 90min in two protective environments - endothermic gas and dissociated ammonia. Presented are graphical relationships of the relative change in the diametric dimensions of the workpieces in dependence on the concentration of phosphorus in them, the type of the protective atmosphere and the duration of sintering.*
KEYWORDS*: POWDER METALLURGY; ENDOTHERMIC GAS; DISSOCIATED AMMONIA IRON POWDERS ASC 100.29; FERROPHOSPHORUS.*

1. Introduction

The powder metallurgy process, which is composed of three main steps - mixing the starting powders, pressing them into the desired shape and subsequently sintering. [1,3,12,13,14]

Sintering is a thermal treatment leading to thickening of free bulk or pressed powder mass. In essence it is a series of physical processes providing more or less fill the pores. In the single-component systems of technological temperature sintering constituted 2/3 ÷ 4/5 of their melting temperature, and multi-component systems are sintered at equal to or slightly higher than the melting temperature of the fusible component at [5.7].

The role of sintering in the making of the final product is different. In the production of highly porous powder products - filters, or in cases where at the final product is not brought great demands on the final set of mechanical properties, sintering is the final operation. In some cases in order to increase density, strength and plasticity of sintered products may need to be re-pressing and sintering secondary [3,4,13]. In practice occurs combined thermo-mechanical treatment - hot forging or hot pressing, and grading has already won products in order to reduce the size tolerances. Iron-copper details or tungsten-copper contacts sealing can be carried out by infiltration of pressed or pre-sintered skeletons of low-melting substances [2.4].

To prevent undesirable oxidation during sintering in industrial furnaces fed restorative or protective gas, and in some cases creating a vacuum.

As a result of caking of powder preparations large part of the separated free energy leads to higher density of sintered workpiece. Driving a spontaneous ongoing process is the difference in free energies of the initial and final state of the substance. The specific ways of reducing these differences consist in a significant reduction of external (surface of the workpieces, open pores) and inner surfaces (closed porosity, grain boundary), and also eliminate the defects in the structure and equilibrium conditions of the system. In the sintering, depending on the nature and state of the system in the powder mass moves a large volume of material, wherein the displacement can be used a number of migration mechanisms [1,2].

Final theory about the processes occurring in sintering at this stage does not exist. There are many unknowns in physical laws describing the process of sintering as a whole and helps to predict to some extent the properties of the sintered materials. In real conditions of sintering run multiple partial processes that depend on each other many cumulative factors - temperature, time, protective atmosphere and others. For example, the combination of surface and boundary diffusion can evolve kineticheski to volume diffusion. In the process of sintering it is possible, and the progress of a number of partial phenomena that are not accompanied by a thickening of the parts.

Analysis of the processes in the kinetic compaction in sintering under the law of the generalized diffusion during this stage does not give satisfactory results. Different authors believe that the main reason for the change in time of the voids in sinter bodies are the size of grains and grain sub, viscosity and reducing the overall concentration of defects. Entered on this basis equations of delay, however, are practically less applicable.

Powder bodies before sintering have generally significant porosity. During the sintering frequently occurs contraction of the pore volume which increases the density of sintering fixtures.

In the most general case of sintering process takes place in three stages.

Heating the sintering samples in the initial stage - 100 ÷ 150˚C, is accompanied by an increase in volume, as occurs the separation of water vapor, gas, vapor or burning grease relaxation of tensions and the like, to reduce flows the total area of contact between the particles.

With increasing temperature to values 0,4 ÷ 0,5 of the melting ends relaxation of tensions, but continued degassing and burning grease and binders and oxide wafers are recovered. As a result of all this non-metallic contacts are replaced with metal and their area is growing. The electrical conductivity of the briquettes increased sharply. At this stage, the occurrence of contact between the partial depends not only on the presence of a partial oxide wafers, but by the mutual arrangement of the particles, the presence of external load and other factors.

The final stage of sintering is carried out at temperatures in the range of 0,7 ÷ 0,9 of the melting temperature of the powder. When it is already complete recovery of the oxide, the contact between particles is fully metallic and run all the basic processes accompanying the heating of: flattening the surface of the particles, spheroidization and koalistsentsiya pore recrystallization and primarily strengthening.

In most instances the process is characterized by the sintering shrinkage the output blanks. For samples molded under high pressure - holding large output density, contraction occurs less in absolute value is less in comparison with the samples pressed at low pressures [13]. The peculiarity of the particulate blanks contraction occurs in that in the event of a subsequent rise in temperature after prolonged isothermal sintering, when the shrinkage is almost stopped, its velocity increases again. The shrinkage in sintering is associated with volume deformation of the particles obtained by volume self-diffusion. Accordingly, the coefficient of self-diffusion change over time, as a result reducing the initial high concentration of defects in the crystal lattice [2].

The change in the values of shrinkage on sintering at a constant temperature is a result of the stabilization of the crystal structures and increase the density of the sintering workpieces, which is accompanied by an increase in the viscosity and influences the kinetics of compacted. The influence of the defects on the process of sintering refers to structural factors, but the influence of the compaction (increasing the density of the porous workpiece, reduces deformations under the action of the same capillary forces increase on account of the contact area) - to geometrical factors [1,3].

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Based on all that the purpose of this study is to trace the impact of technological parameters of the sintering process - duration of sintering and type of protective atmosphere on the amount change of iron powder blanks alloyed with phosphorus.

2. Experimental part

Research are subjected cylindrical specimens with a diameter of 10mm and a length of 50mm. Made of water atomized iron powder ASC 100.29 production company "Höganäs" - Sweden. At present it is the highest quality iron powder produced by the company "Höganäs". It is characterized by very high purity. It has excellent compressibility, which results from the fact that the particles are nearly spherical.

This allows after a single pressing to achieve a density in the range 7,2 ÷ 7,3g / cm^3 [8]. Particularly suitable are those powders in the production of structural articles with high density, as well as for products with specific magnetic characteristics.

To the iron powder was added 0,15 ÷ 0,60% phosphorus and 0,8% lubricant "Kenolube", after which the components of the batch are mixed for 30min in a non-metallic hopper of the mixer with intersecting axes of rotation.

The samples are pressed once struggled 600MRa [13].

Sintering is conducted in a horizontal muffle furnace with a ceramic pipe „Carbolitte“ in protective atmospheres of endogaz and dissociated ammonia - Table №1.

***Table №1**. Composition of protective atmospheres*

Type of atmosphere	Chemical composition, %					
	H_2	N	H_2O	CO	CO_2	CH_4
Dissociated ammonia	75	25	0,5	-	-	-
Endothermic gas	40	40	-	18	1,0	1,0

From previous studies [10,11] has been shown that the most suitable temperature for the sintering of samples from the test system is 1150ºC. For this sintering of the samples was conducted at this temperature for 15÷90min. controlling the velocity of the incoming gas and its dew point.

To prevent oxidation of specimens in the course of sintering they were placed in sealed containers with a backfill of a mixture according to 1 [9]:

$$75\%Al_2O_3 + 15\%FeMn + 10\%C \quad (1)$$

Density of the samples after sintering is determined by the weight method - 7,20g / cm3, according to a methodology developed in [2].

To determine the influence of the duration of sintering on the dimensional changes of the samples in the process of sintering each 15min from the furnace are taken out on 5 samples of which were measured diameters in two mutually perpendicular directions and defined the relative change in dimensions to those of the starting workpieces.

The results for the samples sintered in an environment of about endogaz presented in Table №2, but these sintered in a dissociated ammonia atmosphere of Table №3.

***Table №2** Linear changes in sintering in an environment of endogaz*

t, min	Relative change in the size of preparations, %				
	0%P	0,15%P	0,30%P	0,45%P	0,60%P
15	-0,01	-0,02	-0,04	-0,13	-0,28
30	-0,02	-0,03	-0,05	-0,17	-0,37
45	-0,03	-0,04	-0,06	-0,19	-0,41
60	-0,04	-0,05	-0,08	-0,20	-0,45
75	-0,05	-0,07	-0,09	-0,21	-0,49
90	-0,05	-0,07	-0,10	-0,21	-0,53

***Table №3** Linear changes in sintering under an atmosphere of dissociated ammonia*

t, min	Relative change in the size of preparations,%				
	0%P	0,15%P	0,30%P	0,45%P	0,60%P
15	-0,02	-0,04	-0,08	-0,24	-0,60
30	-0,04	-0,06	-0,10	-0,27	-0,73
45	-0,06	-0,08	-0,12	-0,29	-0,81
60	-0,09	-0,11	-0,14	-0,31	-0,87
75	-0,13	-0,14	-0,16	-0,32	-0,92
90	-0,14	-0,15	-0,17	-0,32	-0,95

The graphical interpretation of the relative change in the straight-line dimensions of the samples at time of sintering 15÷90min is shown in Figure 1 ÷ 6.

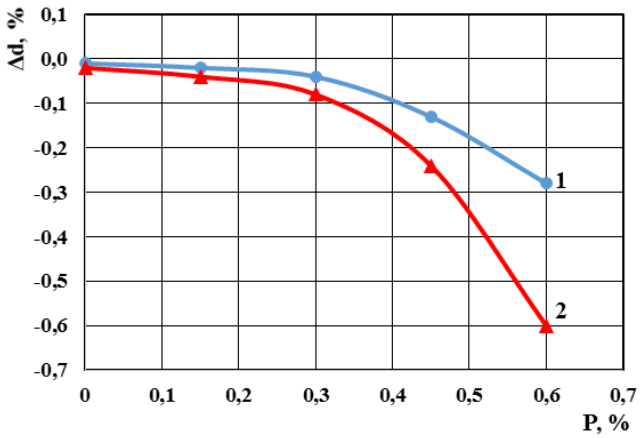

***Fig.1.** Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 15min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

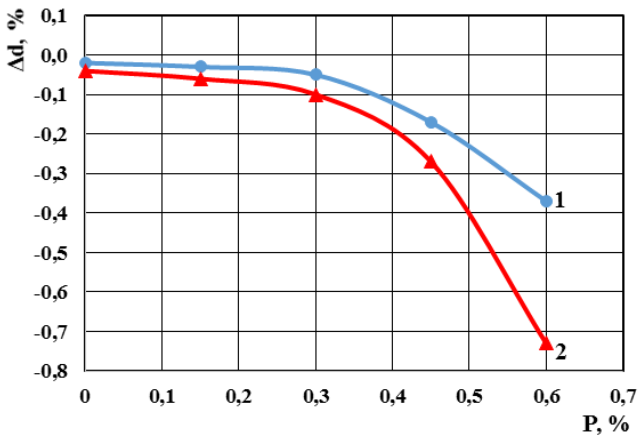

***Fig.2.** Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 30min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

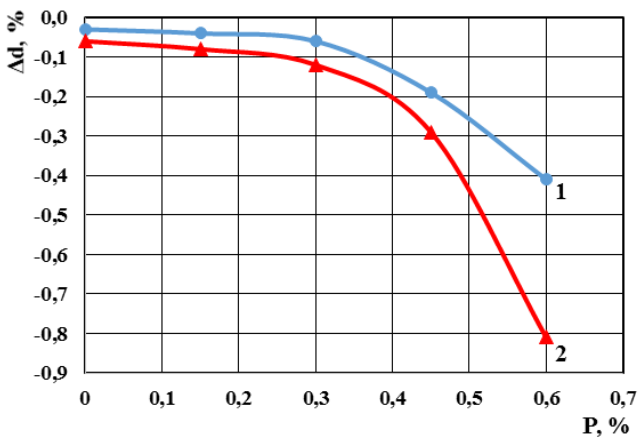

***Fig.3.** Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 45min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

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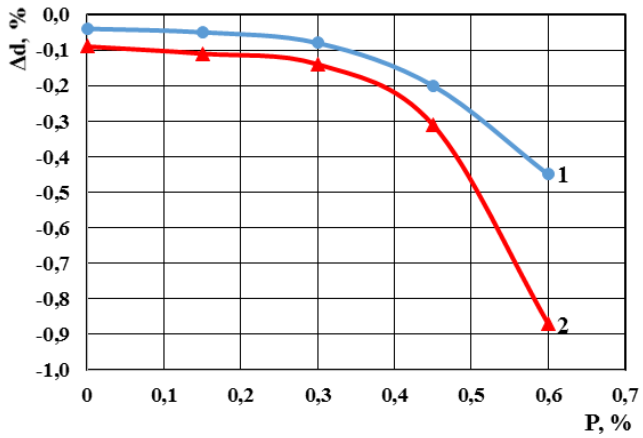

Fig.4. *Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 60min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

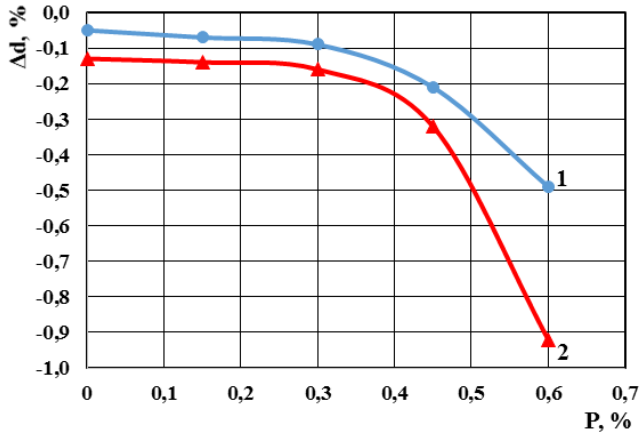

Fig.5. *Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 75min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

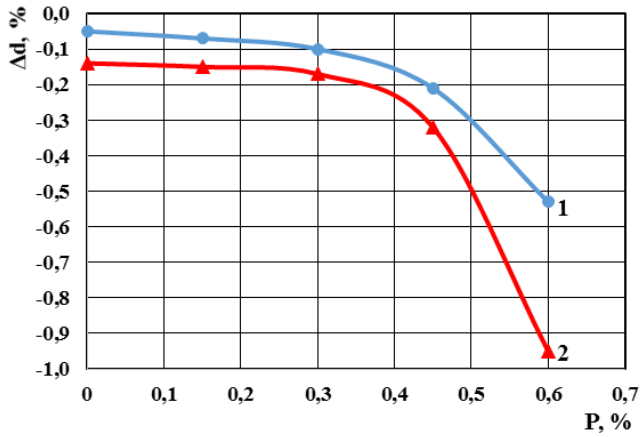

Fig.6. *Relative dimensional changes in the diameters of the workpieces after sintering at 1150ºC for 90min in a medium by: 1 - endogaz; 2 - dissociated ammonia.*

From the obtained experimental results it can be seen that the addition of phosphorus in the iron matrix leads to shrinking dimensions of the samples in all investigated durations of sintering. The graph shows that the process of change in the size of the blanks takes place in three stages conditionally. In the first stage when phosphorus in the iron matrix is of the order of 0,15% registered dimensional changes are minor and can be ignored. Reproving contraction was observed in the samples having a phosphorus concentration of 0,15 ÷ 0,45% and it is in the range of 0,1 ÷ 0,3%. When increasing the concentration of phosphorus over 0,45% shrinkage of the dimensions of the starting workpieces is intensified and can reach values 0,55÷0,95% depending on the type of the protective atmosphere.

This change in size can be explained by the phase equilibrium diagrame iron-phosphorus - fig.7.

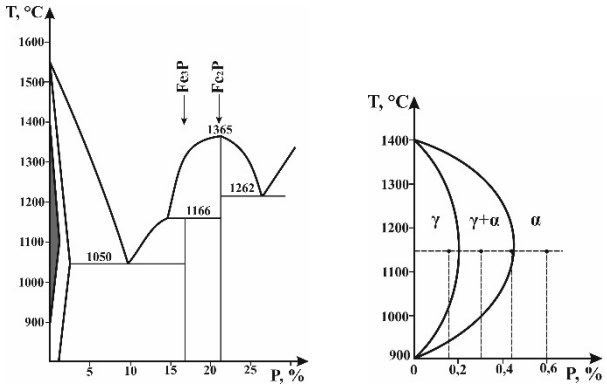

Fig.7. *Phase equilibrium diagrame iron-phosphorus [14].*

It is seen that phosphorus is an element which greatly narrows the austenitic zone. When the temperature of sintering - 1150ºC pure austenitic zone only we have a concentration of phosphorus in the samples 0,15%. Above a concentration of 0,45% P at the temperature of sintering iron matrix is pure ferrite. Since the rate of diffusion in the ferritic steel is significantly greater than that in the austenitic region, it at the same sintering temperature diffusion processes occur in intensive in ferritic zones above 0,45% P. This leads to considerably reduce the volume porosity in the details, and hence the change in their linear dimensions. At a concentration of phosphorus 0,15 ÷ 0,45% at the temperature of sintering the samples are located in the two-phase austenitic-ferritic region, and therefore the change of the linear dimensions of the workpieces is not so pronounced as in those sintered in pure ferritic area of the diagram.

With increasing duration of sintering from 15 to 90min creating conditions except to reduce the total volume porosity of workpieces for smoothing and pore spheroidization. This in turn leads to a further contraction of the tested samples. Regardless of the concentration of phosphorus therein and the type of protective atmosphere to increase the duration of sintering the relative values of dimensional change increased 1,5 ÷ 2,0 times.

From the literature it is known that during sintering in recreational environments is achieved a higher density of samples [1,3,9]. The activity of restorative environments depends mainly on the amount of hydrogen in them. It was with a large amount of hydrogen in the protective atmosphere of dissociated ammonia - 75% is explained by intense change in linear dimensions of samples. It is two times greater than the contraction seen in the other conditions being equal, after sintering in an environment of endogaz wherein the hydrogen concentration is approximately 2 times smaller - 40%.

3. Conclusions

Of the examination and received at the results they can draw the following important conclusions:

- ❑ It is confirmed that addition of phosphorus in the iron matrix of particulate materials is accompanied by a change of the dimensions of the starting preparations after sintering;
- ❑ It was found that the change in the size of blanks is directly dependent on the phase composition of the samples. At concentrations up to 0.15% P in sintering temperature alloys are in austinitnata area of the diagram iron-phosphorus and relative change in size is negligible and can be ignored. The most significant change in size in samples containing 0,45÷0,60% P. These alloys at sintering temperature are present in the ferrite zone where diffusion processes are significantly more intense;

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- It confirmed that with increasing duration of sintering from 15 to 90min occurs further contraction of the samples, which is a consequence of both the reduction in the total volume porosity and by smoothing and spheroidization pore;
- Was confirmed that sintering in a more intense flow diffusion processes in a protective atmosphere containing a larger amount of hydrogen.

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