Investigation of Compaction and Sintering Features of High Porous Materials Produced with Different Pore Formers

L. L. Roganov, N. A. Rudenko, L. V. Popivnenko

Donbass State Engineering Academy

The peculiarities of compaction and sintering of samples obtained from iron powder mixtures with different types of pore-formers (ammonium bicarbonate, sodium hydrocarbonate, sodium chloride) is contemplated. Compaction was performed unilaterally in a closed cylindrical matrix and sintering was carried out in reducing environment in a container with filling. Compression and ejection curves for the samples obtained from specified mixtures in the range of pressure 200-800 MPa were plotted. The influence of pore formers, used in the experiment, on the compaction mixtures of the system "iron – pore-former" is established. The dependencies of the changes in linear dimensions of sintered samples for specified values of compaction pressure within indicated range are built.

Keywords: HIGH-POROUS MATERIALS, COMPACTION PRESSURE, PORE-FORMERS, SHRINKAGE/GROWTH KINETICS

1. Introduction

Among the various types of products manufactured by powder metallurgy a special place occupy high-porous sintered materials. Properties, production technology and the scope of high-porous sintered materials have characteristics that distinguish them into a separate group. These progressive materials are widely used in mechanical engineering, power engineering, medicine, aviation, chemical, oil and metallurgical industries. Technological cycle of production of high-porous sintered materials includes different operations such as preparation of powders for compaction (sieving, annealing), granulation (if necessary), mixing of components, compaction of briquettes, followed by sintering and machining [1-3].

One of the basic properties of high-porous sintered materials is the porosity level. For the porosity increase of such materials different pore-formers are introduced in their composition: plastics, sodium hydrocarbonate, sodium carbonate, ammonium carbonate, carbamide, carbonate, potassium hydrocarbonate, etc. Moreover, achievable level of porosity and pore size completely depends on the volume content and particle size of applied pore-former. After compaction of the mixture of powder material with a pore-former, the pore-former agents are removed from the compacts in various ways: evaporation, thermal decomposition during sintering or dissolution in liquid environment (most frequently in distilled water) [7-10]. Experience has shown that the maximum achievable level of porosity when using pore-formers reaches 75% [11]. Thus the total number of closed pores is about 4-7% and others are open ones.

It is known that during sintering of porous materials there is a change of their size: shrinkage or growth. The degree of dimensional change depends on the powder material nature, sintering conditions (temperature, applied protective atmosphere) and the level of porosity. Shrinkage kinetics during sintering of the samples with different content of pore-formers is not sufficiently investigated and described in scientific literature. Therefore, the purpose of this work is to establish the influence of various pore-formers on shrinkage/growth kinetics during sintering of compacts obtained with their use.

2. Experimental techniques

As the initial materials for experimental procedure were used iron powder, sodium chloride, ammonium bicarbonate and sodium hydrocarbonate. The particles of iron powder have mainly a spongy form with numerous projections; ammonium bicarbonate represents colorless crystals of irregular shape; powders of sodium chloride and sodium bicarbonate are white crystals with the shape close to cubic. For pore obtaining with predetermined size all the powders used in the experiment were sieved into fractions. The amount of pore-former introduced into the iron powder was invariable reaching 50% of volume in all cases. The composition and density of mixtures and particle size of pore-formers are shown in **Table 1**.

Table 1. Composition of powder mixtures and the particle size of pore-formers used in the experiment

Mixture	Fe, weight, g	Pore-former content (vol., %)	Density, g/sm^3	Particle size, μm
Fe+NaCl	13.1	50	5.02	500-1000
Fe+NH$_4$HCO$_3$	13.1	50	4.73	125-250
Fe+NaHCO$_3$	13.1	50	5.2	63-125

Sample weight was determined on the assumption of the size, density, and pore-former proportion content in the mixture of samples according to equation:

$$m_{mix} = V \cdot \rho_{mix}, \quad \text{(Eq. 1)}$$

here m_{mix} – weight of powder mixture, g; V is the volume of compact, cm^3; ρ_{mix} – density of powder mixture, g/cm^3.

The weight of iron powder in all mixtures remained constant (13.1 g) and the sample weight of powder mixtures was the following: mixture iron-sodium chloride – 16.7 g, mixture iron-ammonium bicarbonate – 15.2 g, mixture iron-sodium bicarbonate – 17 g. The sample weight of iron and pore-former was selected regarding to the constancy of the ratio of the sample height to its diameter and taken as a unit ratio. The density of powder mixture is determined by formula evaluation:

$$\rho_{mix} = \rho_{porefor} \cdot X + \rho_{Fe} \cdot (1 - X), \text{(Eq. 2)}$$

here $\rho_{porefor}$ – pore-former density, ρ_{Fe} – iron powder density, g/cm^3; X – pore-former proportion content in the mixture.

Mixing was carried out manually during 15 minutes for all the mixtures. To improve the homogeneity of mixtures 0.5% of kerosene was added (by weight) [12]. Obtained mixtures visually had a uniform distribution of components.

Compaction of the investigated powder mixtures was performed by uniaxially compaction in a rigid matrix of 16.8 mm diameter in specified range of compaction pressure (p_{comp}) of 200-800 MPa with 100 MPa step [13].

Mixture compaction was performed on hydraulic compression testing machine model PSU-50 with nominal force 500 kN without lubrication of the press-instrument working surfaces. Since the compaction was performed within specified values of compaction pressure P_{comp}, then setting the magnitude of compaction pressure p_{comp}, determined the necessary compaction effort by the equation:

$$P_{comp} = 0.785 \cdot d^2 \cdot p_{comp}, \quad \text{(Eq. 3)}$$

here d – green compact diameter, mm.

Compaction of powder mixtures was conducted using calculated values of compaction efforts P_{comp}. Meanwhile a rev-type force indicator of the testing

machine recorded the ejection effort P_{ej}. Obtained compacts were measured and weighed, and then ejection pressure and relative density of the samples were calculated:

$$p_{ej} = \frac{P_{ej}}{\pi \cdot d \cdot h}, \quad \text{(Eq. 4)}$$

here h – green compact height, mm.

$$\rho_{rel} = \frac{m}{0.785 \cdot d^2 \cdot h \cdot \rho_{mix}}, \quad \text{(Eq. 5)}$$

here m – green compact weight, g.

Sintering of compacts was performed in a container with asbestos filling at the temperature of 1150°C during one hour in reducing medium (carbon monoxide) in electric furnace. There was one-step heating at the rate 7 °C/min. Cooling of the samples was carried out inside the container in the furnace.

To determine relative density of sintered samples they were weighed and measured. Then calculations of relative density of sintered compacts (ρ_{rel}^s), magnitude of relative volumetric shrinkage (or growth v_V) and magnitudes of relative linear shrinkage (growth) in height and diameter (l_h, l_d) were performed.

$$\rho_{rel}^s = \frac{m_s}{0.785 \cdot d_s^2 \cdot h_s \cdot \rho_{Fe}}, \quad \text{(Eq. 6)}$$

here m_s – sintered compact weight, g; d_s – sintered compact diameter, mm; h_s – sintered compact height, mm.

$$v_V = \frac{V - V_s}{V}, \quad \text{(Eq. 7)}$$

$$l_d = \frac{d - d_s}{d}, \quad \text{(Eq. 8)}$$

$$l_h = \frac{h - h_s}{h}, \quad \text{(Eq. 9)}$$

here V – green compact volume, mm^3; V_s – sintered compact volume, mm^3.

3. Results and discussion

The compaction curves for mixtures of iron powder with equal content of pore-formers are shown in the **Figure 1**.

As shown in the **Figure 1** with the increase of compacting pressure the relative density of samples rises in all cases, which is associated with a higher ratio of deformation of powder particles forming the mixture. Higher density is achieved for the samples of the system iron-sodium chloride. The lowest density was in the samples of the system iron-sodium bicarbonate. Obviously, this is due to the size of the iron powder particles (63 μm - 125 μm) and sodium chloride (500 μm - 1000 μm). Practice of powder mixtures compaction shows that higher compactibility is achieved for the mixtures of fine and coarse fractions which possess more dense packing at the filling stage [6].

Ejection curves of powder mixtures compacts with 50% of different pore-formers are presented in the **Figure 2**.

As shown in the **Figure 2** with the increase of compaction pressure, the ejection pressure of the samples rises in all cases. It is associated with the increase of lateral pressure stressing the matrix walls. For the specified values of compaction pressure, ejection pressure was the greatest for the sample iron-sodium chloride, and the lowest one for the sample iron-sodium bicarbonate. Also it should be noted that compaction and ejection processes for all the samples was accompanied by a strong sound effect, especially in case of sodium chloride, and insignificant self-oscillations of hydraulic compression testing machine. However, in the specified compaction range samples of all compositions were cracks free.

Diametrical, volumetric and linear shrinkage (growth) dependencies on the compaction pressure for cylindrical samples with different amount of pore-formers (50% by volume) are shown in **Figure 3-5.**

As shown in **Figure 3-4** resizing of the samples obtained from mixtures iron-ammonium bicarbonate and iron-sodium hydrocarbonate are identical: increase in diameter and reduction in height. The volume of sintered samples decreased compared with green compacts.

For the samples obtained from the mixture iron - sodium chloride growth was observed in height and diameter. Accordingly, the volume of sintered samples was greater than volume of green compacts.

Also it should be noted that with the increase of compaction pressure resizing decreases in all cases. It occurs due to the fact that with the increase of compaction pressure increases the density of compacts which slows down shrinkage (growth) kinetics.

Weighing of sintered samples showed that their mass in the process of sintering decreased to the mass of pure iron sample, indicating that pore-formers are removed from the metal matrix.

This demonstrates high efficiency of mentioned above pore-formers for forming of pores of predetermined dimensions in the products. This allows achieving high porosity parts with minimal contamination by pore-former decomposition products.
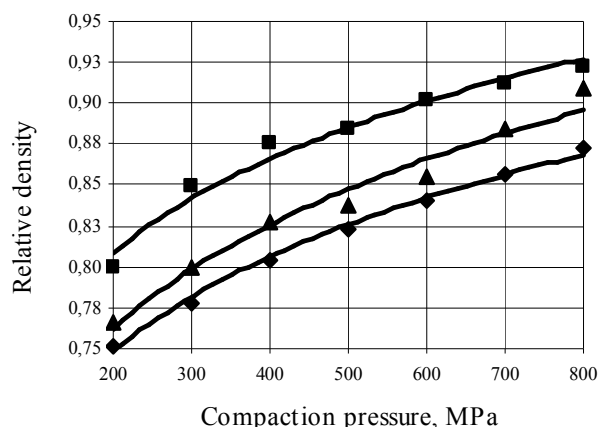

Figure 1. Densification curves of powders: ■ – mixture 50% Fe + 50% NaCl; ▲ – mixture 50% Fe + 50% NH4HCO3; ♦ – mixture of 50% Fe + 50% NaHCO3
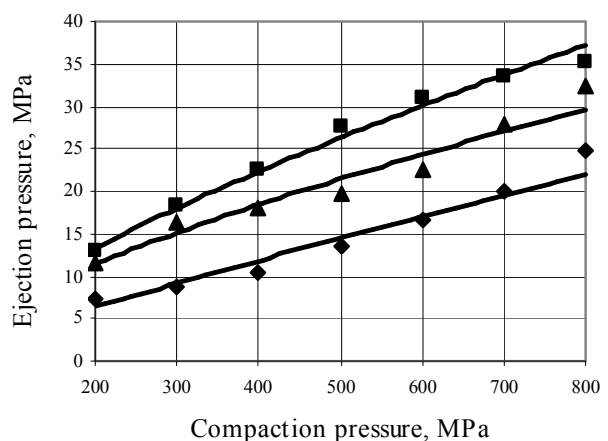


Figure 2. Ejection curves of powders: ■ – mixture 50% Fe + 50% NaCl; ▲ – mixture 50% Fe + 50% NH4HCO3; ♦ – mixture 50% Fe + 50% NaHCO3
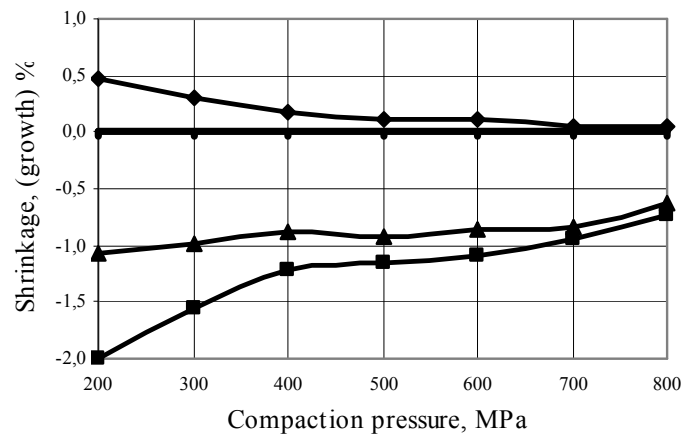
Figure 3. Dependence of shrinkage on the compaction pressure for powder samples with ammonium bicarbonate content 50%: ▲ – volumetric shrinkage; ■ – shrinkage in height; ♦ – growth in diameter
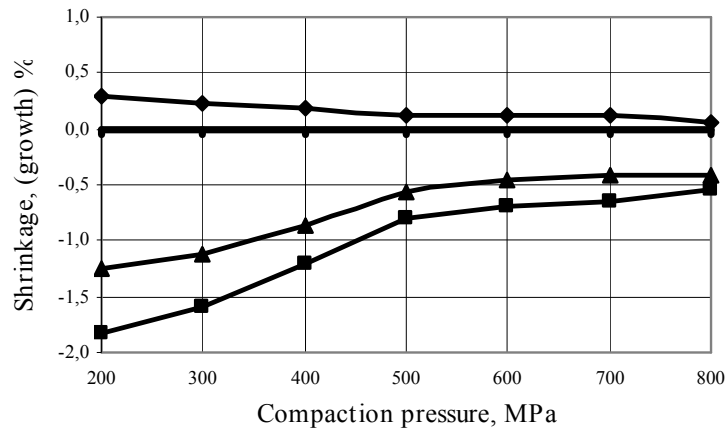
Figure 4. Dependence of shrinkage on the compaction pressure for powder samples with sodium hydrocarbonate content 50%: ▲ – volumetric shrinkage; ■ – shrinkage in height; ♦ – growth in diameter
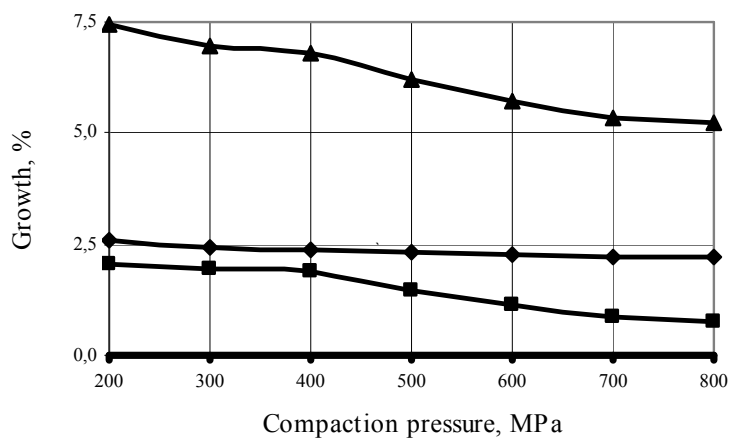
Figure 5. Dependence of growth on the compaction pressure for powder samples with sodium chloride content 50%: ▲ – volume growth; ■ – growth in height; ♦ – growth in diameter

Conclusions

1. With the increase of compaction pressure relative density of samples of all compositions intensifies in all cases. Higher density is achieved with the samples of iron-sodium chloride, and the lowest – with the samples of iron-sodium hydrocarbonate. This is achieved due to the value of size powder particle of sodium chloride and iron. It is explained by the fact that mixtures with such a difference in size of the particles are compacted to a much higher density.

2. With the increase of compaction pressure the ejection pressure is also increased for the samples of all compositions, because lateral pressure on the matrix walls is increased. With the same values of compaction pressure the highest values of ejection pressure are observed for the sample iron-sodium chloride, and the lowest – for the sample iron-sodium hydrocarbonate. Obviously, the use of different pore-formers causes a change in the coefficient of friction between the lateral surface of the sample and the walls of the matrix.

3. Application of different pore-formers determines the nature of dimensional changes of the test specimens. For the samples iron-ammonium bicarbonate and iron-sodium hydrocarbonate resizing had an identical nature: shrinkage in height and diameter growth. For the sample iron-sodium chloride increase in height and diameter is observed. Maximum change occurs in the linear dimensions of the sample iron-sodium chloride.

4. With the increase of compaction pressure resizing of the samples decreased in all cases. It occurs due to the fact that with the increase of compaction pressure increases the density of compacts which slows down shrinkage (growth) kinetics.

5. Particle size of pore-formers determines the size of pores formed during sintering, and the porosity of the products is determined by the amount of pore-former in the mixture. Weighing of the sintered samples shows that their mass in the process of sintering decreases compared to the mass of pure iron sample, indicating that pore-former removes from the metal matrix. This demonstrates high efficiency use of the mentioned above pore-formers for forming pores of desired dimensions in the parts. This allows achieving high porosity parts with minimal contamination by pore-former decomposition products.

References

1. Vityaz P.A., Kaptsevich V.M., Sheleg, V.K. *Porous powder materials and their products*. Minsk: Highest school, 1987, 164 p.
2. Andrievsky R.A. *Porous cermet materials*. Moskow: Metallury, 1964, 180 p.
3. Shibryaev B.F. *Porous penetrable sintered materials*. Moskow: Metallurgy, 1982, 168 p.
4. Belov S.V. *Porous materials in engineering*. Moskow: Engeneering, 1981, 247 p.
5. Li M., Liu Y., Ye J.W., Zhang L.F., Li J., Tu M.J. *Process and compressive properties of porous nickel materials*. Powder Metallurgy, 2006, Vol. 49, pp. 114-116.
6. Erk K.A., Dunand D.C., Shull K.R. *Titanium with controllable pore fractions by thermoreversible gelcasting of TiH2*. Acta Materialia, 2008, Vol. 56, pp. 5147-5157.
7. Rudenko N.A., Laptev A.M: *Influence of pore former type on compaction and properties of highly porous sintered parts*. Resource saving production technology and processing of materials by pressure in engineering, 2010, № 1, pp. 54-60.
8. Ahmed Y.M.Z., Riad M.I., Sayed A.S., Ahlam M.K., Shalabi M.E. *Correlation between factors controlling preparation of porous copper via sintering technique using experimental design*. Powder technology, 2005, Vol. 175, pp. 48-54.
9. Bansiddhi A., Dunand D.C. *Shape – memory NiTi foams produced by solid – state replication with NaF*. Intermetallics, 2007, Vol. 15, pp. 1612-1622.
10. Michailidis N., Stergioudi F. *Establishment of process parameters for producing Al-foam by dissolution and powder sintering method*. Materials and Design, 2011, Vol. 32, pp. 1559-1564.
11. Laptev A., Bram M., Buchkremer H.P., Stoever D. *Study of production route for titanium parts combining very high porosity and complex shape*. Powder metallurgy, 2004, Vol. 47, № 1, pp. 85-92.
12. Libenson G.A. *Manufacturing of sintered parts: textbook for technical school*. Moskow: Metallurgy, 1982, 256 p.
13. Rudenko N.A., Laptev A.M., Popivnenko L.V. *Pressing of powder mixture iron and sodium chloride*. Processing of materials by pressure, 2009, No 1 (20), pp. 326-329.

Исследование особенностей прессования и спекания высокопористых материалов изготовленных с применением различных порообразователей

Роганов Л.Л., Руденко Н.А., Попивненко Л.В.

Рассмотрены особенности прессования и спекания образцов, полученных из смеси порошка железа с различными видами порообразователя (бикарбонат аммония, гидрокарбонат натрия, хлорид натрия). Прессование смесей выполнялось в закрытой цилиндрической матрице по односторонней схеме, а спекание прессовок проводилось в контейнере с засыпкой в восстановительной среде. Построены кривые уплотнения и выпрессовки для образцов, сделанных из указанных смесей для диапазона давлений прессования 200-800 МПа с шагом 100 МПа. Установлено влияние применяемых в эксперименте порообразователей на уплотняемость смесей системы железо – порообразователь. Построены зависимости изменения линейных размеров спеченных образцов для фиксированных значений давлений прессования в указанном диапазоне.