

THE MECHANISM OF IRON REDUCTION FROM MOLTEN SLAG IN ROMELT PROCESS

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ABSTRACT

Investigations of slag samples (including coal char particles and solidified metallic drops) taken out from the Romelt furnace (RF) were carried out using SEM, X-ray and Mossbauer spectroscopy. Results and model experiments allowed to suggest the mechanism of FeO reduction from molten slag in RF. Iron reduction is localized at gas-slag interface in gas bubbles with coal char particles (“active bubbles”) and in gas cavities under primary metal (pig-iron) drops. The process includes the following basic stages:

Adsorption of CO at the gas-slag interface.

Reduction of FeO from slag by CO in adsorption layer.

Recombination of CO₂ at the char surface or at the surface of the pig-iron drops.

Metal phase nucleuses formation of and their carbonization.

Nucleus growth and formation of separate dispersed metal droplets with size 1-10 μm.

Aggregation of the droplets in primary pig-iron drops with sizes 0.1-1 mm.

All stages include mass and charge transport phenomena.

INTRODUCTION

The liquid-phase reduction process Romelt is one of the bath smelting processes of alternative (non-coke) ironmaking. It has become widely known as a method introduced on a pilot scale for non-blast-furnace processing of iron ore feedstock. In this process the mixture of coal and ferrioxide materials (metallurgical sludge, scale, iron ore etc.) is charged top-down on the air-agitated molten slag. Iron reduction and formation of primary pig-iron drops take place in the air-agitated slag bath at $\sim 1400\text{ }^{\circ}\text{C}$, but the physicochemical mechanism of the process is not wholly clear. Analysis of earlier researches together with the results of many years experience in operating a pilot Romelt furnace (RF) installation at Novolipetsk Metallurgical Combine (NLMC) provided a basis for proposing a new approach to understanding the mechanism of liquid-phase iron reduction and pig-iron formation in the Romelt process. According to the proposed model, reduction of ferric oxide dissolved in molten slag is localized at the gas-slag interface in gas bubbles containing coal char particles. The present paper gives the results of experimental verification of this mechanism and details its principal stages on the basis of a study of the morphology and structure of RF-slag specimens.

EXPERIMENTAL AND RESULTS

The slag samples were taken from the air-agitated zone of the NLMC Romelt furnace. The procedure guarantees high cooling rate, rapid solidification and quenching of liquid state morphology, so that the morphological characteristics of the molten slag could be established. The slag samples were examined visually, using magnifying lenses to inspect the outer surface adjoining the steel crucible receptacle and the "interior" surfaces formed when the slag ingots were broken up into individual fragments. Selected fragments were studied in detail by scanning electron microscopy CamScan-44S. To assure electrical conductivity of the samples a thin layer of aluminum ($\sim 10\text{ nm}$) was applied by evaporating.

All produced slag samples looked like glassy ingots of dark green colour and slag chemical compositions were approximately identical on the base components: 35-40 % SiO_2 , 35-40 % CaO , 10-15 % Al_2O_3 , $\sim 10\text{ }\%$ MgO , 3-5 % Fe-oxides. The X-ray analyses showed non-crystalline (amorphous) structure of the slag that proves sufficiently high cooling rate of samples. Mossbauer spectroscopy has shown presence of two different states of iron in slag: Fe^{2+} and Fe^{3+} . The divalent iron prevails above trivalent and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is about 0.2.

After samples fragmentation the numerous sphere-shaped cavities, remaining from gas bubbles in molten slag, were seen. The majority of cavities was empty and had an absolutely sleek surface with characteristic glass brilliance. Nevertheless, in many cavities the small carbon particles and metal pellets (crystallized metal drops) were found out visually. It is important to note that *in all cavities with carbon particles there were the metal ones*. Such bubbles we have named as active bubbles (“active” means the opportunity of iron reduction from slag).

In fig. 1 and 2 the general view of active bubble craters remained from gas bubbles with carbon particles are presented. On a surface of slag some solid metal drops with the size up to 0.5 mm precipitate out. The local analyses (fig. 2f) showed that they were the drops of primary pig-iron. The strong Al-line in a spectrum is connected with Al coating of the sample surface. Ca-line and Si-line exist due to small slag droplets on a surface of metal drops, which are well visible in fig. 2, 3. At higher magnification we could see considerably smaller (1-10 μm) metal droplets and the their conglomerates. Sometimes they formed practically continuous metal films at slag surface (fig. 1d). The small size of these droplets allows to consider that they are products of initial stages of iron reduction from the slag. They can be seen on all surface of slag in a bubble, both close to and at a distance from big metal drops and carbon particle. On the bubble, presented on fig 2 -f the smallest metal droplets (less than 1 μm) were well visible. In this bubble there were no metal drops with the size more than 0.1 mm. It allowed to assume that the reduction process here has not reached yet the high transformation degree. According to it the fine products of initial reduction stage are more visible on a surface of the slag. Dominant morphology of these products is separate, small teardrop-shaped particles of metal phase. The metal nature of these objects, as well as all discussed further, proves to be true by set of obtained spectra, SEI- and BEI-images and images made in characteristic radiation (fig. 3). The particle size and distance between them change from tenths of micron to 1-3 μm , and their arrangement has an ordered character. The localization of particles on gas-slag interface allows to make a conclusion that *the initial stages of process are connected to gas reduction of iron from slag by carbon oxide*.

The study of carbon particles morphology in gas bubbles reveal their porous structure (fig. 4). These carbon particles were coal char, formed during "devolatilization" of coal in slag bath. In large char pores it is possible to observe rather large (up to ~ 0.1 mm) metal pellets and on a surface of particles the huge quantity of smallest metal droplets. Sometimes, the droplets formed practically continuous layer of metal phase on a surface (fig. 4 -f).

Let's note a general conclusion. *The metal drops are always located on gas-slag interface and have lenticular shape.* It is correct for the drops of all sizes (from a several micron to several millimeters). Lenticular shape of drops is well visible after their removing from the slag (fig. 5) and on fracture surfaces of the samples (fig. 6). Another conclusion is that *there are always the gas cavities under the drops in slag* (fig. 5, f and 6 -). Usually cavities are the sphere-shaped and their volume more then metal drop volume. Frequently, cavities consist from several bubbles, separated by thin slag walls (fig. 6d).

The detailed study these cavities under drops of metal (primary pig-iron) has shown again the presence of the smallest particles of metal phase (fig. 6f, 7). These particles with the sizes from tenths of micron to 10 μm formed rather original structures, which frequently had the ordered character. The base of these structures is separate sphere-shaped or teardrop-shaped particles, which had been formed on initial stages of iron reduction. Growth and agglomeration of these particles result in small metal droplets formation (fig. 6f, 7).

The results of RF-slag samples investigations were confirmed in two series of the model experiments, which have been carried out in a reducing atmosphere of Tamman's furnace at temperature $\sim 1400\text{ }^{\circ}\text{C}$. The milled, magnet separated RF-slag with $\sim 4\%$ of Fe-oxides was used in all experiments. Cooling and solidification of samples were carried out in the furnace.

In the first series of experiments we studied an opportunity of iron gas reduction from slag by carbon oxide (CO). Slag was re-melted in alumina crucibles of different height and with different level of a melt. In the experiments with a completely charged crucible the sphere-shaped particles and small droplets of metal phase were found out on slag surface. They were the similar to the particles, which had been found out in RF-slag samples earlier. When we used high crucibles with incomplete charge of slag (the distance between slag melt surface and the top of crucible was 6-7 cm) the surface of slag was clean. In these experiments the recombination CO_2 on the walls of a furnace graphite heater was embarrassed because of the large gas diffusion distance. Thus, *gas reduction of iron from slag by carbon oxide is possible only in the case of intensive $\text{CO}_2 \rightarrow \text{CO}$ recombination.*

In the second set of experiments we studied interaction of slag with pig-iron drops. Pig-iron piece, with weight about 1 g and carbon contents 4.5 %, were dropped in molten slag (high alumina crucibles with incomplete charge were used). After 3-5 sec (after metal preheating and melting) intensive boiling and barbotage of slag were observed. After solidification there were small metal droplets on the slag surface, which formed the concentric

circles. After crucibles splitting the gas bubbles were found out above metal drops (typical results are presented on fig. 8). It is clearly seen that the metal products of iron reduction on gas bubble surface form the structures completely similar to described earlier for RF-slugs. The congestion of these products on a surface of melt slag during the boiling leads to formation of the concentric circles on a surface of model samples. The significant decrease of metal drops carbon concentration to 2.5-3% proves that the reduction of iron proceeded by carbon dissolved in pig-iron.

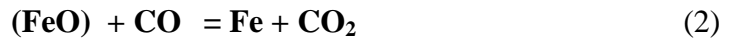
DISCUSSION

The analysis of obtained results has allowed to suggest the mechanism of liquid-phase iron reduction from molten slag and pig-iron formation during Romelt process. The basic position is that **the processes of iron reduction from molten slag and primary pig-iron drops formation proceed in active gas bubbles containing the coal char particles.**

The iron reduction by char carbon («primary reduction») can be described by reaction:



According to our model this process develops in barbotaged slag, in gas bubbles containing char particles (active bubbles) and can be separated on two base stages. The first one is reduction of ferrous oxide dissolved in slag by carbon oxide. The reaction proceeds in an adsorptive layer on gas-slag interface:



The second stage is recombination of CO_2 on gas-char interface:



The detailed study of RF-slag samples morphology, including the char particles and metal drops, confirmed completely the base positions of the suggested model. The primary pig-iron drops with sizes from tenths to several millimeters were found out on gas-slag interface inside active gas bubbles. In a slag matrix under the drops the gas cavities formed due to CO evolution during the development of secondary reduction by dissolved carbon. This process can be described by equation:



The secondary reduction also can be subdivided into two base stages. The equation (2) describes the reduction stage again, but CO_2 recombination is located in gas cavity on “bottom” surface of primary pig-iron drop:



Thus, initial stages of the iron reduction are determined by reaction (2) without dependence on what carbon is the main reduction agent: char or carbon dissolved in metal.

The proofs of reaction (2) realization were obtained both for RF-slugs samples and in model experiments. In particular, the metal particles on slag surface in gas cavities under pig-iron drops were formed without direct contact between slag and drop. So, the only reason of iron reduction from slag can be reaction (2). The results of model experiments have shown that an obligatory stage of process is CO₂ recombination. It is necessary for maintenance of a reduction potential of a gas phase. It is important to mark that only char carbon in active bubbles can ensure long maintenance of reduction process and metal carbonization (reverse reaction to (5) in combination with reaction (3)). The reactions (2), (3), (5) are multistage processes. They take place on gas-slag, gas-char, gas-metal interfaces correspondingly and besides the stages of adsorption-desorption include electrochemical interaction.

SUMMARY AND CONCLUSIONS

Iron reduction from molten slag in Romelt furnace is located on gas-slag interfaces in active gas bubbles with char particles and in gas cavities under drops of primary pig-iron. The iron reduction proceeds due to gas reduction reaction between dissolved FeO and carbon oxide. This stage is the main one for total process. The CO₂ recombination, which is necessary to the process maintenance, is provided by char carbon or carbon dissolved in pig-iron. The obtained results and their analyzes allow to prove and to develop the model of liquid-phase reduction of iron from molten slag and primary pig-iron drops formation during the Romelt process. The mechanism includes the following base stages:

- 1. Dissolution of solid Fe-oxides and mixing coal char particles in slag.**
- 2. Formation of active bubbles within char particles.**
- 3. Carbon oxide adsorption on gas-slag interface.**
- 4. Gas reduction of FeO from slag by CO with the subsequent recombination of CO₂ on char surface.**
- 5. Formation and carbonization of metal phase nucleuses.**
- 6. Growth of nucleuses and formation of separate dispersed metal droplets with micron size.**
- 7. Coalescence of dispersed droplets and primary pig-iron drops formation with the sizes from hundreds micron to several millimeters.**

Intensive barbotage in the slag bath promotes the dissolution of Fe-oxides and char particles mixing in slag. The gas bubble formation with reducing atmosphere around coal char is possible during “devolatilization” of coal and/or direct contact between char and ferri ferro slag. All stages include transport processes. For example, for stage 3 it is a CO diffusion to gas-slag interface, for stage 4 it is CO₂ diffusion to surface of char particle or to pig-iron drop surface and transport of FeO (Fe²⁺ and O²⁻) from slag volume to gas-slag interface. The stages 3-6 can proceed in gas cavities under primary pig-iron drops (the CO₂ recombination occurs on drops surfaces) also. However, the calculation shows that even if the dissolved carbon reacts completely, the drop mass increasing is not more than 5 %.

The obtained results and conclusions can be useful for understanding and operating of Romelt process and other bath smelting processes (for example, HIs melt, AusIron etc.).

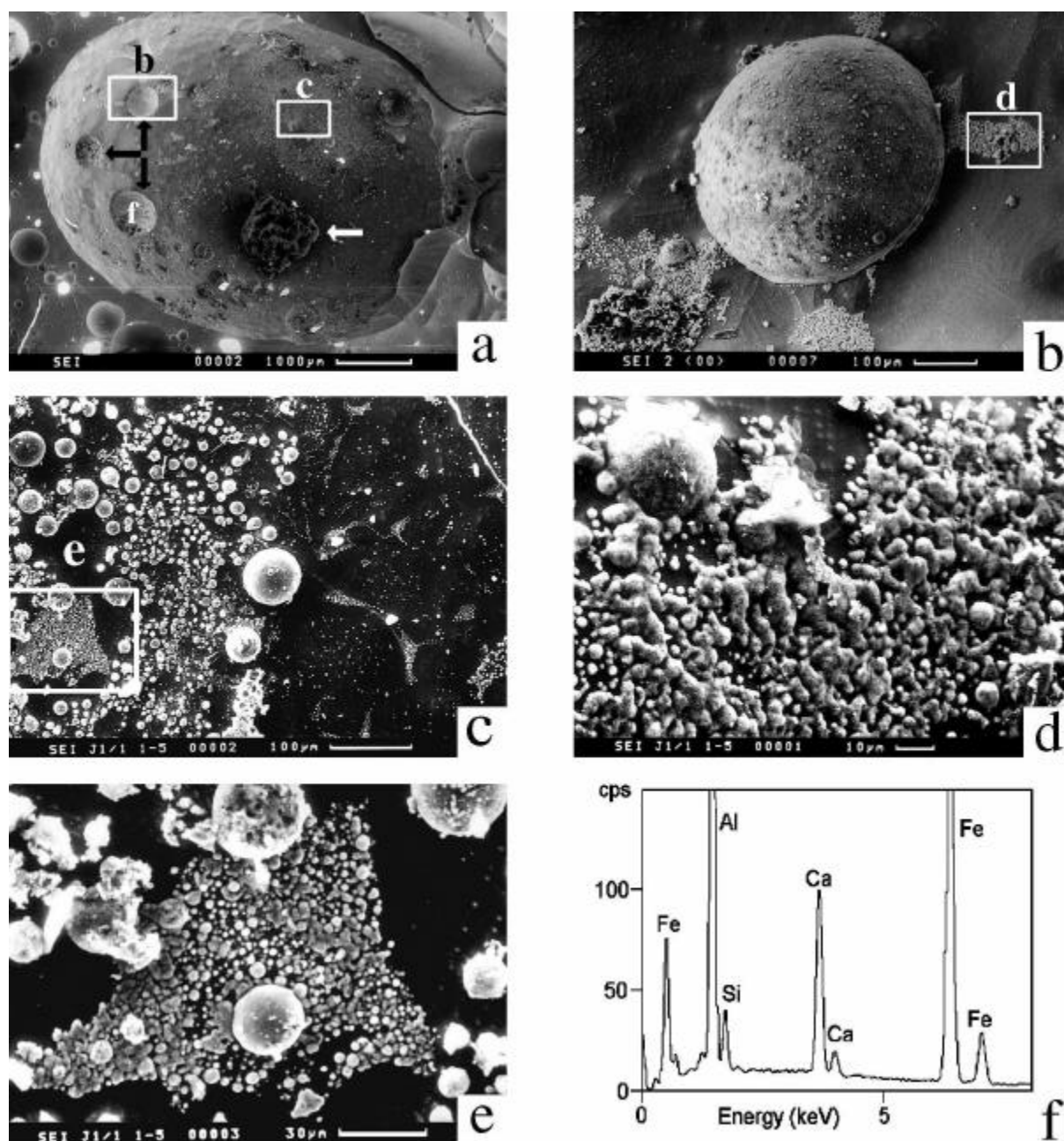


Fig. 1. Crater of active gas bubble on fracture surface of slag sample.

The black arrows point out to the solidified metal drops and the white arrow to coal char particle.

c-e – small metal droplets on the slag surface;

f – X-ray microanalyzes spectrum of metal drop.

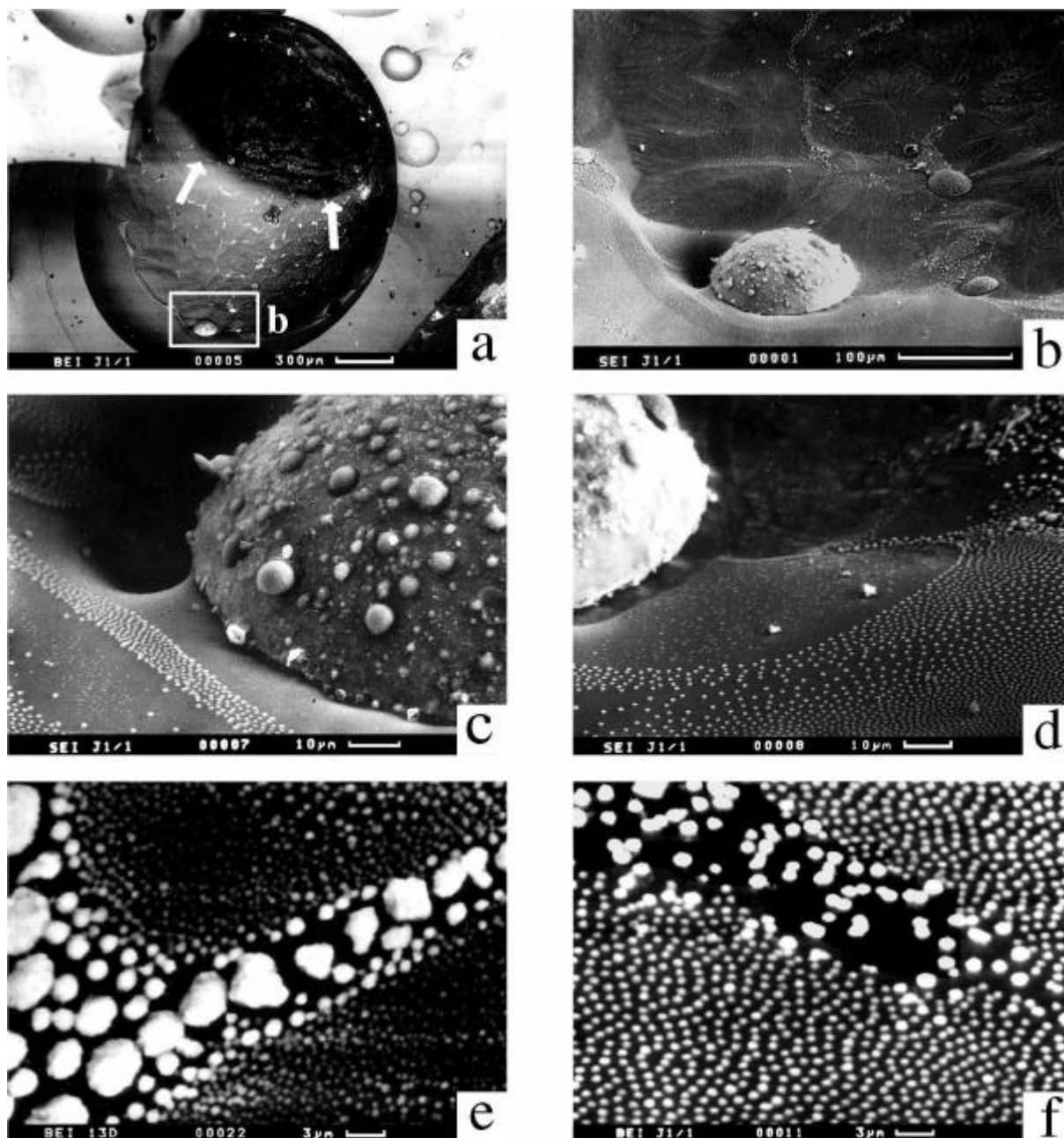


Fig. 2. Crater of active gas bubble on fracture surface of slag sample.

The white arrows point out to coal char particle.
 e, f – fine metal particles on the slag surface.

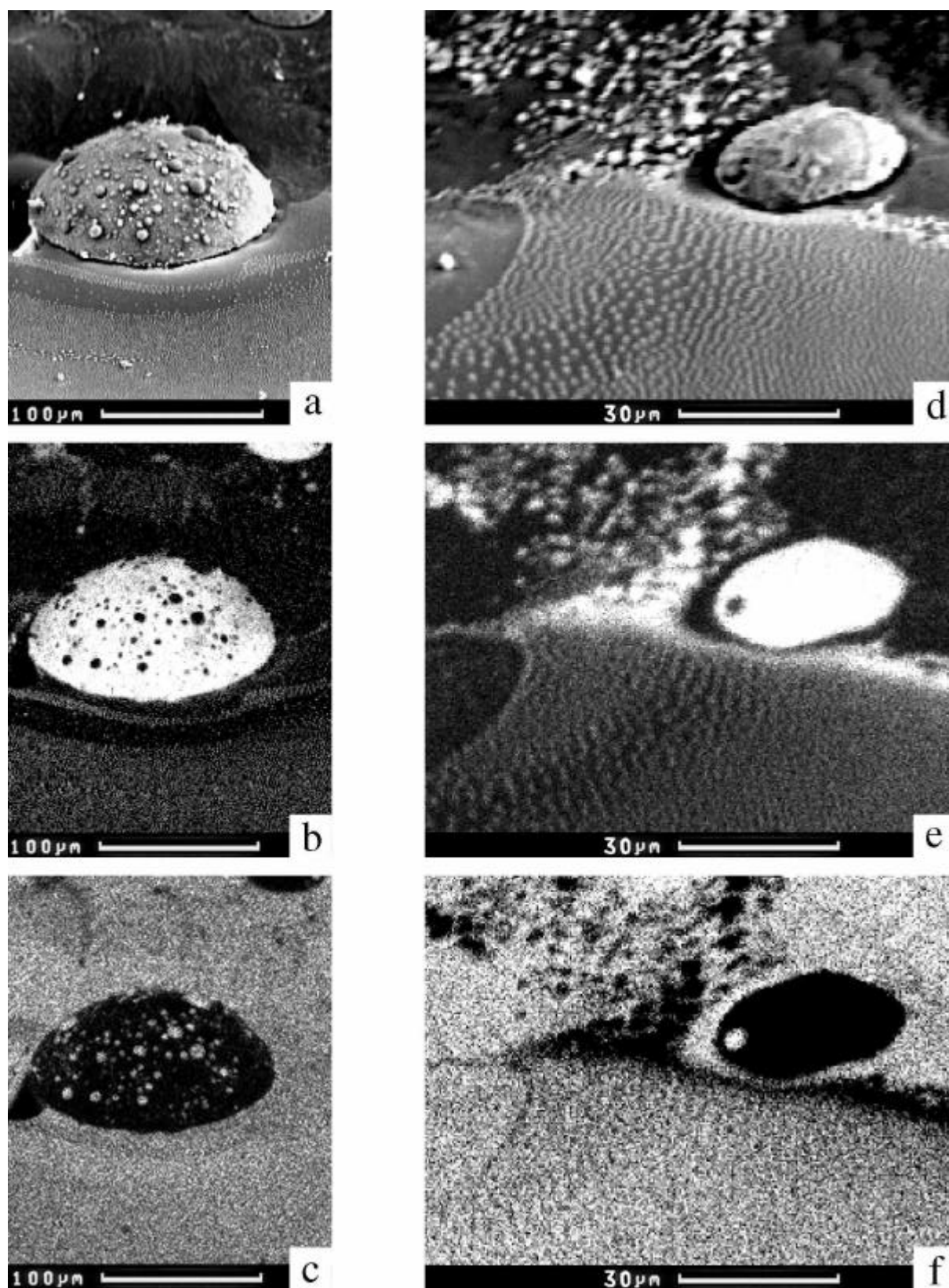


Fig. 3. Metal drops and fine metal particles on the surface of active gas bubble (Fig. 2a).

b, e – Fe K α image;
c, f – Ca K α image.

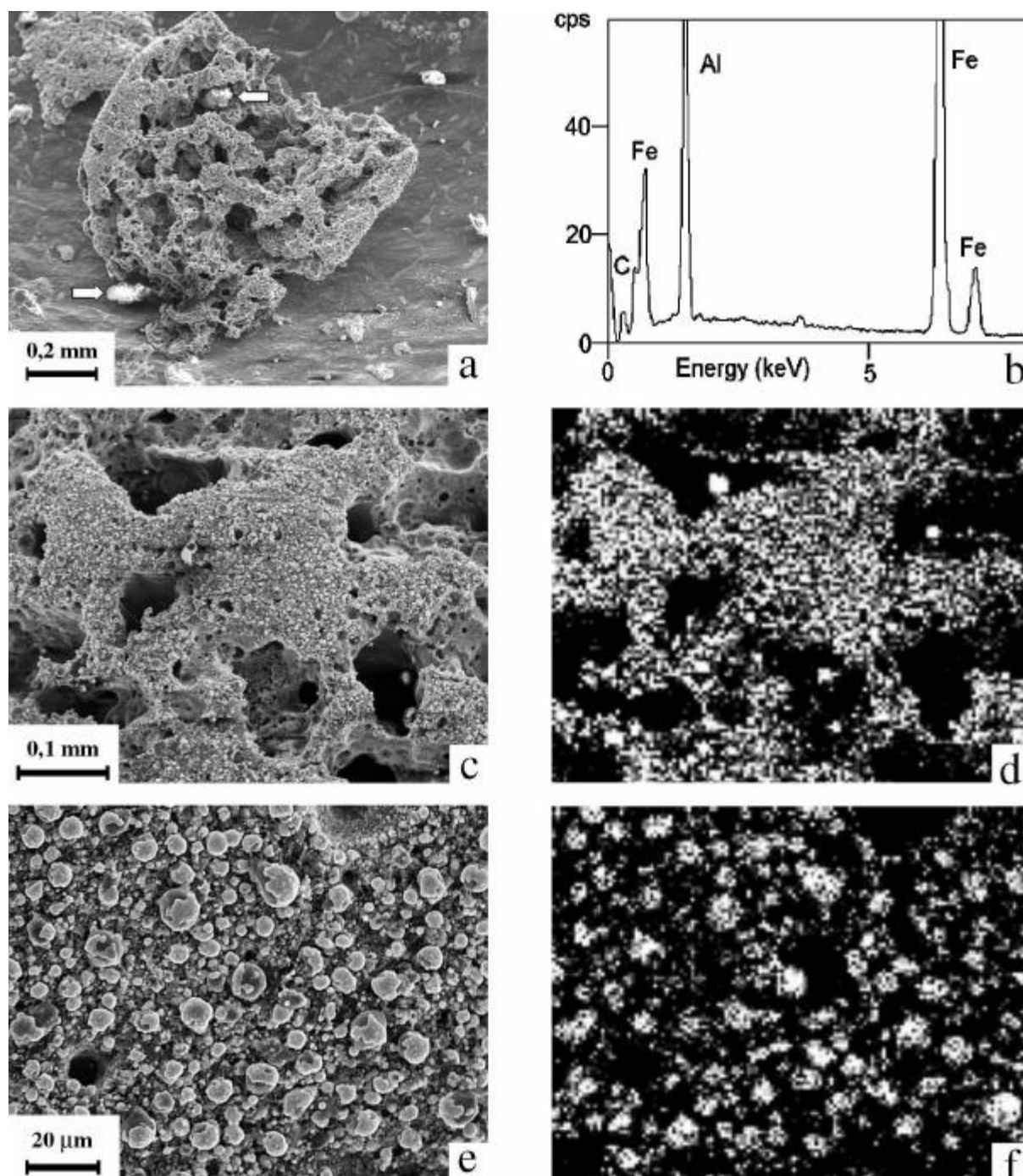


Fig. 4. Coal char particle in active gas bubble (Fig. 1a).

The white arrows point out to the solidified metal pellets
 b – X-ray microanalyzer spectrum of metal pellet;
 c-f – surface of coal char particle (d, f – Fe K α image).

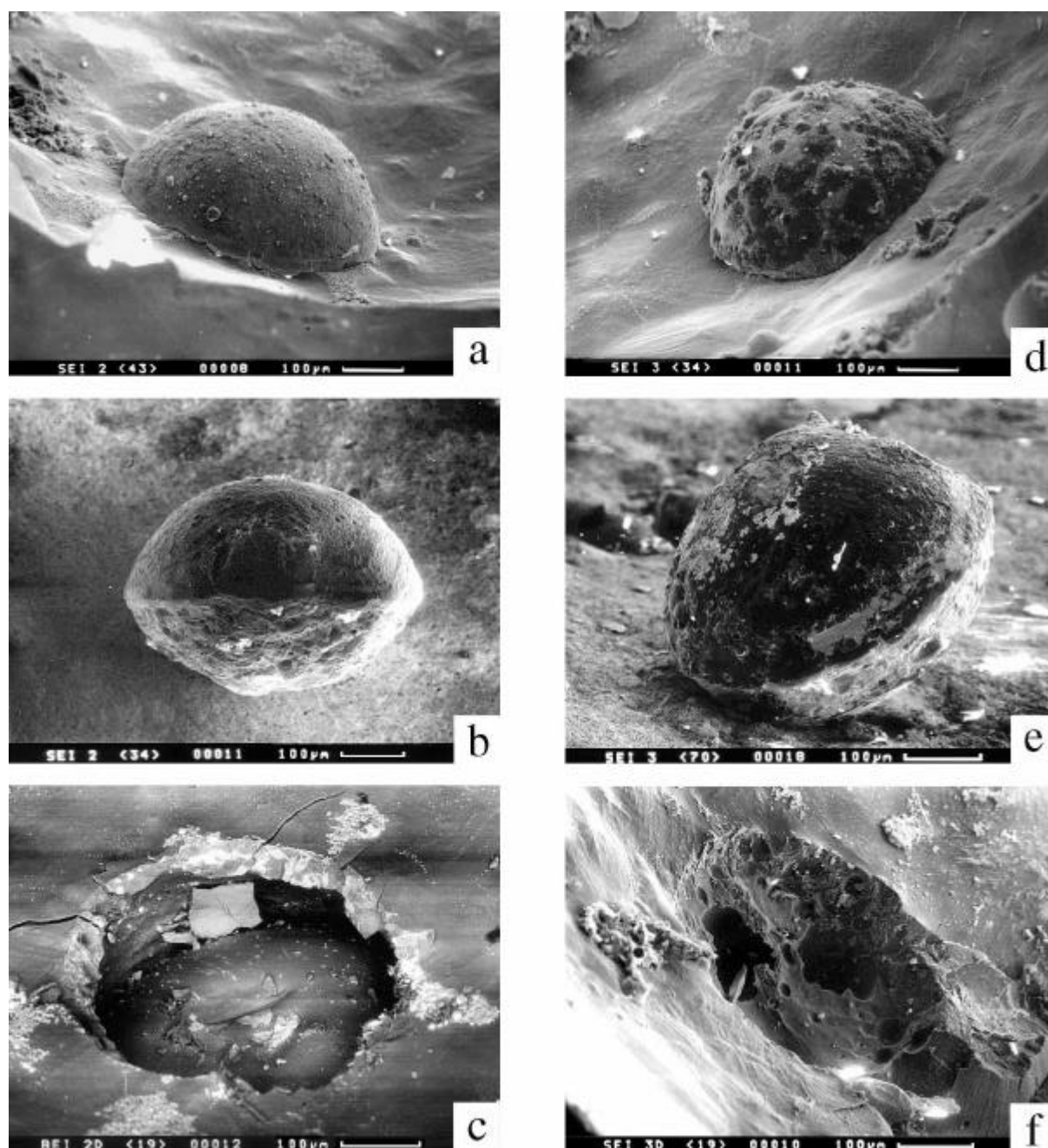


Fig. 5. Metal drops on surface of active gas bubble (Fig. 1a).

- a, d – in situ;
- b, e – after removing from slag;
- c, f – cavities in slag after removing of the drops.

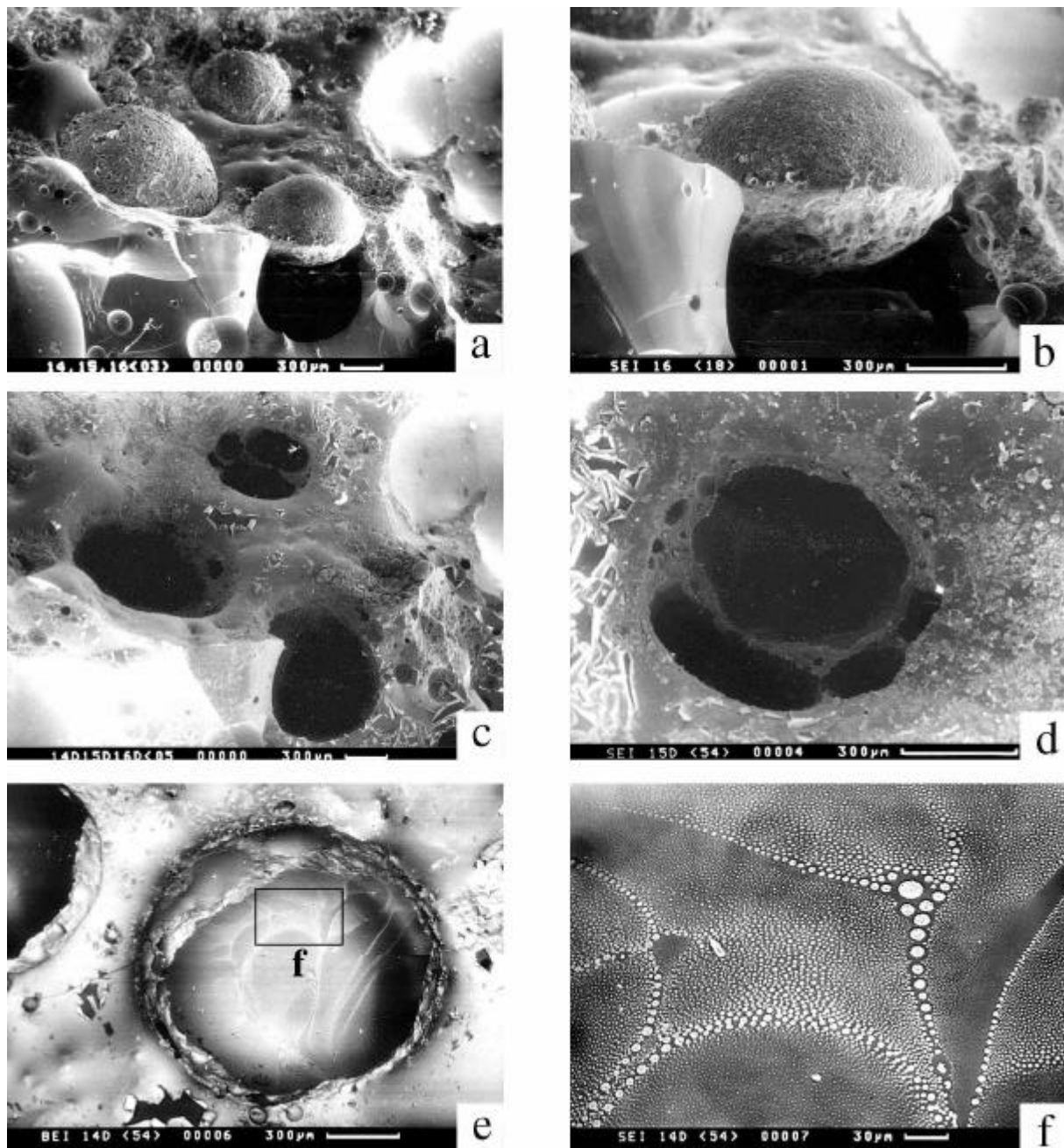


Fig. 6. Pig-iron drops on slag surface.

a, b – in situ;

c-e - cavities in slag after removing of the drops (e – BEI image);

f – fine metal droplets on the slag surface in cavities under pig-iron drop.

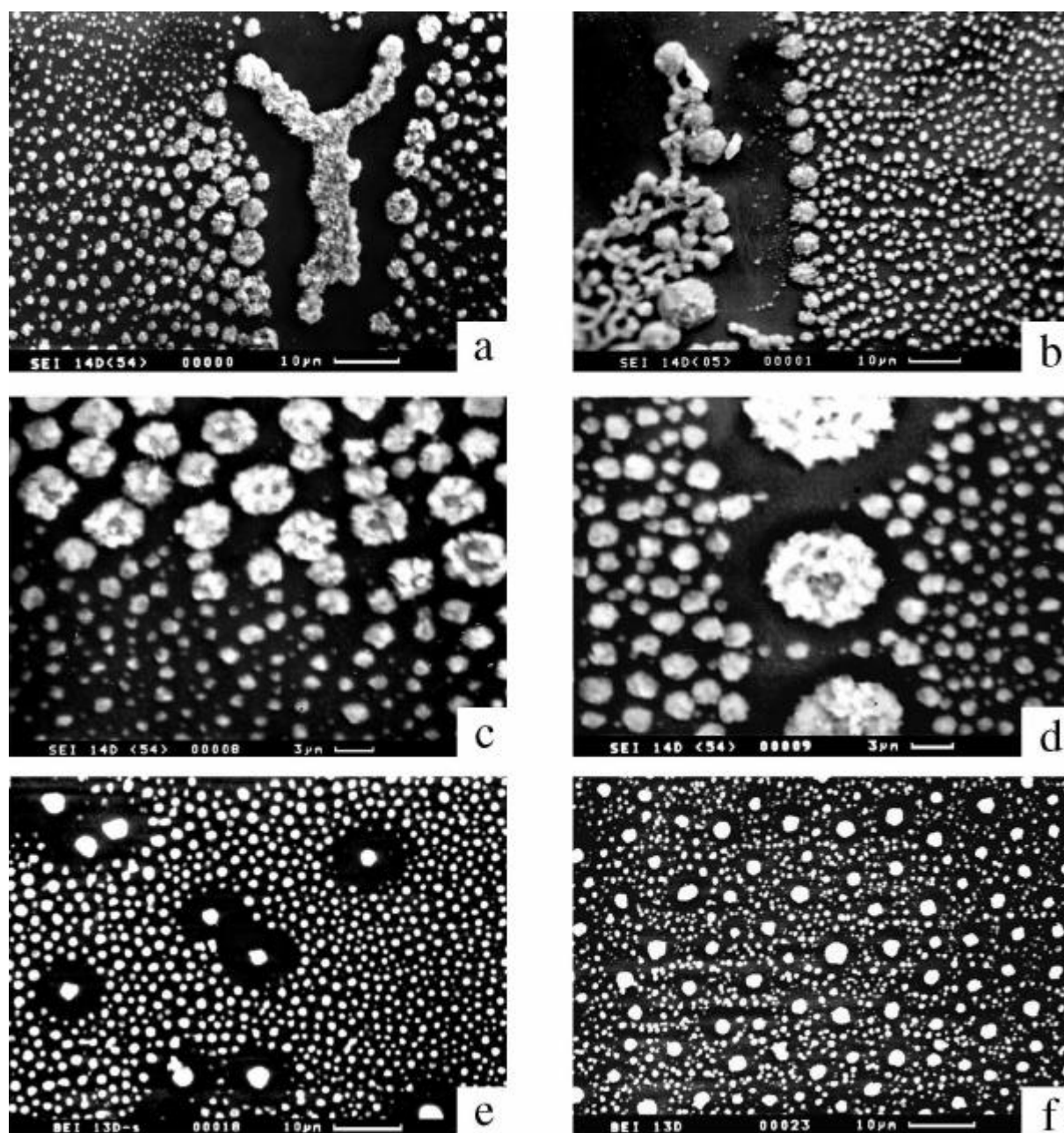


Fig. 7. Structures formed by fine metal particles on the slag surface (Fig. 5e, f).

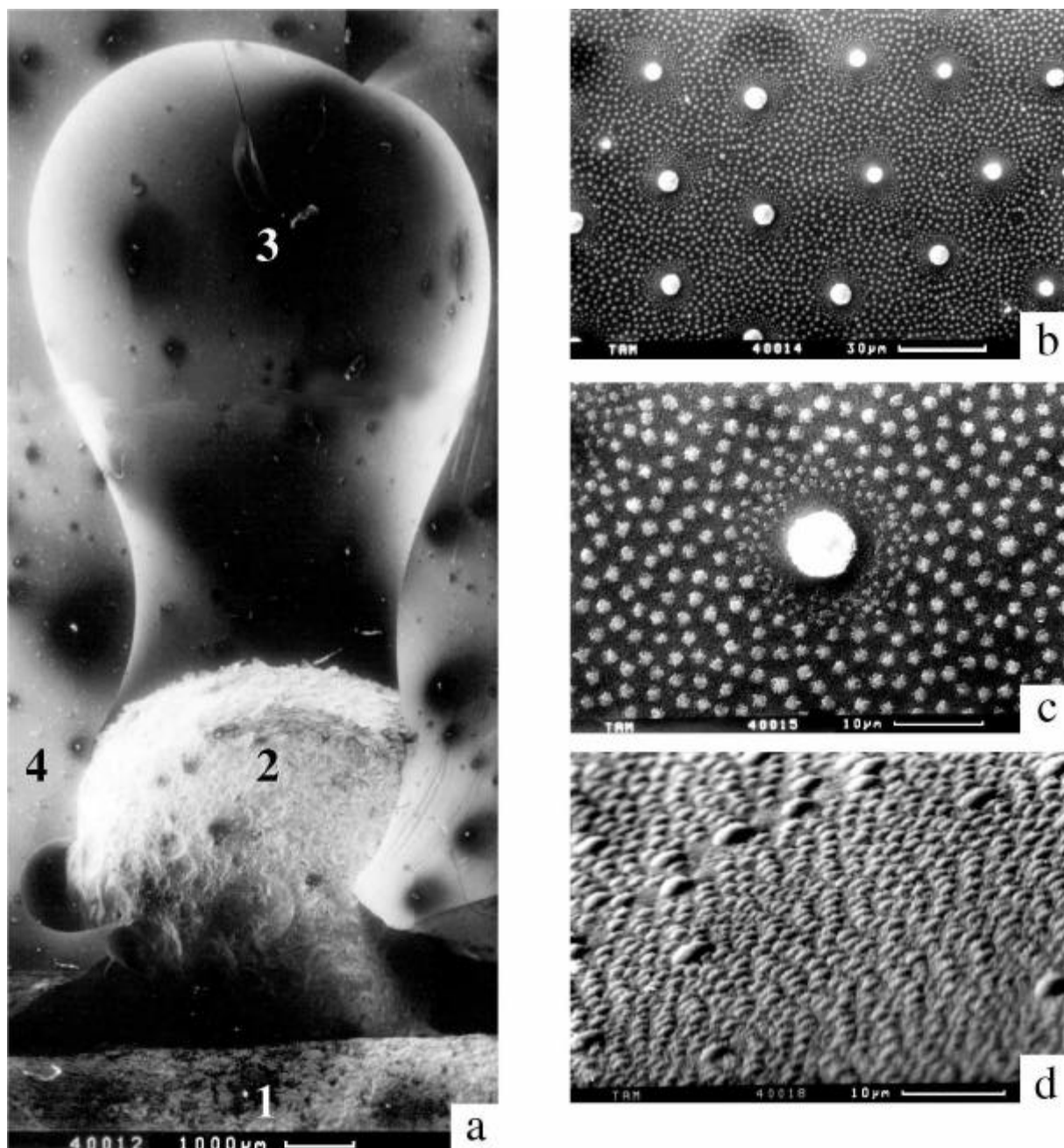


Fig. 8. Morphology of model sample.

a: 1 – alumina crucible; 2 – pig-iron drop; 3 – gas bubble; 4 – slag;
b-d – structures formed by fine metal particles on gas bubble surface.