STRUCTURE AND OPERATIONAL PROPERTIES OF POROUS CERMETS ON THE BASIS OF ALLOYED STEEL SCALE

N.P. Tubalov, O.A. Lebedeva

I.I. Polzunov's Altai state technical university, Barnaul
E-mail: drulya@inbox.ru

Compositions of batches for obtaining porous cermets on the basis of alloyed steel scale with addition of ferrosilicon have been developed. Roentgenograms of the obtained alloys were shown, mechanical durability and porosity of the obtained materials were investigated. The model of formation of porous cermets was offered.

Introduction

Porous cermets (PC) form the basis of many devices and aggregates of modern engineering. Variety of constructive solutions and PC operating conditions [1] supposes the presence of different types of materials of this class directed to their optimal use for concrete aims technically and economically.

The existing methods of obtaining PC are far from being perfect. They are characterized by considerable energy and material expenditures as well as low capacity. The method of self-propagating high-temperature synthesis (SHS) developed in our country has great abilities at PC development [2].

SHS as a method of obtaining porous materials [3] includes low energy capacity, wastelessness and possibility of dynamic variation of structural and other properties of products. These prerequisites allow using economy and simple technology of obtaining porous items.

Selection of batch original components has the great value for obtaining product of high quality. In this work the basis of the batch for obtaining porous materials is industrial wastes of engineering enterprises being metal oxides (alloyed steel scale) and metal powders.

Development of SHS-materials on the basis of metal oxides (alloyed steel scale) has ecology-economic significance besides scientific novelty and urgency. Therefore, the aim of this work consists in determining laws of formation of structures and composition of products on the basis of binary and multicomponent compounds; and development on their basis of new methods and technologies of obtaining porous cermets for their further use as fine filters of gaseous and liquid media in engineering and transport.

It is known that in powder media with porosity more than 30 % (that is typical for the majority of original SHS-systems) mass transfer is implemented through pores.

The existing techniques of experimental diagnostics allow studying to a large extent the SHS method but require perfecting, development of both research devices and upgrading methodological basis.

Structural-methodological diagram of the work is given in Fig. 1.

Industrial wastes of engineering enterprises being metal oxides and metal powders form the basis of the batch for obtaining porous permeable materials.
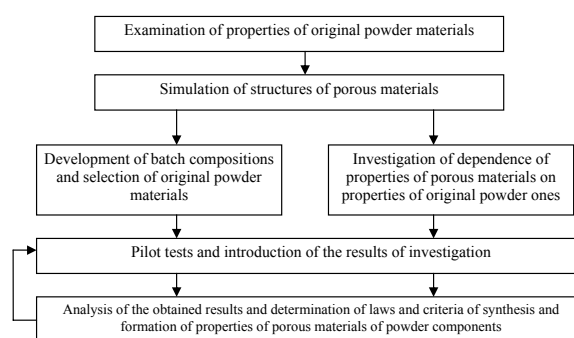

Fig. 1. *Structural-methodological diagram of researches*

We used materials on the basis of scale of alloyed steel hot forging with addition of chromium, chrome oxide and ferrosilicon.

So, for example, in reacting system containing to 65 wt. % of steel scale, to 18 wt. % of chrome oxide (CrO_2) and 17 wt. % of Al the SH-synthesis is possible with obtaining porous permeable material the structure of which is formed spontaneously at synthesis in general owing to melt redistribution in reaction zone and gas desorption from the surface of powder reacting materials.

Studying the structures of reaction products in the system of chrome oxide (IV) (CrO_2) — Al which is the most exothermal of reactions occurring in the compound system the following things were ascertained: intensive reacting of components with product melting; simultaneous phase separation («rise» of oxide product); further crystallization in the form of ingot covered with loose layer of oxide slag. Metal chromium, intermetallic compound Cr_5Al_8 as well as aluminum oxide of composition Al_2O_3 α- and χ-modification (crystal and amorphous structure) form the basis of the product.

The structure of the product is given in Fig. 2. Light inclusions in product structure are identified by the analysis as metal chrome: microhardness of this phase is 4,4...8,6 GPa, (black spots are pores, grey fields are oxide impurity of unreacting particles).

The pattern of distribution of regions of reconstructed chrome allows supposing that metal constituent is well seen in the form of nuclei of average size 1,2...2 mkm where further growth of metal fragments occurs as at substrates. Simultaneously at growth of reconstructed chrome regions the phase separation occurs — chromium motion on discontinuity flaw of porous

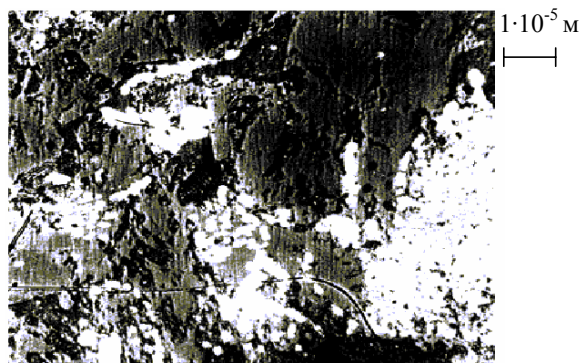aluminum oxide (Fig. 3). Movement pattern of the formed chromium is shown.

$1 \cdot 10^{-5}$ м

Fig. 2. *Microstructure of reaction product in the system chrome oxide–aluminum*

Intermetallic compound Cr_5Al_8 is formed in the regions of reconstructed metal chromium where concentration of dissolved aluminum corresponds to stoichiometry of the given compound that is determined by the parameter of crystal lattice of solid solution aluminum-chromium in the neighborhood of intermetallide extractions.

Oxide Al_2O_3 with parameters of lattice close to equilibrium and microhardness 18,2...20 GPa is the main phase of production as well.
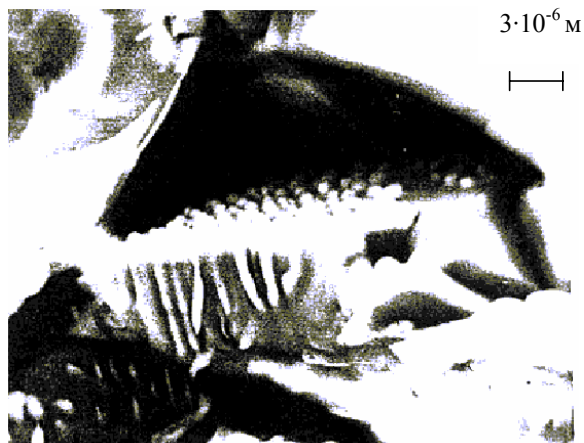

$3 \cdot 10^{-6}$ м

Fig. 3. *Path of phase separation in structure of reaction product of the system chrome oxide–aluminum*

Structure of reaction products in the system of steel scale – aluminum

Interaction of aluminum with steel scale occurs at low efficiency and temperature than alumothermic reduction CrO_2 (IV). It is conditioned by scale phase composition including the lowest and nonstoichiometric iron oxides characterized by lower exothermicity of reduction reaction. Significant content of iron (ferrite) forming 40...48 wt. % affects the thermokinetic parameters of reduction reaction as well.

In the structure of end product ferrite attends in the form of fields with the size from 10 to 300 mkm the structure of which is similar to the structure of chromium reduction regions in products of reduction reaction of

chrome oxide (IV). Mechanism of formation of ferrite fields includes stages of melting scale original ferrite, formation of primary nuclei as a result of reduction reaction, their growth and coalescence into extended regions at phase separation, as it may be concluded from the investigation of the structure of the product. Ferrite fields are characterized by fine-grained equilibrium structure of crystal grains, field microhardness changes weakly by microsection area amounting to 1,8...2,1 GPa (Fig. 4).
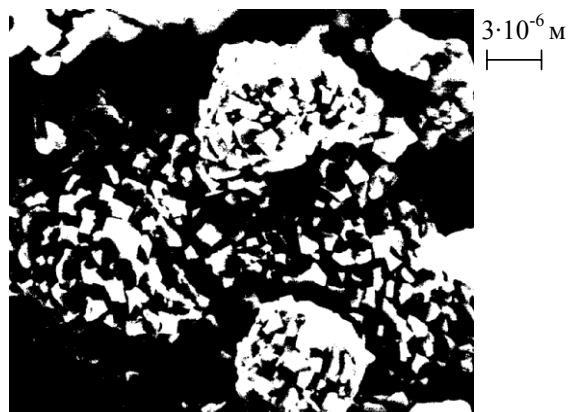

$3 \cdot 10^{-6}$ м

Fig. 4. *Microstructure of reaction product of alloyed steel scale – aluminum*

$5 \cdot 10^{-6}$ м

Fig. 5. *Particles of aluminum and iron oxide in reaction product structure in the system of alloyed steel scale – aluminum*

Oxide matrix the basis of which is aluminum oxide with inclusion of residual iron oxides Fe_2O_3 and which has accurate perfect faceting is also presented in product structure (Fig. 5). There, where aluminum oxide composition differs from stoichiometric and there are iron impurities and its compounds in oxide the type of oxide material differs considerably (Fig. 6).

Matrix on the basis of ferric oxides the composition of which changes from Fe_2O_3 to FeO is typical constituent of reaction product in complex system. Oxides are formed, obviously, at metal-reduction reaction in sequence Fe_2O_3, Fe_3O_4 – FeO. In this case plates of FeO grow owing to reactionary reduction of disperse particles of magnetite Fe_3O_4 being a constituent phase of the original scale.

Parallel reactions between aluminum and CrO_2 (IV) as well as between aluminum and scale results in formation of compound oxides of composition $FeO(Al)_2O_3$ in product structure; they are presented in the form of par-

ticles of complex faceting and occupy to 80 % of a sample (Fig. 7). Space change of spinel particles faceting indicating the variable composition of compound oxides is typical. Spinels are the hardest component of material – particles, microhardness amounts to 7,5...8,4 GPa and depends on their composition.
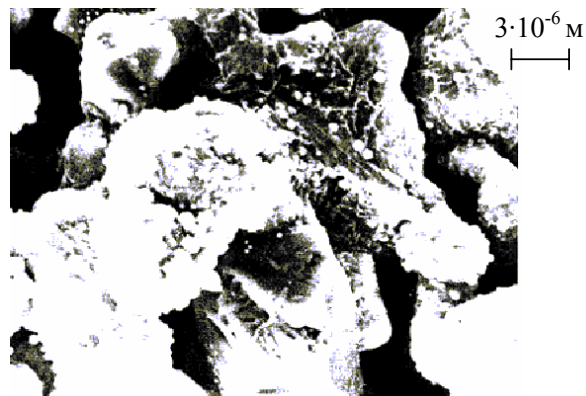

$3 \cdot 10^{-6}$ м

Fig. 6. *Particles of nonstoichiometric aluminum oxide*
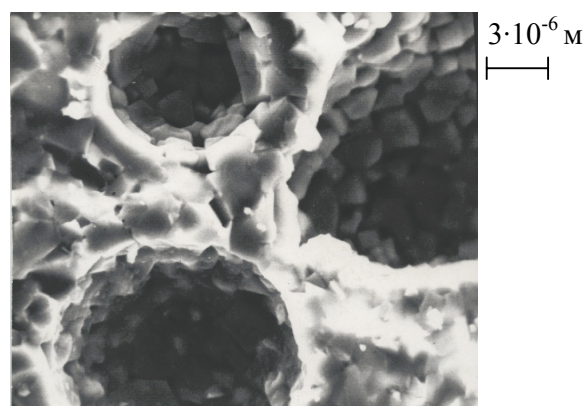

$3 \cdot 10^{-6}$ м

Fig. 7. *Microstructure of reaction product of the system scale – chrome oxide – aluminum*

Phase inhomogeneity of the obtained product as well as very nonuniform distribution of constituent phases by volume of material samples caused by phase separation at structure-formation are the factors capable of negatively affecting the material service properties first of all mechanical strength (owing to inhomogeneity of destruction type) and corrosion resistance (by the reason of possibility of formation of microgalvanic pairs in the frame). In order to improve material properties the experiments on formation of more homogeneous structure of material were carried out.

One of procedures was introduction of powdery chromium into original reaction mixture. It is capable of homogenizing solid-liquid reactionary medium due to spreading at combustion temperature as well as screening local areas of intensive heat-segregation owing to significant heat capacity. Melting temperature of chromium higher than that of iron allows narrowing the interval of existence of solid-liquid medium raising its solidus and increasing melt viscosity. Thus, there is kinetic resistance to medium redistribution at phase separation.

As the experiments showed chromium introduction into the mixture in the amount to14 wt. % does not cause

principle change of product phase composition. However, expansion of regions of solid solution on the basis of iron-chromium accompanying by increase of microhardness of fields of solid solution to 9,7...11,1 GPa was observed. It was ascertained that chromium introduction into the mixture results in more uniform distribution of metal component in frame structure, alignment of microhardness and crystal lattice parameter of solid solution by microsection area and therefore, solid solution homogenization. Decrease of sizes of oxide matrix fields was noted. In the whole structure of the material containing chromium is characterized by higher uniformity than structure of basic samples (Fig. 8 and 9) where structures of sample frames of basic system and system expanded by chromium introduction are compared.
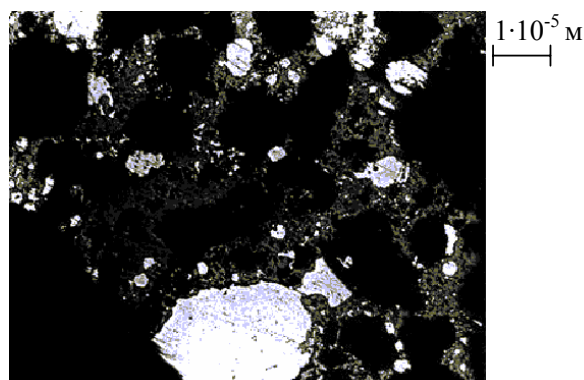

$1 \cdot 10^{-5}$ м

Fig. 8. *Microstructure of reaction product in three-component system of steel scale – chrome oxide (IV) – aluminum*

Thus, structure and phase composition of SHS-synthesis reaction products in the compound system at metal-reduction reactions were studied.
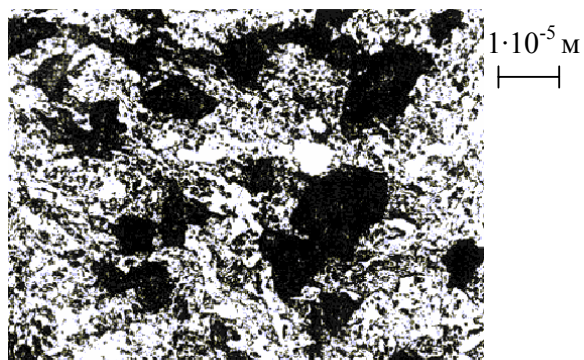

$1 \cdot 10^{-5}$ м

Fig. 9. *Microstructure of reaction product in three-component system of steel scale – chrome oxide – aluminum expanded by chromium introduction*

Introduction of powdery ferrosilicon FS-70 SS1415-7 in the amount of 1...5 wt. % containing 70...75 wt. % of silicon into the batch increases combustion temperature of mixture and implies increase of liquid phase volume and as a result significant growth of mechanical compressive and bending strength. Ferrosilicon deoxidizes the obtained metal-ceramic basis of material frame due to binding silicon with oxygen i. e. results in considerable increase of mechanical strength in 8...10 times. In this case, silica covers pore walls decreasing material conductance to zero.
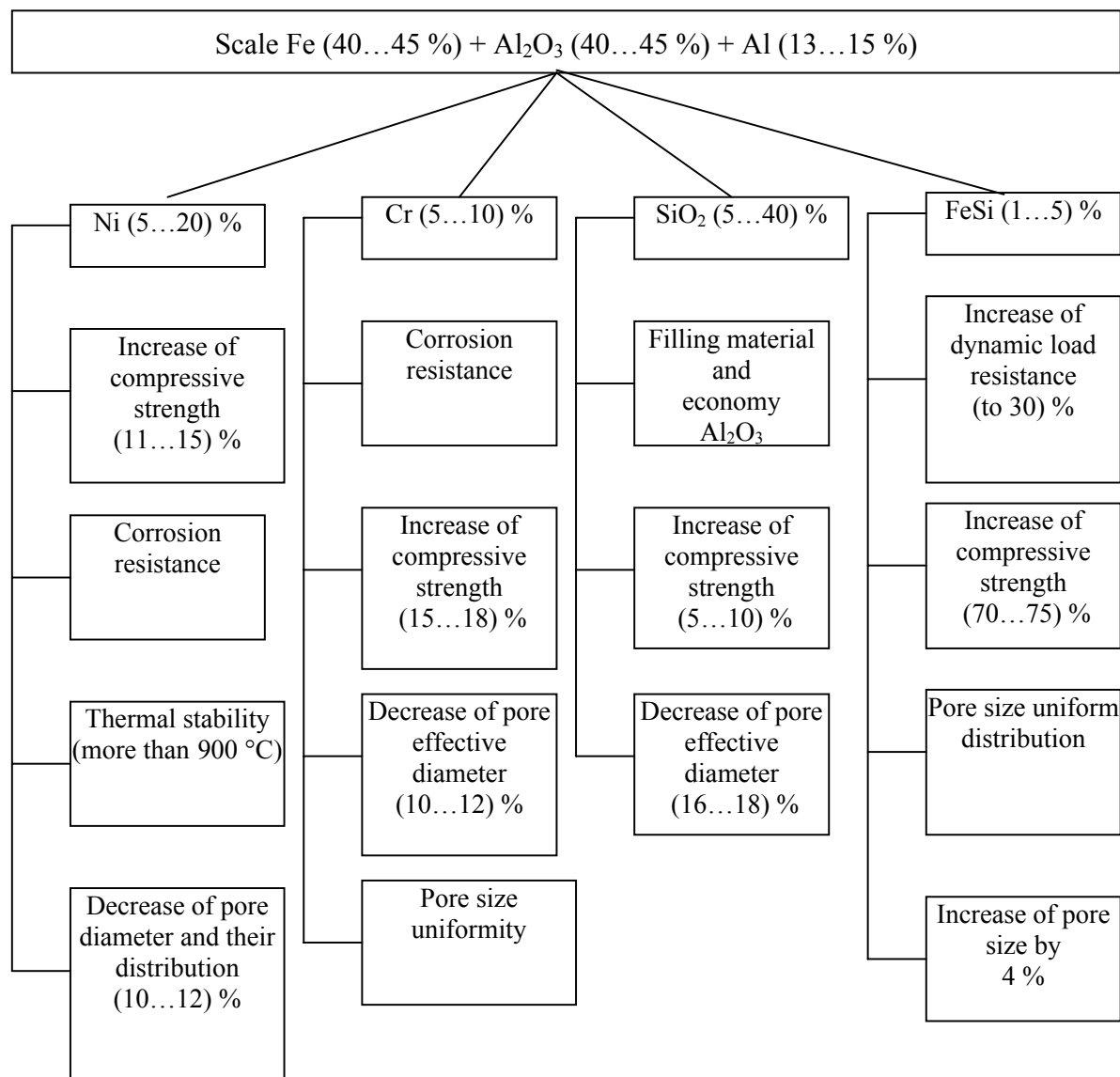
Scale Fe (40…45 %) + Al$_2$O$_3$ (40…45 %) + Al (13…15 %)

Ni (5…20) %
- Increase of compressive strength (11…15) %
- Corrosion resistance
- Thermal stability (more than 900 °C)
- Decrease of pore diameter and their distribution (10…12) %

Cr (5…10) %
- Corrosion resistance
- Increase of compressive strength (15…18) %
- Decrease of pore effective diameter (10…12) %
- Pore size uniformity

SiO$_2$ (5…40) %
- Filling material and economy Al$_2$O$_3$
- Increase of compressive strength (5…10) %
- Decrease of pore effective diameter (16…18) %

FeSi (1…5) %
- Increase of dynamic load resistance (to 30) %
- Increase of compressive strength (70…75) %
- Pore size uniform distribution
- Increase of pore size by 4 %

Fig. 10. *Properties of cermets with different admixtures*

Increase of mechanical strength expands sphere of application of items of porous permeable material and increases their resistance to dynamic and static loads.

Properties of PC with different admixtures changing operating characteristics are given in Fig. 10.

Conclusion

1. Phenomenological model of mechanism of formation of porous cermets on the basis of oxides of ferric and aluminum – aluminum and alloy additions consisting in the following was developed:
   - at the primary stage of SH-synthesis fragile ceramic frame of Al$_2$O$_3$ is formed;
   - reduction of iron in reaction Fe$_2$O$_3$ + Al$_2$O$_3$ + Al and coalescence of liquid iron melt round solid frame of Al$_2$O$_3$ forming crystallizable drops (globules) which change their form, increase size of pores between them under the influence of expanding gas pressure at intensive heat extraction.

2. It was ascertained that introduction of ferrosilicon into the original batch results at synthesis in increasing liquid phase volume, its spreading and further oxidation of iron free surface, increasing wettability at interfaces of globule adjacent particles.

3. It was proved that introduction of 8...10 % of aluminum into the system ferric oxide (scale) – aluminum oxide supports occurrence of self-propagating high-temperature synthesis due to iron reduction of oxides. The selected concentration range of reaction system components determined steady-state combustion of mixture obtaining porous material. Porous items with specified properties were obtained: average size of pores is 100...150 mkm, porosity 45...60 %, fraction of one-side open and close porosity at its value less than 0,18 amounts to 2...5 % of total porosity of material, mechanical compressive stress varies from 15,4 to 1,7 MPa and bending stress varies from 4,2 to 1,0 MPa.

REFERENCES

1. Volkov V.I. Filtering turbulence mode // Increase of environmental safety of automotive engineering: Article collection. – Barnaul, 1999. – P. 72–77.

2. Evstigneev V.V., Volpe B.M., Gorkol D.A. Development of principles of generalized SHS-technologies of dispersed composite material // Altai STU works. – 1993. – Issue 1. – P. 3–18.

3. Tubalov N.P., Lebedeva O.A., Vereschagin V.I. Porous composite ceramic materials obtained by self-propagating high-temperature synthesis in the system F_2O_3-Al_2O_3-Al // Novye Ogneupory. – 2003. – № 9. – P. 40.

UDC 66.796.2

PURIFICATION OF GAS AND LIQUID MEDIA BY METAL–CERAMIC SHS–FILTERS

A.A. Geyneman, V.D. Goncharov, A.L. Novoselov, N.Yu. Shchetinkina

I.I. Polzunov's Altai state technical university, Barnaul
E-mail: drulya@inbox.ru

Industrial samples of fine filters of gas and liquid media from mechanical microparticles have been developed. Porous permeable cermets obtained by self-propagating high-temperature synthesis are the basis of filters.

On the basis of self-propagating high-temperature synthesis (SHS) the technology of obtaining porous permeable materials which may be used for fine purification of liquids and gases was proposed [1–3]. Scale of alloyed steel, metal powders and ferrosilicon were used as original components of batch [4].

The principle stages of the process of obtaining porous materials is the diagram, Fig. 1, including grinding original materials, powder screening, batch preparing, component matching and gauging , synthesizing and product improvement.
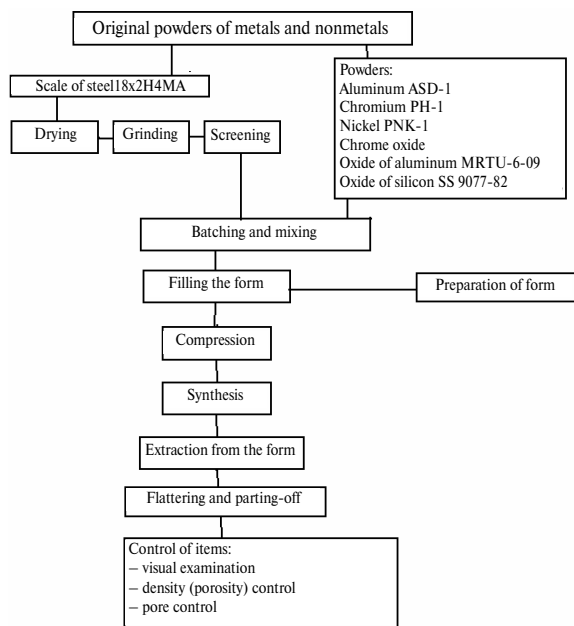

Fig. 1. *Diagram of technology of obtaining porous permeable product by SHS method*

Technological experiments showed that the highest efficiency of grinding is achieved at its carrying out in two stages; at the first stage the foregrinding occurs, at the second stage fine grinding with obtaining rather narrow required fraction (through the sieve) occurs.

Investigation of scale powders obtained by processing original material at the grinder KID-100, showed that the primary type of material decomposition is intercrystalline fracture; particles of the obtained powder of various fractions have similar morphology repeating morphology of crystal grains of ferrite of original material.

On the basis of the extracted fractions of steel scale powder the reaction mixtures of constant concentration composition were prepared; samples of porous material were later prepared from them.

Filters for purification of gas media

The determining properties of material for gas purification are average pore size (Fig. 2) and mechanical strength at compression and bending (Fig. 3). This implies that at increase of steel scale concentration from 45 to 60 % by mass the mechanical strength decreases.

Filtration of exhaust gases in porous materials may be divided into several stages. Firstly, solid particles which should be separated from the flow of exhaust gases are supplied to the surface of filter, then they abut to filter surface and at the next stage penetrate filter surface and are trapped in pores. The larger particle size the high the probability of its trapping in porous wall. The absorption factor of solid particles by porous SHS-filter owing to engagement may be presented as:

$$\delta_n = \frac{\delta_{cm}}{2\delta_{c\pi}^2 \cdot \sqrt{3}}\left(\tau_{cm} \cdot \bar{\upsilon} + \frac{3r_{m\iota}^2}{\delta_{cm} + \delta_{c\pi}}\right), \qquad (1)$$