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Experimental Determination of the Interparticle Contact Structure in Densified Iron Powders

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Despite being one of the oldest objects of materials science, powder structures still are of great interest. Significant information can be provided by analysis of interactions between particles in powder medium. This article discusses the experimental results from measurements of dynamics of probing solvent removal from pore volume, linked to interparticle contacts. The concept of topological uniformity of pore space in powder bodies is formulated and distributions of three-dimensional interparticle contacts by volumes are analyzed.

Keywords interparticle contacts, isostatic/axial/step radial pressing, porous space, powder/compact

1. Introduction

The quantitative parameters of a porous system are closely related to the properties of materials produced by the powder consolidation. This statement is so much obvious and trivial that it hardly needs supporting by the analysis of publications on the subject. At present, there are certain well-established stereotypes of understanding geometry, topological features, and, as a whole, the role of pores in the behavior of powder compacts. Some of them are formulated in an explicit form and lie at the basis of commonly accepted methods to study pores, e.g., the radius (or volume) distribution of pores. However, the real pore space of a powder body does not consist of some set of pores of certain sizes. It is a complex network of canals having a sharply defined isometric nature of sections. There is no way of unambiguously telling where a pore of one size ends and a pore of another size starts. Of course, the above pore radius (or volume) distributions are very useful, as they indirectly reflect the structure evolution of a powder body under various actions. However, they are not directly related to the properties of powder compacts. Understanding the powder medium structure at the mesoscale demands formulation of new models for interparticle interactions (Ref 1, 2).

Another widespread notion, which automatically, without a clear formulation, is used as the basis for the analysis of powder bodies' behavior, is the idea of the absolute topological uniformity of the pore space. In practice, this should have resulted in the fact that properties of two compacts of the same porosity produced from the same powder are uniform regardless of the technological prehistory and the way of consolidation. According to experimental data and computer simulations, the compact prehistory affects properties of a powder body even more strongly than the dispersity of particles and volume fraction of pores (Ref 3, 4).

Unlike such an object like a "pore with a certain volume and surface," which is a pure abstraction, interparticle contacts are real physical objects. The quantity and parameters of them are directly related to the prehistory and properties of powder compacts. Investigation and prediction of properties of powder bodies based on the quantity and structure of interparticle contacts present in them have not been widely used because of the difficulties associated with experiments. The works by Skorokhod et al. on determining the sections of interparticle contacts in compacts of electroconductive powders are worth mentioning (Ref 5, 6).

In our opinion, the difficulties associated with experimental studies of interparticle contacts are caused by the use of the obvious concept, according to which a contact is a flat (in any case two-dimensional) region of the direct contact of two powder particles. The determination of a total area of these regions and the size distribution of them is hardly possible even for an arbitrary single-component system of particles with a narrow dispersed composition.

The aim of this article is to analyze some new possibilities and results relevant to the use of a new concept of considering interparticle contacts as being three-dimensional objects. According to this concept, the pore space of a powder body is topologically nonuniform. One may define regions, in which the compact pore space has special properties.

In probing the pore space by removing the liquid, which fills pores, the segments of trajectories of probing molecules that are equal in length will be identical in shape for any section in the pore volume. This is the evidence of the metric uniformity of the pore space. At the same time, the energy required from probing molecules to overcome these geometrically identical segments of the path may prove to be different in different regions of pore space. This is the manifestation of the space topological nonuniformity. A fraction of the compact pore space is considered, which differs in properties from the basic pore volume, as the volume associated with interparticle contacts.

Because of this, the main tasks of the present work were the experimental determination of the constituent of the pore

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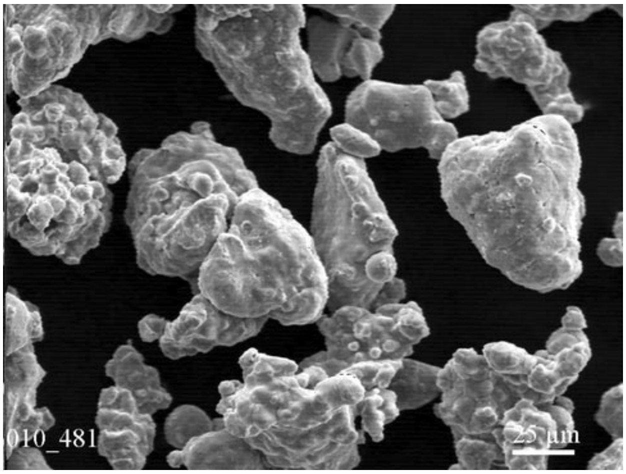

Fig. 1 Sputtered powder

volume in powder compacts related to interparticle contacts (later on a contact volume); the separation of individual interparticle contacts and the assessment of their distribution by size of contact volume.

A contact volume of pores in a powder compact may be defined by various methods. At the basis of the experiment presented here is the filling of the compact pores with a solvent, which then is removed by heating or decompression. Solvent molecules being removed probe the pore space of the compact. The information about the absolute value of the contact volume in the compact and about the distribution of the contact by volume is contained in the data on the dynamics of removing the residual solvent from pores.

According to this interpretation, the contact volume is a certain portion of the compact pore space, which requires from the substance molecules (probes) migrating in the above portion more energy to overcome a unit path length than the bulk of pores. This means that a final stage of probing is of interest.

2. Objectives

The porous compacts used in the following experiments were produced from iron powders of various origins, produced by the Brovary plant for powder metallurgy in Ukraine. Some of the powders used had particles of fragmentation shape, produced by spraying; other powders had particles of spherical shape, produced by the decomposition of iron pentacarbonyl. The photos in Fig. 1 and 2 display the characteristic particle shapes for powders of these types.

The choice of powders is dictated by a strong difference in particle morphology and dispersion, which is important for the assessment of the versatility of the proposed approach. The dispersed compositions of powders, as measured with an Accu Sizer 780/DPS optical sensing device, are shown in Table 1 and 2.

3. Experimental

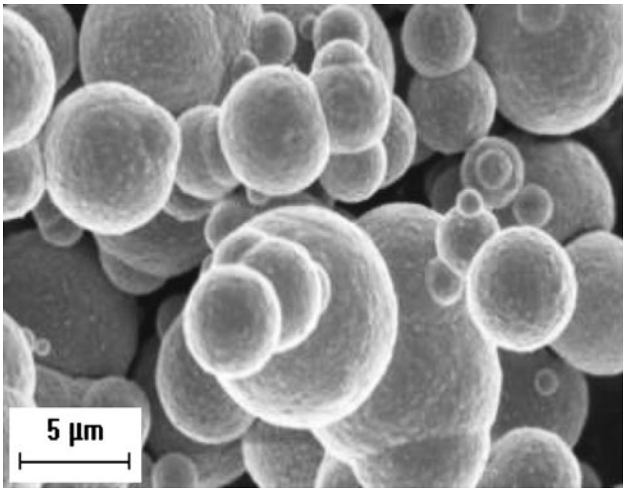

Fig. 2 Carbonyl powder

Table 1 Sputtered powder

Fraction, μm	125/100	100/80	80/63	63/50	50/40
The content of fraction, % on mass	15.3	33.8	27.1	18.5	6.3

Table 2 Carbonyl powder

Fraction, μm	10/7	7/5	5/3	3/1	1/0
The content of fraction, % on mass	3.8	16.0	30.1	43.4	6.7

Fraction boundaries in μm and concentration of fraction in wt.%
Specific surface of powder is 0.28 and 1.38 m^2/g for sputtered powder and carbonyl powder respectively

A sample, in the form of a compact or a loose powder saturated with a solvent by infiltration or capillary condensation of vapor was placed into a heating cell, at the rate of 10-20 K/s. The basic amount of the solvent was previously removed. A residual solvent evaporating from the compact (as a rule, $<1\%$ of the initial, as measured by weighing the specimen with a precision balance) was supplied to a JMS-T100LP mass-spectrometer with a flow of an inert gas. The requirements for the solvent were:

- not a very low boiling temperature (in the range from 373 to 423 K),
- absence of a chemical interaction with the powder substance,
- absence of specific adsorption interaction with the powder particles surface.

Based on these criteria, dimethyl sulfoxide was chosen as a probing agent for iron powders.

4. Results and Discussion

The curves obtained at various heating rates and different solvent-loose powder ratios (Fig. 3) are equivalent to each other. That's why the final segment of any of these curves can be used as a base line for the analysis of the final segment of the curve of the solvent evaporation from a loose powder. The final

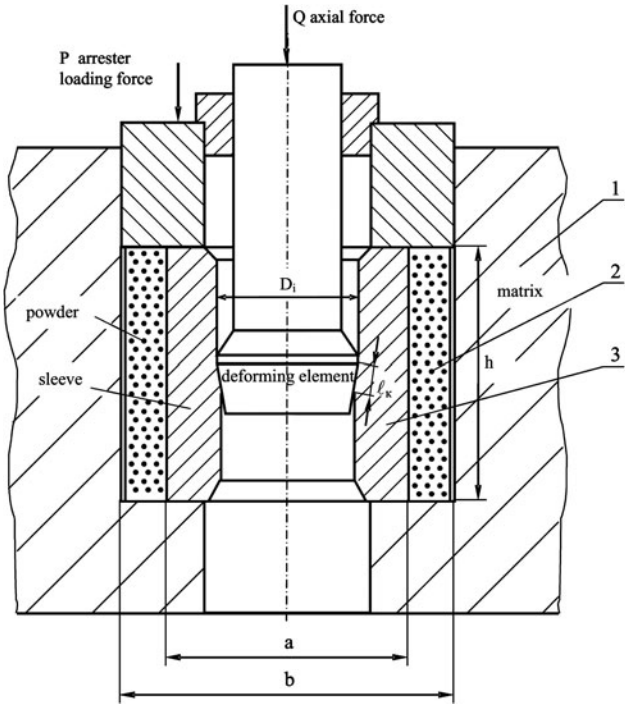

Fig. 3 Schematic diagram of the radial step deformation powder compaction method

segment of the curve of the solvent evaporation from a loose powder was assumed as the base line for each compact. The initial solvent-powder ratio corresponded to the solvent content of the compact when its pores are completely filled. The heating rates of samples (a loose powder wetted and a compact impregnated with a solvent) were equal in both cases. The volume of samples has no influence on the evaporation path within the range of volumes 0.5-2 cm^3. Also, the fact that the part of the specimen demonstrates the same evaporation path, as the whole specimen is indicative of homogenous wetting, even when solvent content is below 1%.

For samples of powders subjected to compaction or ultrasound treatment, the shape of the final segment of the solvent evaporation curve changes qualitatively. A system of peaks appears in the curve. The peak shape, quantity, and position for the same powder are essentially dependent on the conditions of compaction or treatment (Fig. 4). The absolute volume of the solvent that remains in the compact pores by the time of the first deviation of the evaporation curve from the base line is the assessment of the special portion of the pore space, which is associated with interparticle contacts (from here on the term a "near-contact volume" will be used).

For further analysis, the results of mass-spectrometric experiments were presented as a function of the increment of the solvent quantity removed from the compact (the Δm increment, positive or negative, was measured relative to the base line) on the absolute solvent quantity, which is removed from a sample of the loose powder. It is presented as the number of solvent molecules removed from the bulk of the loose powder.

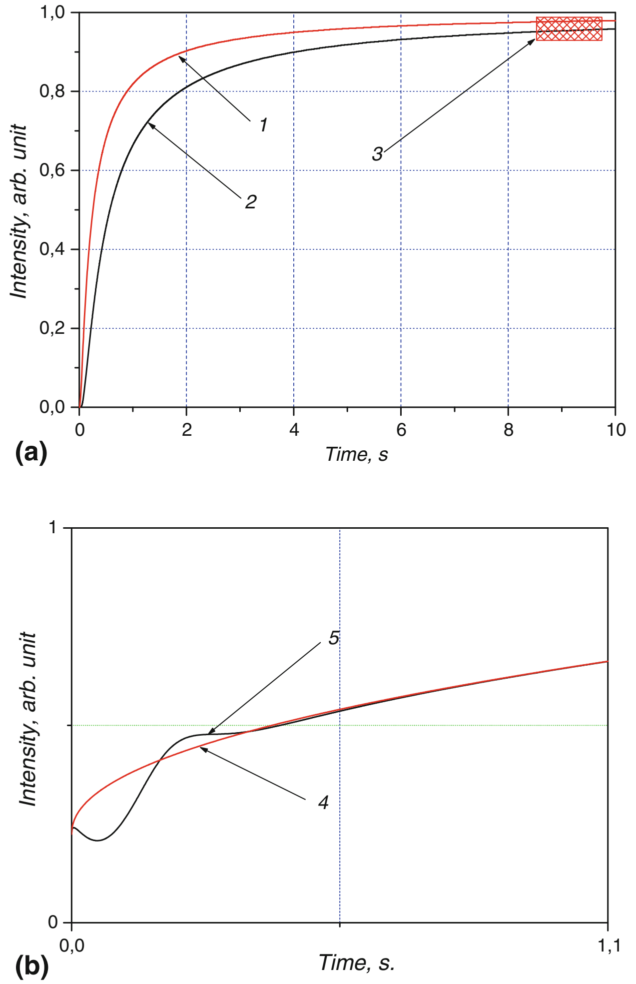

Fig. 4 (a) Full curves for sounding solvent evacuation: (1) drop of solvent (~0.03 cm^3), (2) free powder saturated with solvent, and (3) final study of sounding. (b). Final stage of sounding solvent evacuation: (1) drop of solvent (~0.03 cm^3) and (2) free powder saturated with solvent

The process of removing a solvent from pores can be considered as the dispersion of the flow of probing molecules by the compact pore space. From this point of view, the dependence given in Fig. 4 presents a shape of a scattering wave. Then, using the Fourier transform, the density of the distribution of compact interparticle contacts by volume is obtained. The curves obtained were normalized using a coefficient, which is equal to the absolute value of the near-contact volume of the given sample.

This approach makes it possible not only to determine the distribution of interparticle contacts by volume, but also to assess the absolute quantities of contacts in powder samples, which were compacted using various methods and subjected to ultrasonic treatment.

To assess the effect of the technological prehistory on the characteristics of the contact volume in compacted iron powders, the latter were subjected to compaction by various methods. The samples were produced by conventional axial pressing, isostatic pressing, and radial stepped plastic deformation in a closed system (Ref 7, 8).

Typical curves of the density of the distribution of interparticle contacts by volumes for the compacts of above three types are shown in Fig. 5. These results refer to powders with a specific surface of 0.28 m^2/g produced by sputtering.

As kinematic features of the used compaction schemes differed greatly, it was advisable to consider as a variable not the

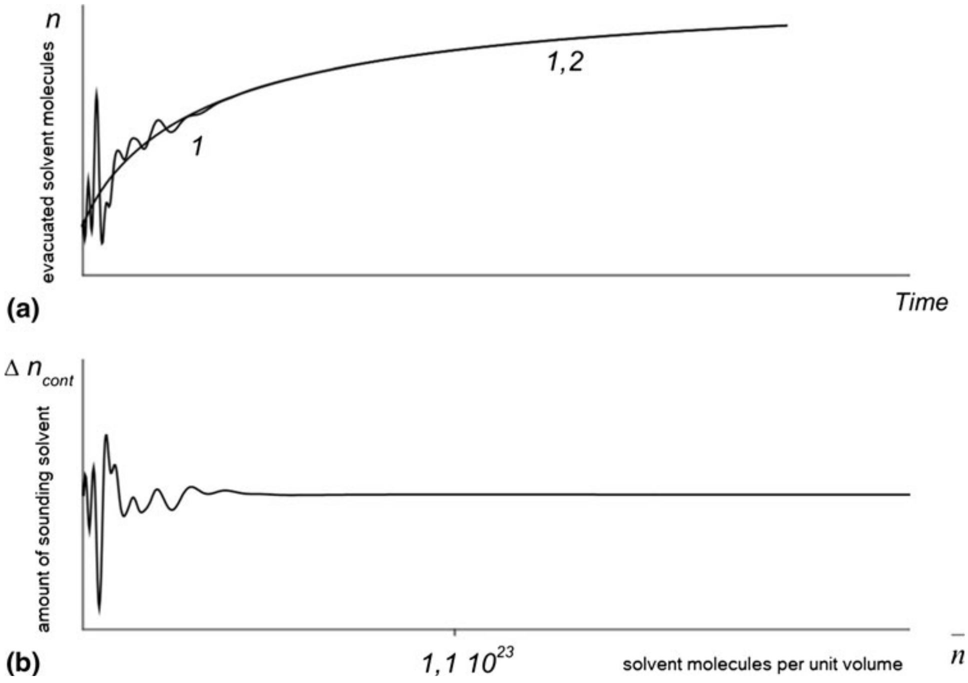

Fig. 5 (a) Final stage of sounding solvent evacuation: (1) compact, saturated with solvent and (2) base line. (b) Graph plotting the dependence of amount of sounding solvent, evaluated from interparticle contacts of compact on quantity of solvent molecules per unit volume of free powder specimen, evacuated by corresponding time

pressing force, but the compact porosity. The compaction pressure to achieve a given density varies with the compaction scheme, but in all cases was 70-300 MPa. Ultrasound vibration treatment enhances the loose powder's density, but also averages the state of symmetry by the volume of powder forming the system of interparticle contacts as three-dimensional objects.

Contacts of various structures (a large amount of peaks in the distribution curve) are observed in iron powders compacted by axial pressing. Volumes of single contacts lie in the wide range. In this case, contacts, whose volumes are near the upper and lower boundaries of the distribution, prevail. With increasing pressing force, the contributions of these two groups of contacts continue to increase through contacts of the medium volume.

Samples produced by isostatic compaction are characterized by a rather wide composite peak of the distribution relating to contacts of the medium volume. In this case, the amount of components of distribution corresponding to contacts of various structures is much lower than for compacts produced by the axial compression. As the compaction force increases, they merge into one restricted peak, which is indicative of the uniformity of the structure of contacts in the volume of the powder body.

In the case of the radial stepped compaction, the distribution density of contacts starting with a relatively low compaction force is characterized by two peaks. One of them is a narrow peak that relates to contacts, which are similar in nature and have small characteristic volumes. It is assumed that this type of contacts forms in cooperative displacement of particles in the course of radial plastic deformation of a powder medium. The second peak is wide and probably composite. It stems from the axial precompaction. As the compaction force increases, a redistribution of contacts in favor of a narrow peak with a smaller characteristic volume takes place.

Density curves of the distribution of contacts by volume for compacted powders of carbonyl iron (a specific surface of 1.38 m^2/g) are shown in Fig. 6. In this case, the peaks in curves are sharper, more clearly defined, and look single-mode, which points to the common physicochemical nature of particle surface portions that are linked to the corresponding contacts. In this case, the minimal elementary volume that corresponds to the leftmost peak of the distribution tends to be larger than the minimal volume registered for the powder having coarser particles of irregular shape (Fig. 5). This difference might be attributable to a regular (spherical) shape of particles of carbonyl iron powder and higher structure uniformity of their surface layers.

The notion of interparticle contact as of a three-dimensional object with a certain volume does not fully correlate with a simple obvious interpretation of a contact as a portion, where two particles closest approach each other that is seen in micrographs and has a certain section. In our opinion, each such portion of the particle maximal approach (i.e., contact in a traditional interpretation) can include several three-dimensional contacts having different volumes and even belonging to various distribution peaks (shown in Fig. 5, 6).

The effects shown in Fig. 5 and 6 are not the result of the interaction of iron powders with a solvent (e.g., dimethyl sulfoxide). With another suitable solvent (criteria have been defined above), e.g., *o*-xylene (Fig. 7), curves of the density of distributions exhibit somewhat changed shapes of peaks but their areas and positions of the maxima are maintained to a high accuracy. This also applies to various rates of heating samples, containing probing solvent (Fig. 8).

The idea of separating three-dimensional contacts as microscopic portions of the compact pore space that are localized near "points of a real particle contact" is based on the concept of the topological nonuniformity of the pore space of a powder

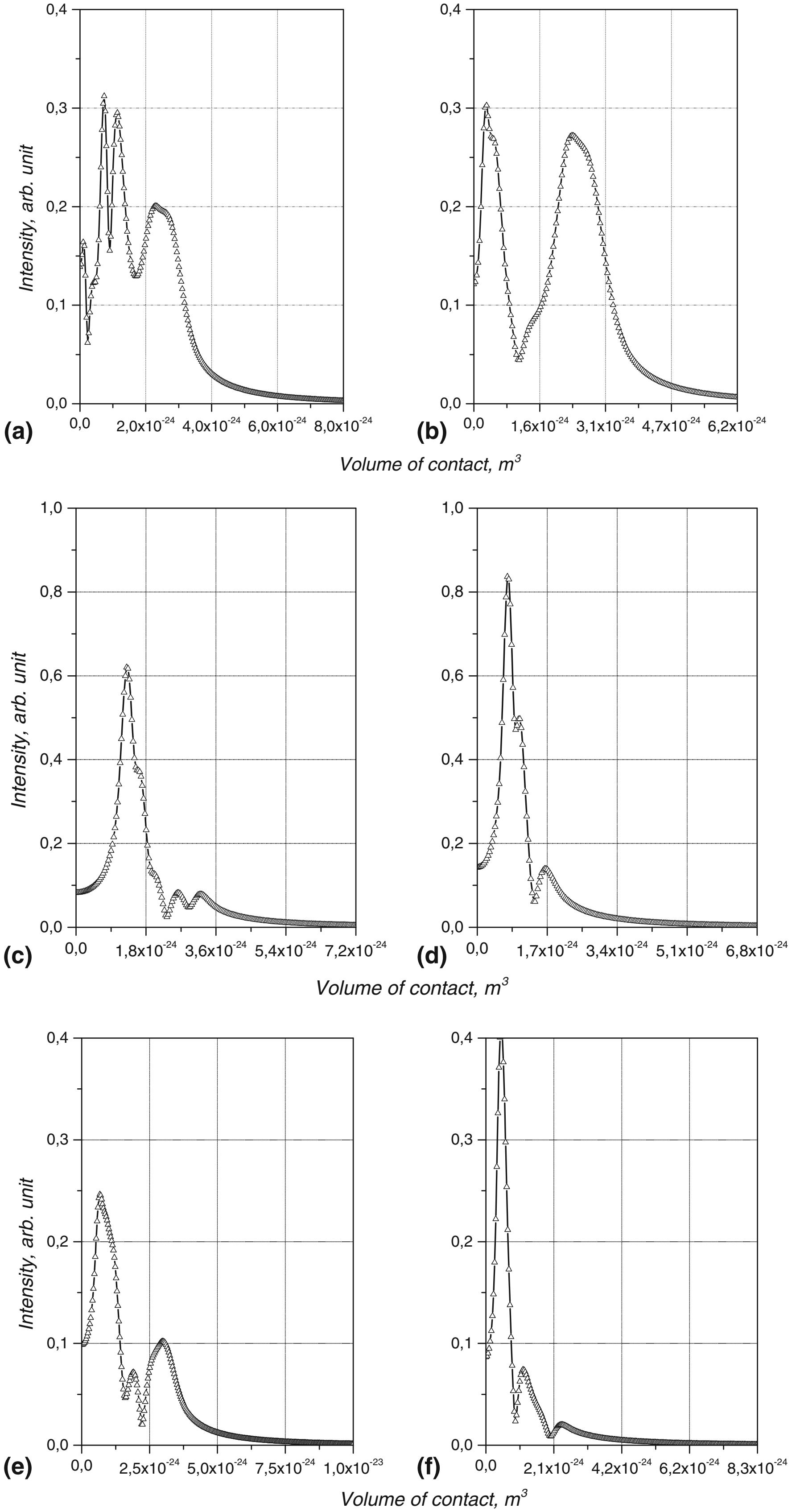

Fig. 6 Distribution of interparticle contacts in iron powder compacts by volumes; splinter shape powder, 0.28 m^2/g. (a) axial pressing, porosity 25%, (b) axial pressing, porosity 10%, (c) isostatic compaction, porosity 18%, (d) isostatic compaction, porosity 9%, (e) stepped radial compaction, porosity 22%, and (f) stepped radial compaction, porosity 7.5%

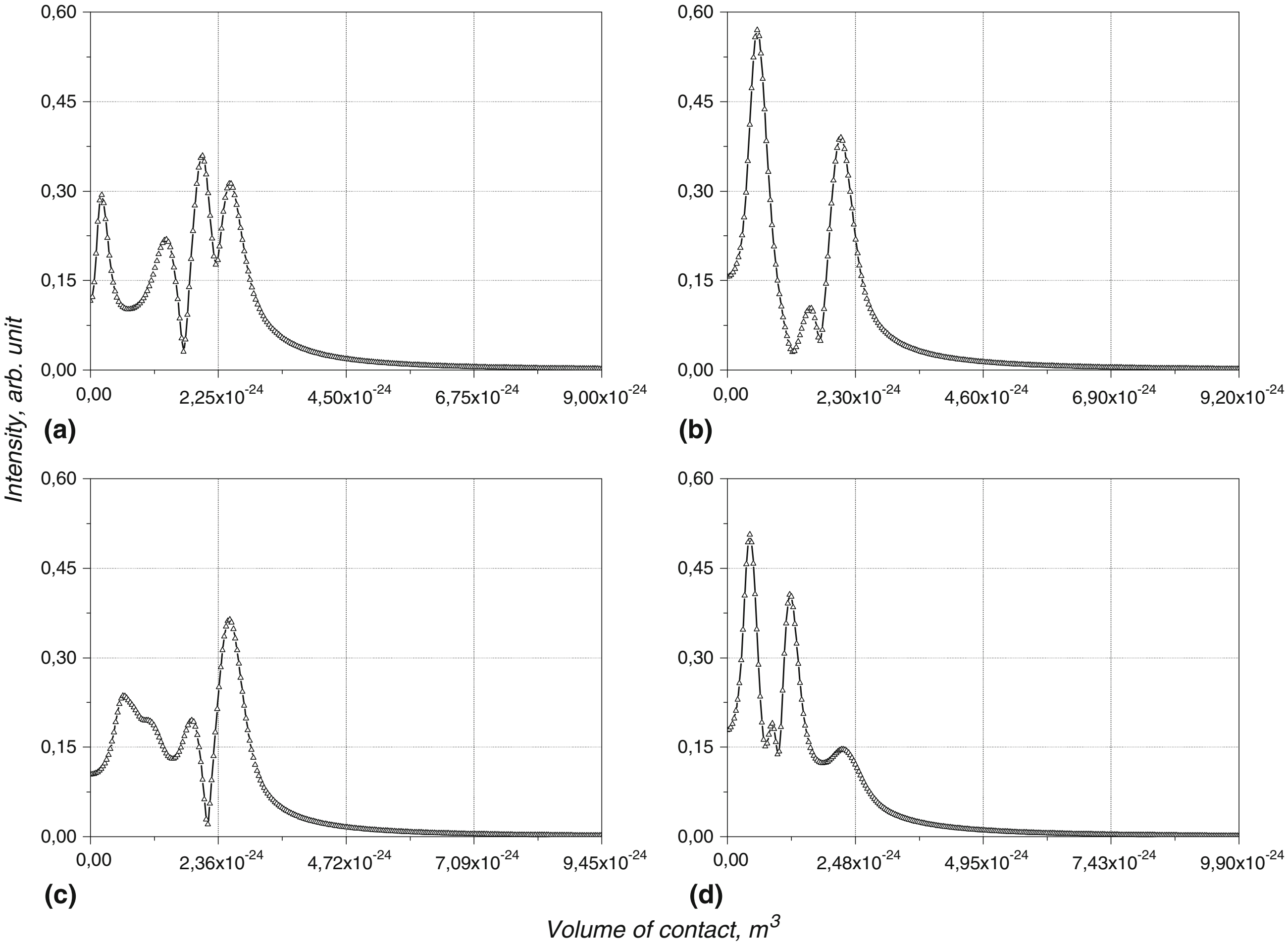

Fig. 7 Distribution of interparticle contacts in iron powder compacts by volumes; carbonyl spheric shape powder, 1.38 m^2/g. (a) Axial pressing, porosity 30%, (b) axial pressing, porosity 16%, (c) isostatic compaction, porosity 27.5%, and (d) isostatic compaction, porosity 14.5%

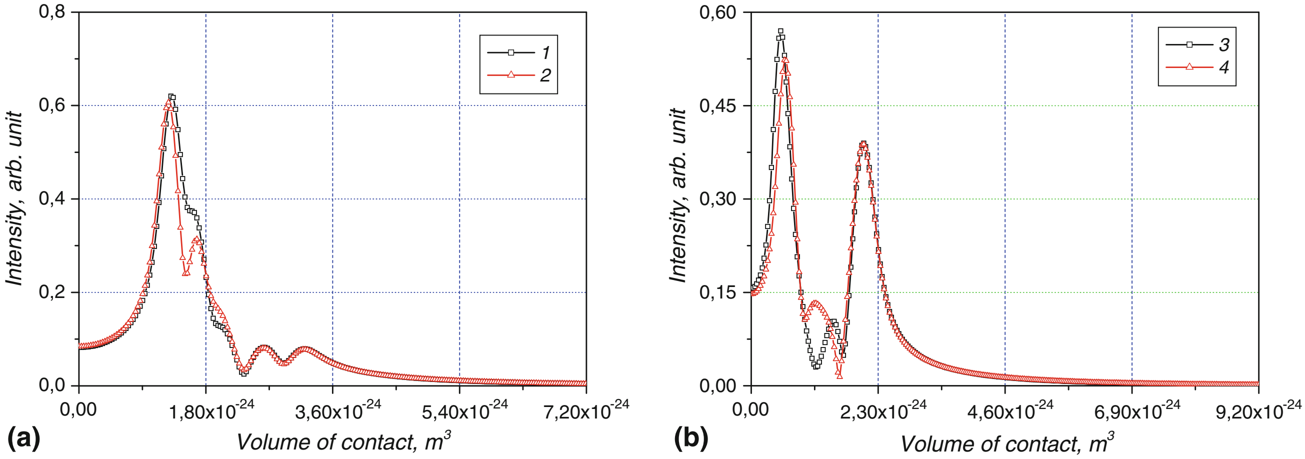

Fig. 8 Effect diverse solvents (a) and heating rates (b) on the shape of contacts' volume distribution. (1) dimethylsulphoxide (B.P. 462 K, $P = 40$ mmHg at 373 K), (2) xylene (B.P. 418 K, $P = 200$ mmHg at 373 K), and (3/4) heating rate correlation 2.5/1

body. In the portion of the pore space adjacent to interparticle contacts the conditions for the displacement of the probing solvent molecules are markedly changed as compared with that in the bulk of pores. As a result, the probing curve shape reflects the information about the quantity and characteristic volumes of contacts as three-dimensional objects.

In fact a three-dimensional contact is a region around the "point of contact" of two powder particles with all peculiarities of their geometry, oxide and other surface films, adsorbed molecules, etc. In this region, the physical phenomena, which are caused by an interaction between the most approached solid surfaces, show up essentially. The analysis of the mechanisms of these phenomena and the attempts to correlate them with the shape of the contact distribution by volume are beyond the scope of the present paper. One can only suggest that the above processes are associated with the formation of local nonequilibrium electronic states, emission, and formation of fluctuating interference. A certain analogy with the processes taking place between a probe of a tunnel microscope and a solid surface is also possible.

5. Conclusions

A new concept of interparticle contacts in powder media was developed. It was demonstrated that it is possible to regard such contacts as three-dimensional objects with a certain distribution of volumes. A significant correlation between the shapes of distributions and the trajectories of compaction was proved. The next step of the study will be the formulation of quantitative criteria, which will allow relating the structure of a set of interparticle contacts to the conditions of the powder compaction, as well as with the compact properties. These numerical characteristics will be based on experimental densities of the distribution of contacts by volume.

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