MORPHOLOGY AND PROPERTIES OF ROMELT PROCESS SLAGS

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ABSTRACT

Slag samples were taken out from agitated slag zone of Romelt furnace (RF). The procedure guarantees high cooling rate and quenching of liquid state morphology. Samples morphology and RF-slag components properties were investigated by SEM, X-ray, Mossbauer spectroscopy, etc. RF-slag is a very complicated heterogeneous system. The base of the system is a foaming molten slag (gas bubbles fraction up to 60% vol.). Slag contains coal char particles and primary pig-iron drops. In gas bubbles with char particles on the gas-slag interface there are always the products of iron reduction initial stages (1-5 μm separate metallic droplets) and primary pig-iron lenticular drops (0.1-1 mm). Pig-iron drops with the size up to 5 mm are stable on the gas-slag surface due to surface tension factor. Gas cavities are found out under the metal drops in slag. They are formed as result of FeO reduction from slag by carbon dissolved in drops. On their surface the iron reduction products are also seen.

INTRODUCTION

Environmental pollution over coke ovens emissions, limited coke coal reserves and high coke prices, problem of Fe-oxides metallurgical waste recycling has stimulated the interest in a variety of non-coke ironmaking processes. The liquid-phase reduction process Romelt is one of the bath smelting processes of alternative ironmaking. It introduced on a pilot scale at Novolipetsk Metallurgical Combine (NLMC). In Romelt furnace (RF) the mixture of noncoking coal and ferrioxide materials (blast-furnace and BOF metallurgical sludge, scale, iron ore etc.) is charged top-down on the surface of air-agitated molten slag. Iron reduction and formation of primary pig-iron drops take place in the air-agitated slag bath at ~ 1400 °C. So, investigations of properties and morphology of Romelt furnace slags (RF-slags) are very important for better understanding the mechanism of iron reduction and pig-iron formation in the Romelt process.

EXPERIMENTAL

The slag samples were taken from the air-agitated zone of the NLMC Romelt furnace (hard or light noncoking coal and BOF sludge or iron ore are charged in furnace during sampling). The slag samples were taken from different depth of the RF slag bath. The samplers were introduced through the charging inlet of the furnace. The sampler consisted of a thick-walled cardboard tube (an outside diameter of ~ 11 cm and a length of ~ 25 cm) with plywood bottom and cover. A steel collapsible cylinder crucible-receptacle was located within tube. A steel crucible (a wall thickness of 8 mm, an outside diameter of 90 mm and a height of 165 mm) had interior steel plate partition with a thickness of 10 mm. This partition separated the cylinder volume of crucible (~ 600 cm^3) on to equal parts. A detachable steel riser of 50 mm height in the form of a tube was installed on the top part of the crucible. The sidewall of the riser had a 40-mm hole that conjugated with a similar hole in the wall of the cardboard tube. The slag ran through these holes into the receptacles when the outer protective paper layers burned out, i.e., when the sampler was already immersed in the molten slag. The large heat capacity of the steel crucible and its good thermal isolation ensured quenching and rapid solidification of the slag during sampling, so that the morphological characteristics of the molten slag could be established. As a result of each sampling two slag ingots in a form of semicylinder were obtained (fig. 1a).

The sampling from the surface of RF slag bath was made with the use of sampler

without upper cover. The sampler was put down into the bath, taken out quickly and steel crucible was cooled immediately with water stream.

Morphology of 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. The slag structural components were studied in detail by scanning electron microscopy CamScan-44S. Selected fragments were melted in a Wood's metal cup, and a thin layer of aluminum (~10 nm) was applied to the specimen surface to assure electrical conductivity.

Chemical composition and structure of the samples were investigated by chemical and X-ray analyzes and Mossbauer spectroscopy. For density determination the bottle method was used. Coal char particles specific surface was measured by Ar adsorption method with the use of AccuSorb 2100E surface analyzer. The chemical analyses of carbon and sulfur in metal drops were made with Leco CS-46 analyzer.

RESULTS AND DISCUSSION

All obtained slag samples looked like glassy ingots of dark green colour. The slag chemical compositions were approximately identical. The base components content: 35-40 % SiO_2, 35-40 % CaO, 10-15 % Al_2O_3, ~10 % MgO, 3-5 % Fe-oxides, ~ 1 % MnO. The slag chemical composition was virtually independent on sampling depth that indicates good slag mixing in the air-agitated zone of the furnace. The X-ray analyzes showed that slag had almost amorphous structure in all samples. It proves sufficiently high cooling rate and rapid solidification of samples. Mossbauer spectroscopy has shown presence of two different states of iron (Fe^{2+} and Fe^{3+}) in slag amorphous matrix, but there were no tracks of crystalline Fe-oxides or other iron-containing phases. It means that intensive barbotage and mixing leads to complete dissolving of ferrioxide materials in molten slag in RF. The divalent iron prevails above trivalent and the Fe^{3+}/Fe^{2+} ratio in slag is about 0.2. This result is in a good accordance with results of Fe^{2+} and Fe^{3+} chemical analyses.

When the slag ingots were fragmented, their interior was found to contain individual carbon particles (up to 5-10 mm) and solidified metal drops (up to 3-5 mm). More often these particles and drops were in ingots exterior part. The number of such relatively large carbon particles and metal drops was small and not exceeds a few per sample. For the samples taken from the surface of the slag bath their quantity, especially the carbon particles, was much more. It must be noted that both the carbon and metal particles in ingot volume were always

located in spherical voids and cavities and were quite weakly bounded to the slag (fig. 1). The carbon particles and large metal pellets and solid drops were often detached from their original positions during sample fragmentation.

The chemical analyses of metal drops (4.0-4.5% C, 0.05-0.1% S, ~0.1% Mn and less then 0.01% Si) show that they are primary pig-iron drops. They were sphere-shaped and their size was from tenths to several millimeters. The most part of the drops was of practically ideal lenticular form (fig. 2a, b). Often, the rough edges, "pockmarks" and depression in the surface were clearly seen on the one of spherical segments (fig.1b, c and 4a), and sometimes, there is a something like «faceting» of the drop surface (fig. 2d).

The carbon particles were coal char, formed during "devolatilization" of coal in slag bath. Char particles could be characterized by strongly developed pore structure. It is clear because the particle effective density is low and value of specific surface is rather high (about 4 m^2/g). The char effective density determined by non-wetting liquid (water) and the density determined by wetting liquid (ethyl alcohol) were different: 1.20-1.25 g/cm^3 and 1.65-1.70 g/cm^3 correspondingly, so char porosity is approximately 25%. The char density is significantly more than density of coal (~1.35 g/cm^3), that is connected with evolving of coal-volatile matter during "devolatilization".

The effective density of char particles is sufficiently less than molten slag density (~2.8 g/cm^3). It explains why the char particles fraction in surface area much more than for volume of slag bath. Char particles can get to the bath volume only as a result of mixing, connected with molten slag intensive barbotage. Wetting of these particles promotes the char mixing to slag. It is well known that molten slag does not wet carbon. However, char particles carbon in surface area burns out. Thus, the coal ash layer appears on the char surface. The base of the coal ash is SiO_2 and Al_2O_3 (about 55 % and 25 % correspondingly). Coal ash covering formation promotes char particles wetting with molten slag and their mixing to the slag bath volume consequently.

The effective density of slag ingots for samples taken from volume of slag bath changes in a wide range: from 1.6 to 2.3 g/cm^3 but the correlation between effective density and sampling depth was found: the less is sampling depth the less is an effective density. For the surface area slag the effective density decreases to 1.0 g/cm^3. The last value corresponds to 60% of porosity. High sample porosity was discovered after ingot fragmentation. This procedure showed that main structural inhomogeneity in all samples was the presence of numerous cavities and voids remained from gas bubbles in the molten slag. The visually

detectable cavities ranged in size from a fraction of a millimeter to several millimeters (~ 5 mm or even more). An enormous number of cavities and voids were observed on the lateral surface of the ingots; their shape generally resembled a sphere segment. They were also encountered within the specimens, where the cavities were almost ideally spherical. The extremely large number of cavities undoubtedly indicated a high degree of gas saturation and intense slag agitation in the Romelt process. The morphology of surface area slag is almost identical to morphology of foaming slag (Fig.3a, b).

The overwhelming majority of the cavities was empty and had an absolutely smooth surface with a characteristic glassy luster. Nevertheless, small (1-3 mm or less) char particles and pig-iron drops (with the size about 1 mm or less) were observed with the unaided eye or under low magnification in some of them (Fig. 1a-c). We might remark that the metal drops were localized on the gas-slag interface in bubbles with the char particles. Such bubbles we have named active bubbles ("active" means the opportunity of iron reduction from molten slag and iron carbonization and maintenance of these processes during a long time). Significantly smaller char particles and metal droplets became visible at higher magnifications. The small metal droplets were localized exclusively in the gas bubbles containing char (the active bubbles). This was true both for the cavities in the interior and for the craters at the surface, which were formed as a result of displacement of the gas bubbles toward the surface of the steel crucible during pouring and solidification of the molten slag.

As the experimental data show, even relatively large metal drops (1-3 mm in size) were stable on gas-slag interface and they did not go into the slag, despite the significant difference in density. Besides, the gas cavities were always seen under the pig-iron drops and large metal drops are located in a something like gas bag (fig. 1b, c and 4a). The smallest metal particles can be found out on the slag surface of such cavities and gas bags (fig. 4b-d). They are similar to the particles existed in active bubbles. These droplets appear during the initial stages of iron reduction by carbon oxide from the slag. The process develops due to carbon dissolved in pig-iron drops. The iron reduction by carbon dissolved in pig-iron drops we have called «secondary reduction» in contrast to iron reduction by carbon char («primary reduction»).

The secondary reduction explains pig-iron drops morphological characteristics mentioned above. The carbon concentration in the drops is quite enough for development of secondary reduction process. The beginning of the process leads to formation of the CO micro-bubbles on the bottom drop segment, which is deepened in slag. (fig. 3f and 5-I). Such micro-bubbles get into the metal drop, tracking the surface. That is why the depressions and

holes can be seen on the surface of solidified drops (fig. 2c). The secondary reduction development leads to growth and coalescence of gas micro-bubbles. The metal drop is situated among several gas bubbles (fig. 5-II). It gives original faceting of the drops after crystallization (fig. 2c). Further process development leads to formation of single spherical cavity under the metal drop (fig. 5-III) and drop become of lenticular shape (fig. 2a, b)

High porosity and gas bubbles content of RF-slags are stipulated not only by intensive air-agitating and barbotage but by iron reduction also. The iron reduction process results CO formation without dependence on state of carbon (coal char particles or pig-iron drops):

$$\textbf{(FeO)} + \textbf{C}(\text{char, iron}) = \textbf{Fe} + \textbf{CO} \tag{1}$$

The process 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 of active bubbles or gas cavities under primary pig-iron drops:

$$\textbf{(FeO)} + \textbf{CO} = \textbf{Fe} + \textbf{CO}_2 \tag{2}$$
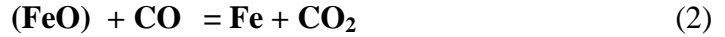
The second stage is recombination of CO_2 on gas-char or gas-metal interfaces:

$$\textbf{C}(\text{char, iron}) + \textbf{CO}_2 = \textbf{2CO} \tag{3}$$

We need only note that presence of a char particle in the gas bubble is an obligatory condition for liquid-phase reduction to occur continuously. It is only in this case that the CO_2, formed during FeO reduction or iron carbonization (reverse reaction to (3)) can be regenerated and hence that a reductive CO atmosphere can be preserved and maintained in the gas bubble.

Estimation shows that volume of CO, evolved during reaction (1) is approximately 17000 times more, than the metal drop volume. Thus CO evolving during iron reduction leads to formation of huge number of gas bubbles. Obviously, in slag surface area, saturated by char particles, iron reduction and, consequently, CO evolving is much more intensive than in slag bath volume. So, there, the quantity of gas bubbles is much more too.

If the gas bubble radius is 1.5 times more than metal drop one, the effective density of the complex bubble-drop is equal to molten slag density. Thus, gas bubble formation around metal drop during secondary iron reduction increases sufficiently the drop stability and its lifetime in slag bath. Pig-iron drops float to slag surface area and there they can be carbonized during the contact with char particles. Repeating of "secondary reduction" – "flotation" – "carbonization" – "secondary reduction" cycles increases dramatically the reduction ability of pig-iron drops, because even if the dissolved carbon reacts completely, the drop mass increasing is not more than 5 %. We observed pig-iron drops with sizes up to 5 mm, which were stable in the bubbling slag and so, they could participate in the iron reduction process in

RF bath smelting. The tendency to the falling down dominates for the drops with sizes more than 5-10 mm only.

SUMMARY AND CONCLUSIONS

Air-agitated RF-slag is a very complicated heterogeneous system. The base of the system is a foaming molten slag (gas bubbles fraction up to 60% vol.). Slag contains the coal char particles and the primary pig-iron drops. The char particles and metal the drops content is much more in surface area of slag bath in comparison with the volume of the furnace. In gas bubbles with the char particles on the gas-slag interface there are always the products of iron reduction (1-5 µm separate metallic droplets) and primary pig-iron lenticular drops (0.1-1 mm). Pig-iron drops with the size up to 5 mm are stable on the gas-slag surface due to surface tension factor. Gas cavities are formed under the metal droplets in active gas bubbles with char particles. Besides, gas bubbles appear around the big (several millimeters) pig-iron drops. Both processes are the result of CO evolving during FeO reduction from slag by carbon dissolved in metal drops. On these new surfaces the iron reduction process (secondary reduction) start and the smallest metal phase particles are also seen. Gas bubble formation around metal drop during secondary iron reduction increases sufficiently the drop stability and its lifetime in slag bath.

Our results permit to draw the following conclusions, which are important for understanding the mechanism of liquid-phase reduction and primary pig-iron drop formation in the Romelt process:

- Reduction of the ferric oxide dissolved in the molten slag takes place in active gas bubbles containing coal char particles. Formation of primary pig-iron droplets is localized on the slag-gas interface.
- oal char particles fraction is much more in the surface layer of slag bath. Intensive barbotage of molten slag is necessary for char particles mixing into slag bath volume.
- Pig-iron drops are stable on the slag-gas interface and do not enter into the molten slag, at least if their size is about 5 mm or less.
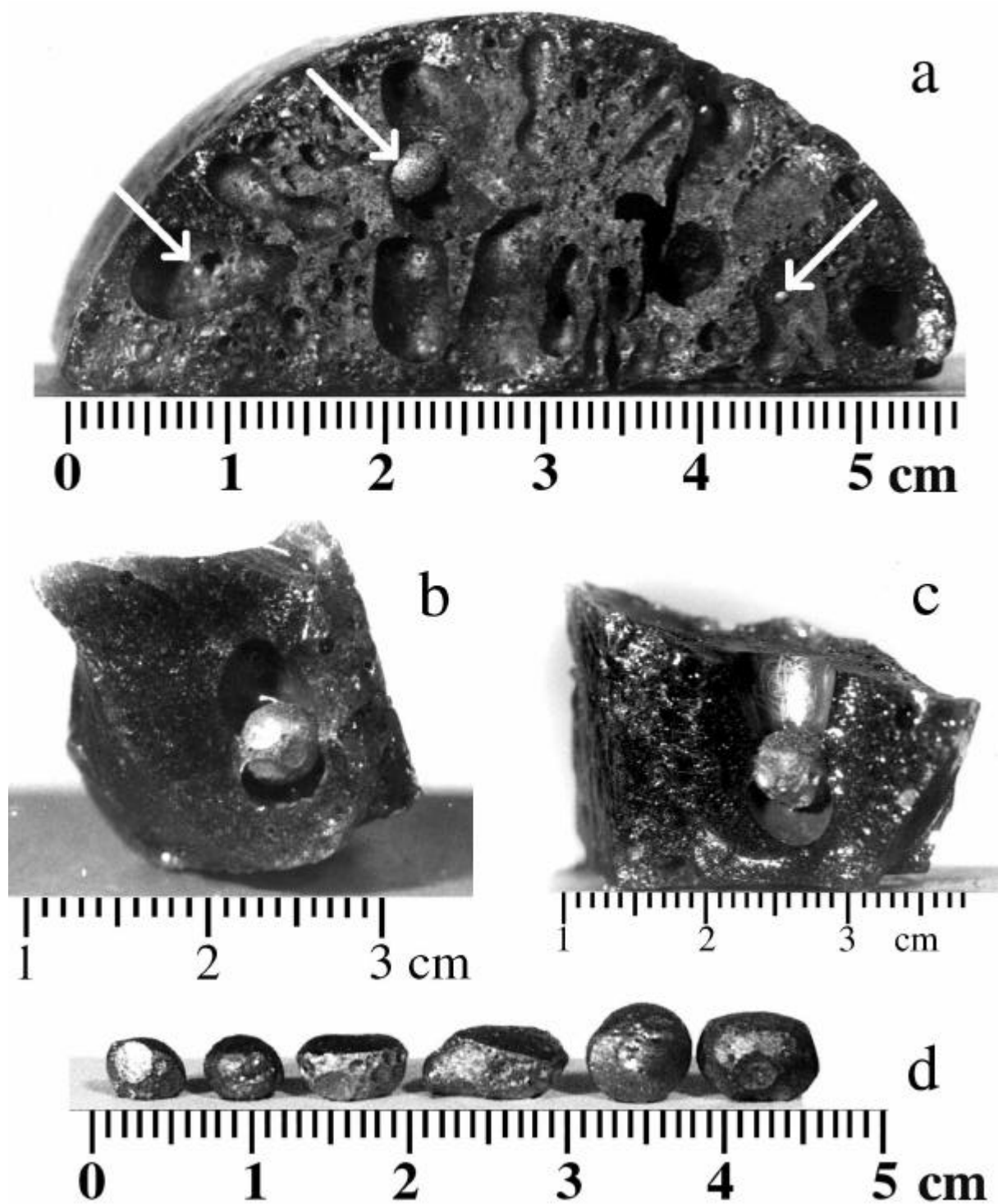
Fig. 1. Metal drops in slag ingots (optical photos).

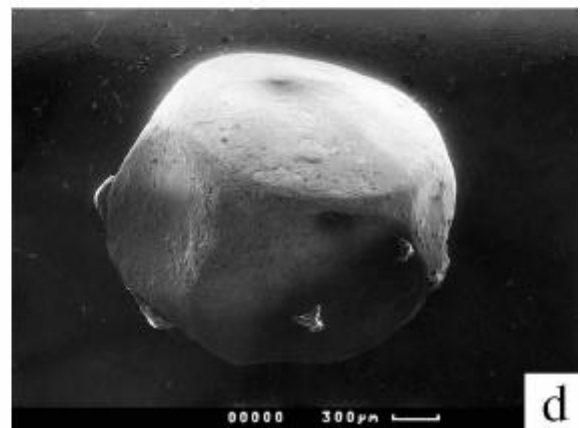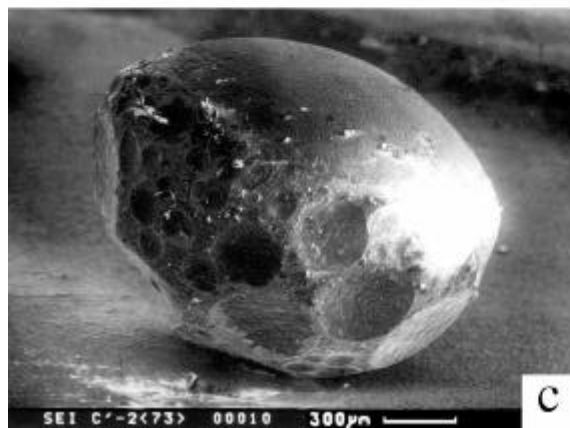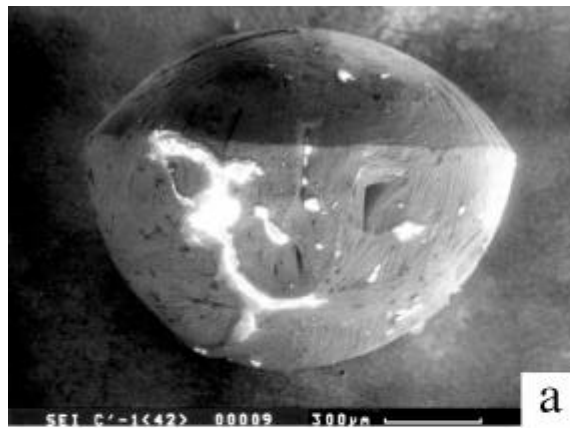The white arrows point out to the solidified metal drop in gas bubble.

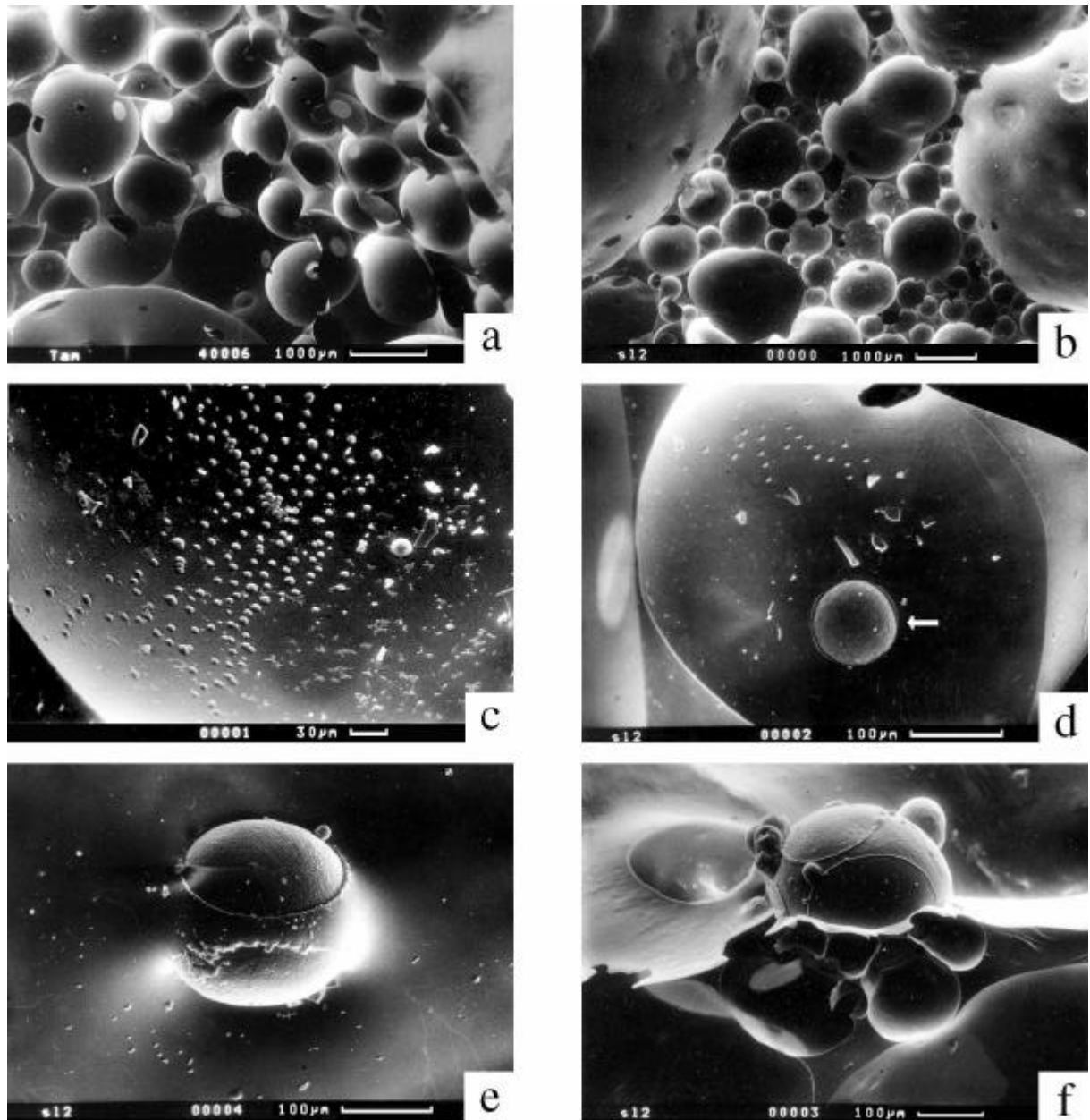Fig. 2. Metal drops from slag ingots (SEM).

Fig. 3. Morphology of surface foaming slag.

The white arrow point out to the pig-iron drop on the gas bubble surface.
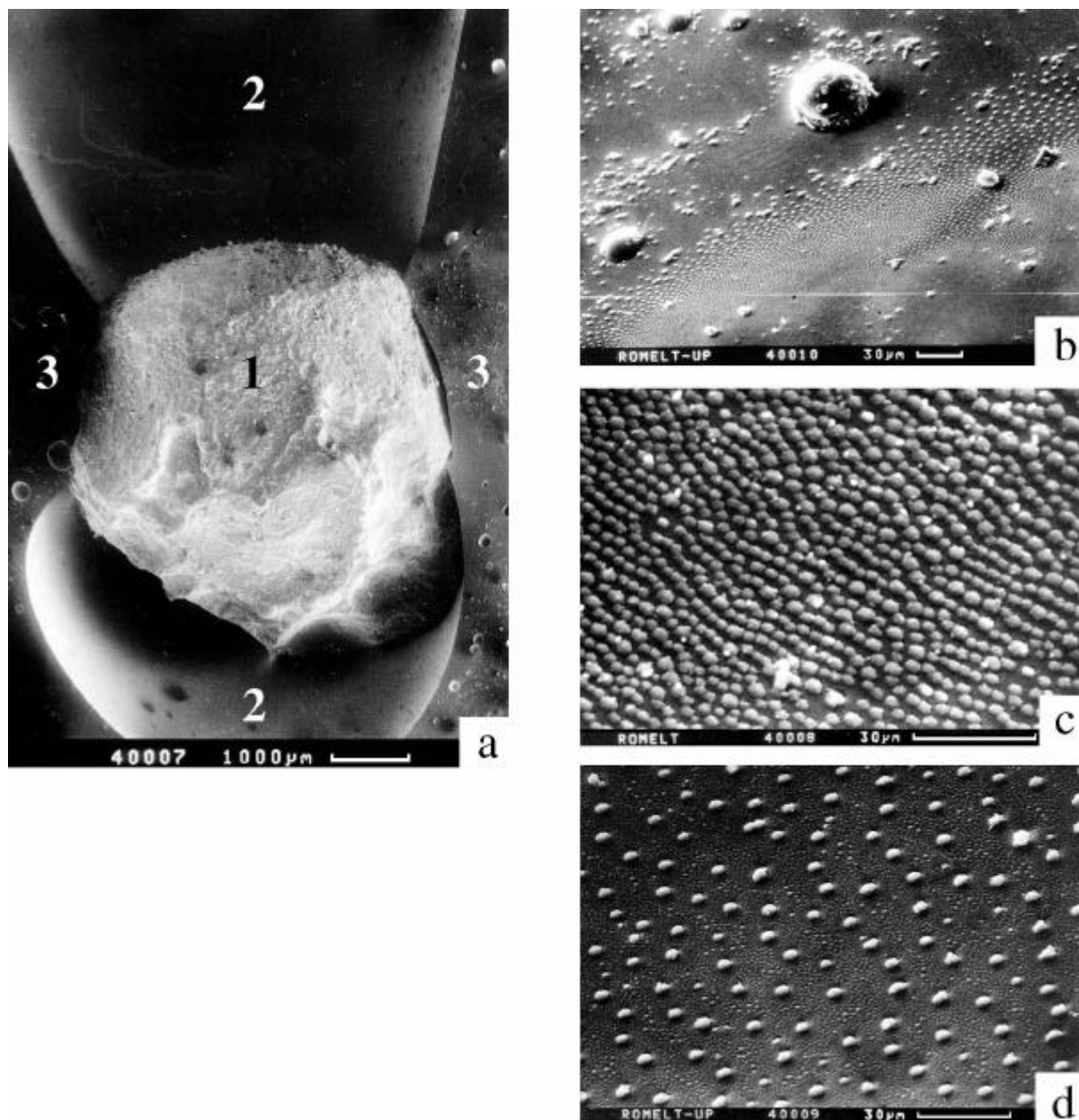
Fig. 4. Pig-iron drop in slag.

a: 1 – metal drop; 2 – gas babble; 3 – slag.
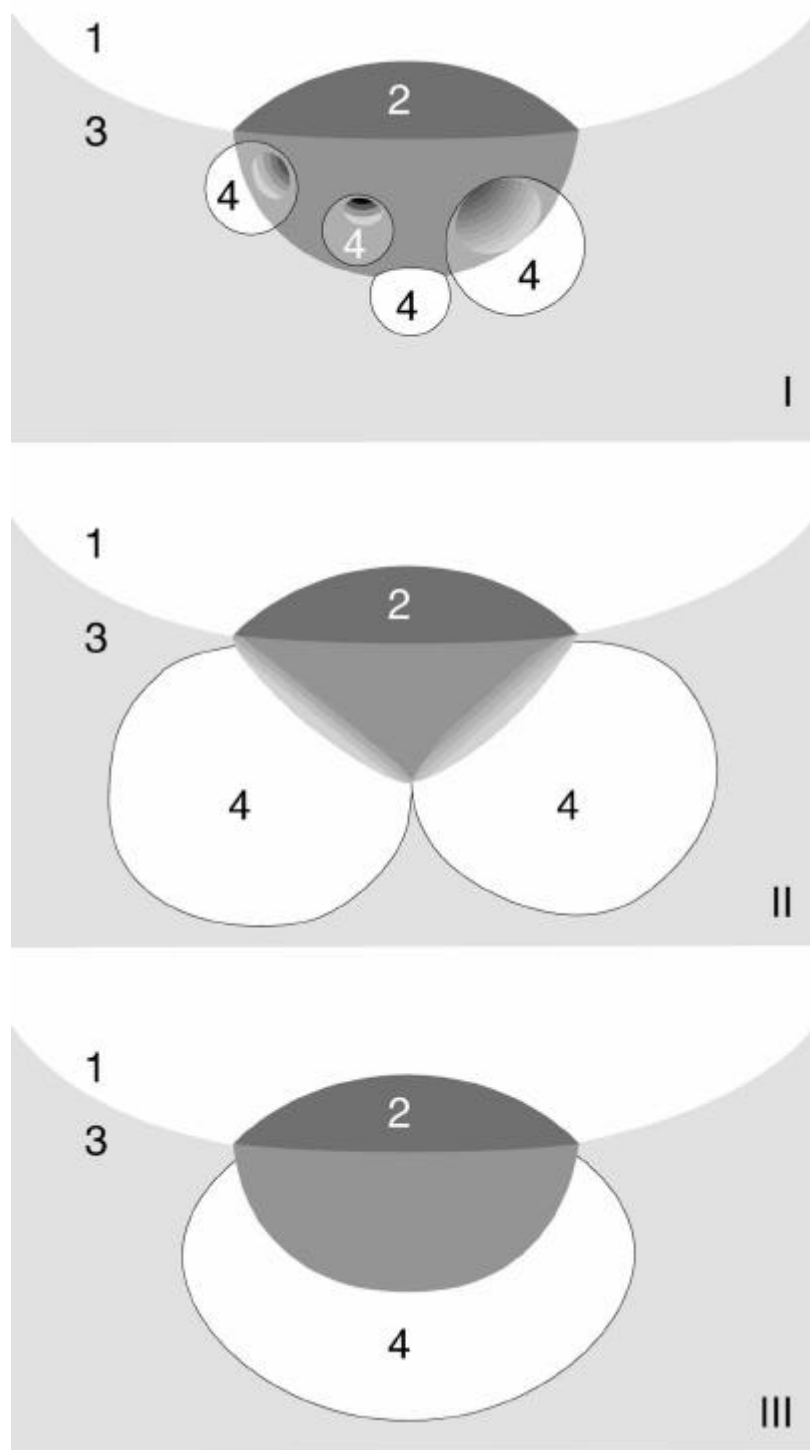b-d – structures formed by fine metal particles on gas bubble surface.

Fig. 5. Schematically presentation of metal drop shape formation process in active gas bubble.

1 – active gas bubble, 2 – metal drop, 3 – slag, 4 – gas cavities.