MODERN VIEW ON COMPOSITION OF AUTOGENOUS SMELTING SLAGS AND METHODS OF THEIR DECOPPERING

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ABSTRACT

The knowledge of the true phase composition of the liquid slag is a very important problem, mastering of which grants the possibilities for the scientifically founded choosing of decoppering method of the autogenous smelting slags. The investigation using different methods of the phase composition of the flash quenched autogenous copper melt slags has shown, that the most effective method of the slag decoppering during smelting with matte production is the flotation of the recrystallized slags.

In this work the authors posed the problem to realize the slag quenching with the rates similar to those, which are used in modern investigations devoted to the flash quenching of the iron-containing alloys, with the subsequent study of the quenched samples using the Mössbauer spectroscopy methods in order to establish the connection between a liquid slag structure and the metals losses with the slag.

INTRODUCTION

The real composition of copper containing smelting slags is rather little-known, since the overwhelming majority of investigations in this field is based on the results of analysis of recrystallized slags of quenching with the rates, that do not provide conservation of the liquid slag composition (overcooled liquid). Smelting slags, in a first approximation, could be analysed according to a composition, as implantation solutions [1], with ions of metals implanted in the interstitial sites of two types - octahedral and tetrahedral, formed by the ions of oxygen, and solubility of the ions of metals in a liquid slag is more considerable than in a solid slag, defined by a constitution diagram.

This work posed the problem of realization of slags quenching with the rates similar to those used in modern investigations in the sphere of ultra-rapid quenching of the iron-containing alloys with a subsequent study of the quenched samples using Mössbauer spectroscopy method for establishing a connection between a liquid slag structure and non-ferrous metals losses with this slag.

EXPERIMENTAL

The authors of this work used the method of a liquid slag quenching at the surface of the rotating copper disk – the spinning method [2]. The slags had been obtained by the method of alloying of chemically pure oxides over the layer of matte, containing 75% of copper. Two samples of synthetic slags had been studied simultaneously with the production samples of the copper smelting slags, obtained in the process of matte smelting, containing 38% of copper.

Slags composition is shown in Table. The composition of the slags shown in Table could be written in the following form: 36 FeO II $Fe_2O_3 \cdot (53-X) SiO_2$ XCaO, where X=3, 17, 33 for slags C, A and B, accordingly.

NGR-spectra (nuclear-gamma-resonance spectra) had been obtained by the instrument NGRS-4 with the source ^{57}Co in a chromium matrix. All measurements had been made at an indoor temperature with a value of graduation for one channel 0,116 mm/s.

RESULTS

The ultra-rapid quenching slags spectra represent asymmetric doublets of wide lines (see Figure 1). One of the doublets refers to the Fe^{3+} ions, two other doublets are linked to Fe^{2+} in different composition states.

Revelation of positions conforming to the Fe^{3+} ions and the $Fe^{2+}_{okt.}$ ions and the $Fe^{2+}_{tet.}$ ions (octahedral and tetrahedral positions, accordingly), had been made with the use of a computer. Revelation of the positional distribution for the Fe^{3+} ions had not been made in view of a small intensity of lines from ferric iron. A small relative (~30%) content of Fe^{3+} does not allow to reliably identify its distribution according to the octahedral and tetrahedral positions. We had been interested mainly in the Fe^{2+} ions performance because this performance of the Fe^{2+} ions, as well as of the Ca^{2+}, is linked with isomorphic replacement of the Fe^{2+} ions for the Cu^{2+}, the Pb^{2+}, the Ni^{2+} ions when analysing the problem of possible losses of these metals with the slags. Data on a correlation of the Fe^{3+} ions and the Fe^{2+} ions, obtained for recrystallized slags, do not reflect their true correlation in melts (glass).

The fraction of the Fe^{2+} ions (α), that are present in the octahedral and tetrahedral positions depending on CaO content in the slag, is shown on Figure 2.

For the octahedral positions - $\alpha_{oct.} = Fe^{2+}_{oct.}/Fe^{2+} + Fe^{3+}$, for the tetrahedral positions - $\alpha_{tet.} = Fe^{2+}_{tet.}/Fe^{2+} + Fe^{3+}$, where $Fe^{2+}_{oct.} + Fe^{2+}_{tet.} + Fe^{3+} = 1$ and $Fe^{2+} = Fe^{2+}_{oct.} + Fe^{2+}_{tet.}$

Figure 2 illustrates such changes in the fraction of Fe^{2+}(R) depending on Ca concentration in the slag. It is evident that the value $R = Fe^{2+}/Fe^{2+} + Fe^{3+}$ tends to increment with the growth of CaO concentration in a liquid slag. The fact of growth of Fe^{2+} content in the glass when the content of CaO in it was increasing, had been also pointed out in the work [3]. Thus, in our opinion, Ca in liquid slags makes for slag reduction. It is connected with the fact, that Ca has a negative affinity for an electron, i.e. Ca can only eject electrons and not capture them, thus being a typical reductant. Figure 2 also demonstrates that as the Ca ions content is growing in a slag, the fraction of the Fe^{2+} ions in the octahedral positions is decreasing and, accordingly, the fraction of the Fe^{2+} ions in the tetrahedral positions is increasing. One could be made an assumption that the Ca^{2+} ions displace the Fe^{2+} ions from the octahedral and tetrahedral positions.

Figure 3 illustrates the Fe^{2+} fraction in the octahedral and tetrahedral positions depending on the parameter $X = Ca^{2+}/Fe^{2+}$. The parameter X characterizes the degree of replacement of the Fe^{2+} ions by the Ca^{2+} ions. Under complete replacement of the Fe^{2+} ions by the Ca^{2+} ions the value of X = I. The fraction $\beta_{oct., tet.} = Fe^{2+}_{oct.,tet.}/Fe^{2+}_{oct.} + Fe^{2+}_{tet.}$ is plotted on the ordinate. The value of $\beta_{oct.}$ and X are linked by a simple dependence $\beta_{oct.} = 1 - ax$, where a is a coefficient, which characterizes the probability of isomorphic relacement. As it is clear from Figure 3, when X = 1, not all ions of Fe^{2+} are replaced from the octahedral positions, 30% of the Fe^{2+} ions are at their places and some additional portions of Ca are necessary for their replacement. The processing of the experimental data given in Figure 3, resulted in value $a = 0,7$, i.e the probability of isomorphic relacement $Ca^{2+} \rightarrow Fe^{2+}$ makes up 70% for this system. This may be connected with the fact that 30% of the Ca ions

interact with the octahedral voids, that are constantly present in the system and not with the Fe^{2+} ions. For a complete replacement of the Fe^{2+} ions from the octahedral positions into the tetrahedral positions, Ca^{2+} should be taken 1,4 more than the Fe^{2+} ions (where X = 1,4; $\alpha_{oct.}$ = =0).

NGR-spectra of a bar test of the silicate-calcium slag (slag B) and dumping production slag (slag C) had been taken. The spectrum of a complete recrystallized slag had been also taken for the type B slag (retarded quenching with the furnace). Those spectra are illustrated at Figure 4 and Figure 5. As it is clear from Figure 4, a bar test does not reflect a true compositional and material state of the slag. For the slags (C) in bar test a partial crystallization with isolation of the phyllite phase ($Fe_2 SiO_4$) (up to 60%) is observed and only 40% of iron atoms are in glass. In silicate-calcium slags in a bar test almost complete crystallization with FeO formation (20%) and spinel formation on the basis of Fe_3O_4 (80%) are observed. A bar test characterizes the interim state between liquid slag (glass) and the crystallized state.

DISCUSSION

On the basis of the results obtained we can suggest the following scheme of possible maximum losses with the slags of bivalent metals ions (Cu^{2+}, Pb^{2+} and others).

The slags are represented as a set of different oxides, the anions in which there are oxygen and sulphur atoms. When describing the melts, it is evidently necessary to proceed from the principle of the closest packing of anions, as the sizes of the latter are much larger than the sizes of the cations. The anions form the closest packing and cations are placed in voids that are formed when packing the anions. In the closest packings one can differentiate two types of voids. Some voids – tetrahedral (A-positions)– are formed by four anions, placed at the top of the tetrahedron. The coordination number for the tetrahedral environment equals to 4. Other voids – octahedral (B-positions) (the coordination number 8) – are formed by eight atoms of anions, placed at the top of the octahedron. For every n atoms of anions falls n octahedral voids and $2n$ – tetrahedral ones. This correlation does not depend on the type of packings, which can form the atoms of anions in melts. The octahedral voids are much larger in size than tetrahedral ones. Many cations for their size could not be placed in tetrahedral voids and are placed only in octahedral voids. The ions of calcium refer to this type of cations. The atoms of the silicon ions, on the contrary, are placed only in tetrahedral voids, forming the group SiO_4^{4-}. It is known that the higher valence, the smaller ionic radius of a cation. The Fe^{3+} ions can be placed in the octahedral voids as well as in tetrahedral ones, the Fe^{2+} ions prefer to spread in the octahedral voids and only in the extreme cases, e.g. in their isomorphic relacement by the Ca^{2+} ions, they move to the tetrahedral voids. The Ca^{2+} ions, as was stated above, occupy only octahedral positions.

Thus, the quantity of anions in a melt (for the slags - the atoms of oxygen and sulphur) will define the number of octahedral and tetrahedral voids, in which the atoms of cations are placed (for our slags these are the ions of Fe^{2+}, Fe^{3+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Si^{4+}). As was mentioned above, the silicon ions will occupy only tetrahedral positions (A-sites) increasing by this the quantity of unoccupied B-sites (of the octahedral voids). Since the losses of bivalent metals (Cu^{2+}, Pb^{2+}, Ni^{2+}) are connected mainly with occupation of B-sites, the presence of silicon in a slag should increase possible bivalent metals losses with slags.

A number of octahedral voids equals to a number of anions in a system (oxygen, sulphur). The atoms of Si, Fe, Ca, Cu, Ni, etc., may be the cations. The difference between a maximum number of octahedral pores (Σ 0,5) and octahedral pores occupied by cations, defines the number of free octahedral pores, i.e. vacancies. The more vacancies in a system, the more possible metal losses with slags. Octahedral sites, occupied by the Fe^{2+} ions may be

isomorphically replaced by the Cu^{2+}, Pb^{2+}, Ni^{2+} ions, therefore it is efficient to fill the octahedral sites by the Ca^{2+}, Na^{2+} ions, which, as was experimentally illustrated above, replace the Fe^{2+} ions into tetrahedral positions, removing them from the process, but the Fe^{2+} ions could not be displaced from octahedral pores by other ions.

When the Ca^{2+} ions replace in octahedral positions all Fe^{2+} ions, displacing them into tetrahedral positions, then the conditions are formde for diminishing possible bivalent metals losses with slags, as they can't displace the Ca^{2+} ions from B-sites. It is also expedient to diminish the oxygen and silicon concentration in a slag, for a number of initial vacant B-sites depends on their concentration.

CONCLUSIONS

A proposed physical conception of assessment of metals losses with slags demonstrates, that the content of ions of oxygen, calcium and silicon in a slag is very important in assessing the non-ferrous metals losses with a slag. It is shown here that these losses will decrease in the row: silicate, silicate-calcium, ferrite-calcium slags. The minimum losses of the Me^{2+} ions with slags are expected in ferrite-calcium slags. This conclusion had been proved by numerous applied research on copper losses with slags [4-8]. The atoms of silicon are almost lacking in these slags and there are very few atoms of ferrous iron there, that can be isomorphically replaced, thus favouring the minimum losses. Decrease of losses is also linked with the occupation of the octahedral positions by the Ca^{2+} ions, that decreases the number of the octahedral positions, where the ions of the basic metal Me^{2+} could present. When analysing the slag composition it should be also taken itno account, that a bar test reflects a process of transition from glass to a recrystallized condition of slags. The less Ca in slags and the more silicon, the closer is a bar test to a glass condition, that could be obtained under ultra-rapid quenching of slags.

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Table

Composition of tested slags

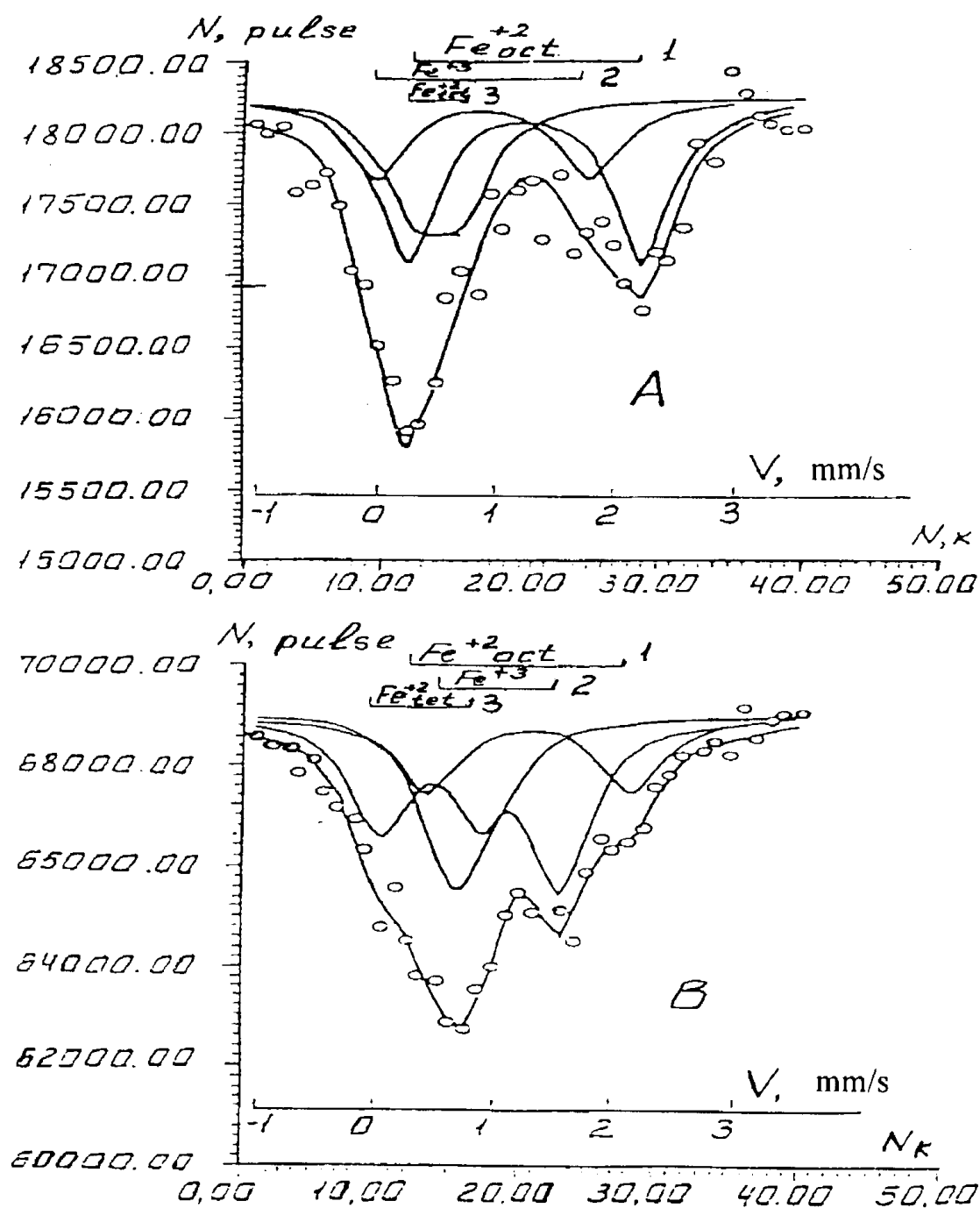| Type of slag	Composition:% mass.% molecule					Compositin:% at.				
	FeO	Fe$_2$O$_3$	SiO$_2$	CaO	ratio CaO/ SiO$_2$	Fe^{2+}	Fe^{3+}	Si^{4+}	Ca^{2+}	O^{2-}
Silico-calcic A	$\dfrac{33}{36}$	$\dfrac{24}{11}$	$\dfrac{30}{36}$	$\dfrac{13}{17}$	0,47	13,5	8,2	13,5	6,3	58,5
High-base ferrite-calcic B	$\dfrac{33}{36}$	$\dfrac{25}{11}$	$\dfrac{17}{20}$	$\dfrac{26}{33}$	1,65	14,2	8,7	7,9	13,0	56,1
Production C	$\dfrac{33}{36}$	$\dfrac{24}{11}$	$\dfrac{41}{50}$	$\dfrac{2}{3}$	0,06	12,5	8,5	17,5	1,0	60,5
Copper content in slag A –1,8% at., in slag B – 1,2% at.										

N, pulse

18500.00

18000.00

17500.00

17000.00

16500.00

16000.00

15500.00

15000.00

Fe$^{+2}_{oct}$ 1

Fe^{+3} 2

Fe$^{+2}_{tet}$ 3

A

V, mm/s

-1   0   1   2   3

N, к

0.00   10.00   20.00   30.00   40.00   50.00

N, pulse

70000.00

68000.00

65000.00

64000.00

62000.00

60000.00

Fe$^{+2}_{oct}$ 1

Fe^{+3} 2

Fe$^{+2}_{tet}$ 3

B

V, mm/s

-1   0   1   2   3

N к

0.00   10.00   20.00   30.00   40.00   50.00

Figure 1 - **NGR-specta of ultra-rapid quenched slags A and B**
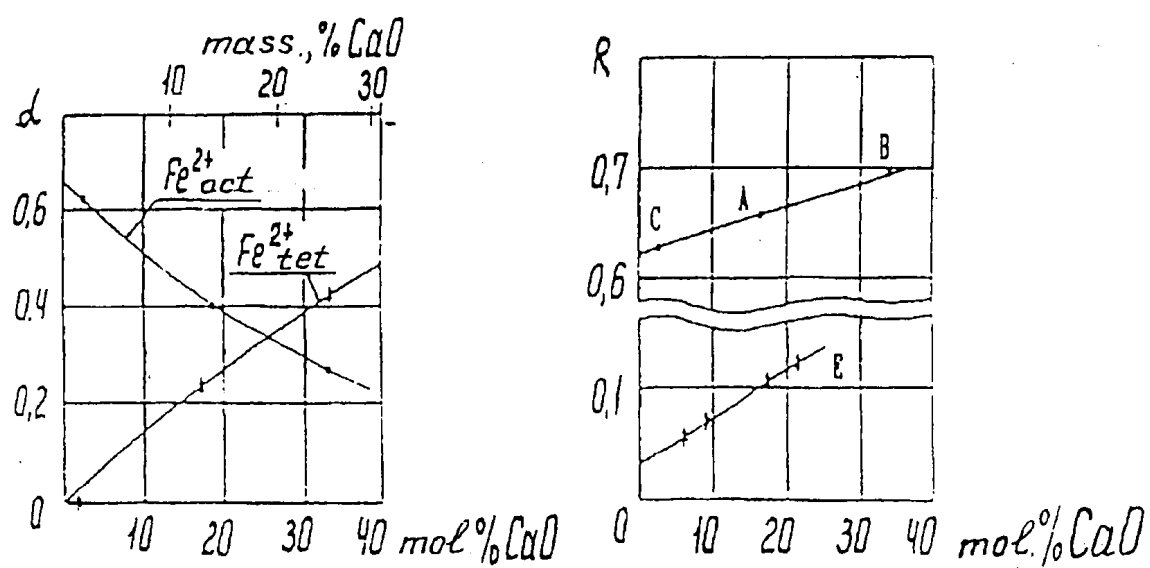
Figure 2 - **Dependence of the Fe^{2+}(R) ions fraction and their positions (α) on CaO content in a slag:**
A – silico-calcic; B – high-base ferrite-calcium;
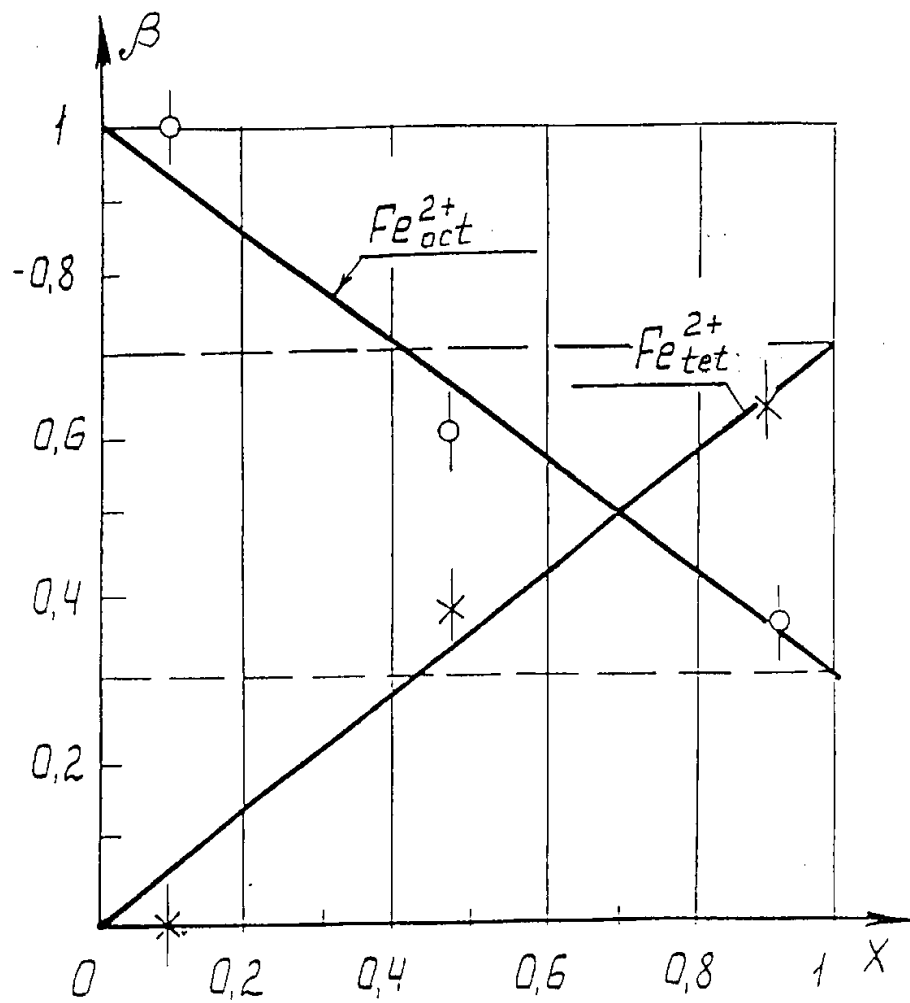C – production; E – according to Bowker's data [3]

Figure 3 - **Fraction of the Fe^{2+} ions in octahedral and tetrahedral positions depending on parameter $X=Ca^{2+}/Fe^{2+}$**
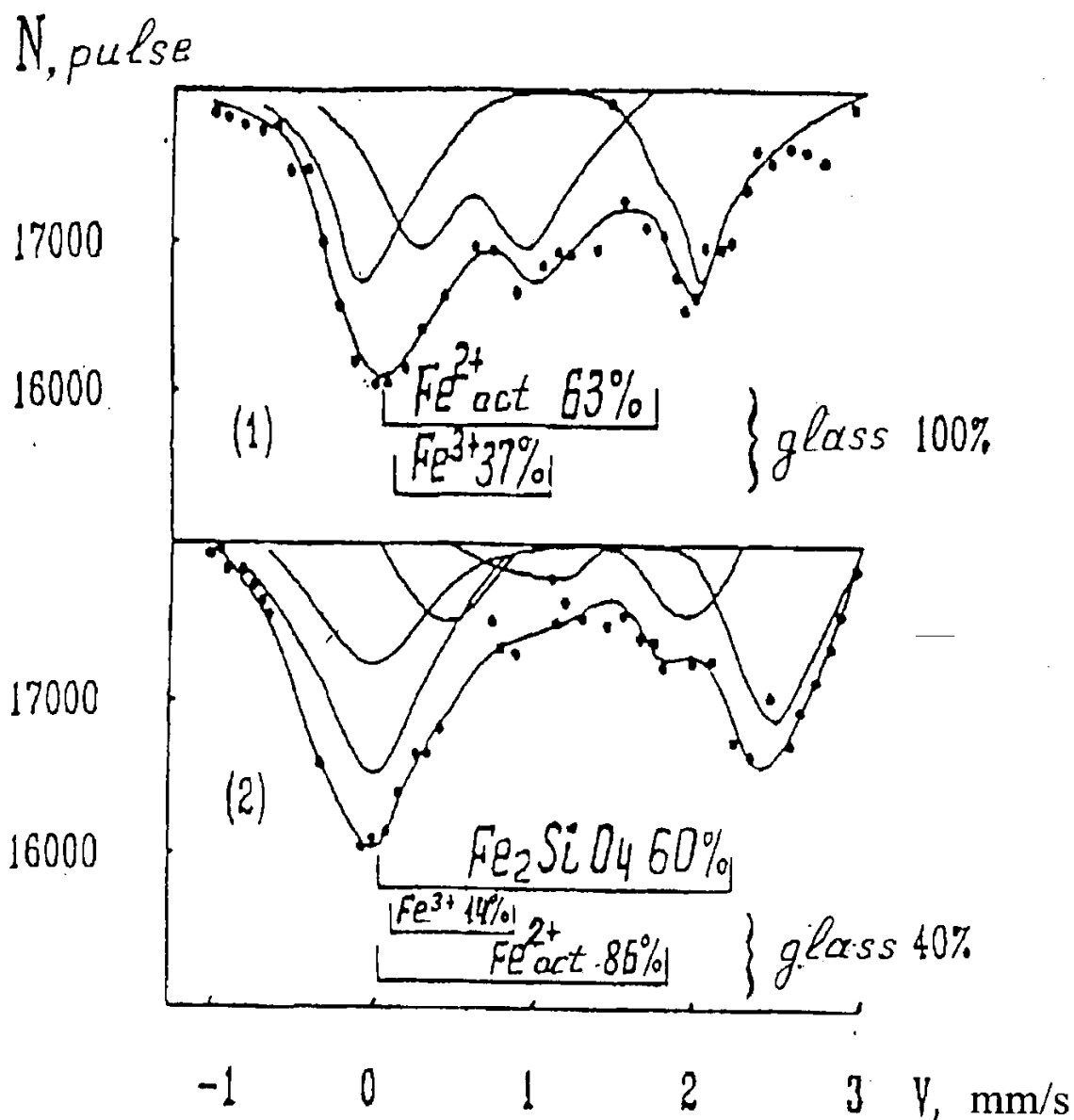
Figure 4 - **NGR – spectra of production slag:**
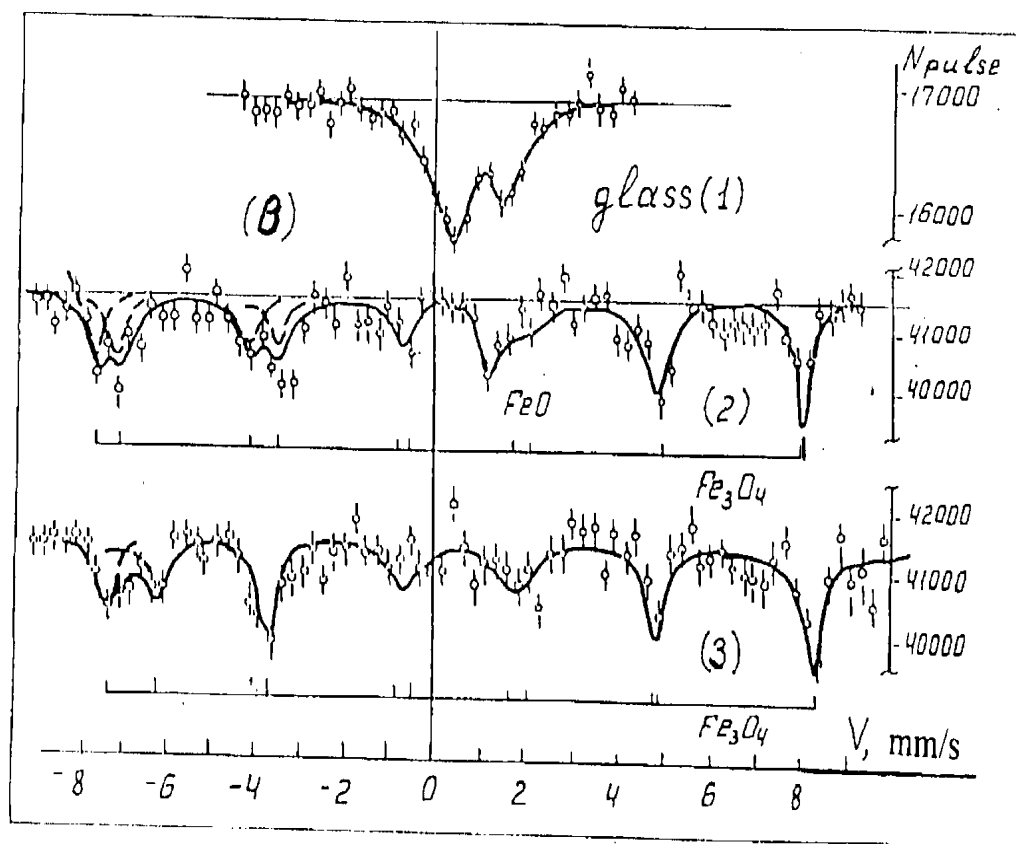1 - Ultra-rapid quenching (glass); 2 - Bar test

Figure 5 - **NGR-spectra of bar and recrystallized tests of a slag B (1,2) and production slag (3):**

1,3-bar tests; 2 – recrystallized test