Structure and Behaviour of Oxide Melts.

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ABSTRACT

Modern understanding of the structure of oxide melts does not satisfy the needs of metallurgical practices and can not be used with necessary authenticity forecasting of mechanism of chemical reactions in liquid media especially at high temperatures. The purpose of the work was to study the behaviour and properties of oxide melts in order to determine the principles of formation of liquid structure and establish the factors influencing the reactionary processes in melts. As the result of the study it was found that under the influence of mechanical vibrations on the slag melt with the composition (%): SiO_2-31.4, Al_2O_3-16.7, iron oxides-23.6, CaO-27.5 were formed 3 layers containing, (%): SiO_2-27.0, 29.1, 28.8; CaO-23.0, 24.0, 22.4; Al_2O_3-22.35, 20.25, 20.4 and oxidized iron-15.2, 16.8, 16.4 correspondingly. Similar results were obtained for a slags with the wide range of compositions, excluding noniron slag with the structure containing phases of pseudo-wollastonite type. As the object of the study we used synthetic oxide melts consisting of SiO_2, Al_2O_3, CaO and FeO. The iron oxide content in slags was 0 - 52.0%.

When magnetic fields were applied perpendicular to the crucible height, the electric conductivity of slags decreased with the increase of the temperature and at 1459°C was 0.07 $Ohm^{-1}\times cm^{-1}$. At the disconnection of the solenoid the electric conductivity increased 12 times. When temperature was decreased from 1489 to 1285°C conductivity of the slag increased and at the further decrease of the temperature it decreased according to the normal laws.

In case of the slag with the composition, (%): SiO_2-42.1, Al_2O_3-18.65, CaO-39.25 slag became conductive under the temperature of 1450°C i.e. after increasing the temperature of the slag by 230°C over the liquidus line. The conductivity temperature coincides with the thermal effect under cooling.

It was also established, that phase transition of the first type does not brake the monotony of the slag conductivity change depending on the temperature.

As the result of the conducted study there was established that:

- coacervation of melts is promoted with the help of combined electromagnetic fields and mechanical vibrations;
- the structure of the melts depends not only on the chemical composition and temperature but also on any other energy factors actively influencing the melts;
- the law introduced by N.I.Usanovich on anomality of electric conductivity in water solutions may be applied to melts;
- spontaneous electric dissociation can not be considered as a principle of formation of structural elements of liquids;
- slags from various processes have a strictly individual structure and properties determined by the structure;
- the behaviour and properties of melts can be described from the point of view of the molecular structure of slags;
- melts have the electron type of conductivity.

INTRODUCTION

Complex chemical composition of the raw materials processed in metallurgy, increasing demands for the environment protection and the increasing cost of energy resources make the improvement of physical-chemical processes in metallurgy extreamly necessary. First of all it applied to a liquid media in the barbotage smelting.

No methods exist for direct determination of structural elements in liquids[1,2] that is why it is impossible to predict the exact mechanism of chemical reactions and the behaviour of the components in technological processes.

The determination of the structure of liquid is mostly based on measurements of viscosity[3,4] and electric conductivity. In some cases the determination of this parameters is considered as a direct proof of the forms of the structural elements of a liquid phase[5,6,7]. Most modern theories of structures of water solutions, melts, etc. are based on the recognition of existence of spontaneous electrolytic dissociation of solid compounds during their transition into liquid state. Thus the abbility "of some substances called electrolytes to dissociate into particles with opposite charges - ions, during the dissolution in certain solvents, for example in water, " is considered as a main proof of electrolytic dissociation theory[9]. Such an approach to the formation of structural elements in a liquid during melting of solid substances or their dissolution in water or other solvents, leads to the consideration that liquid is a continuum sufficiently homogenous in all its mass. This continuum sufficiently providing the transfere of electrical current by movement of charged elements of the structure of liquid. All the continual conceptions of liquid structures are going back to the conception of "physical dissolution"[10,11] and the theory two electricities - positive and negative ones[12].

Development of the experimental base of electrochemistry, introduction of electrochemical technologies and barbotage processes in pyrometallurgy give the basis for the revision of current theories of liquid system formation[8]. The introduction of the conception of "ion conductor" into the scientific practice significantly limited the approaches to predict chemical reactions in liquid media[13], and the development of chemical sources of power has become in fact empirical[14]. The prevailing role of such conception of the formation of liquids was also due to the draw backs of molecular theories: the absence or complete neglection of the problem of transport of electric current through the liquid, the causes of molecular movement in liquids under the energy influence, structural changes in liquids under the combined influence of energy factors[15,16].

We have worked out methods of analysis of structural changes and transport of electric current through the liquid[17-20]. The molecular or quasi-colloidal principle of formation of water solution of non-organic compounds was developed by V.D.Ponomarev in his theory of dissolutional peptization. M.I.Usanovich came to the conclusion that anomalous electric conductivity of liquid is rather a rule than an exclusion. The V.D.Ponomarev's postulate, saying that any real physical-chemical system is macro- and microheterogeneous, became a background for the research, investigating the mechanism of chemical reactions in alkali solutions.

For the melts a number of experimental methods of structure determination are limited. We used the method of inductive concordance[21,22] to combine the results of different analytical and experimental methods. The purpouse of our experimental work was to transform microheterogenities into macroheterogenity and to define the structural transformations under combined energy influence. We compared the changes of viscosity and conductivity caused by molecular motion with phenomena corresponding to the motion of macroobjects in a melt. Having a large number of systematic experimental facts we can established validity of different theories on description of structure of liquids and its formation.

EXPERIMENTAL

The influence of mechanical oscillations on the liquid structure was studied by the application of vibration directly on the melt in vibroviscometer. The oscillations were transferred by a molybdenum rod with 2.5-5.0 mm diameter and the frequency of 56-58 Hz. Weight of the sample was 110-120 g. The temperature interval was 1150-1550°C. Method of the four - probe measurement cell was used for the experiments studying the influence of combined electromagnetic fields on the melt. The four - probe measurement cell for determination of conductivity of melts is a combination of a four probe cell with a solenoid used as source of electromagnetic field and simultaneously as a melt heater (this was a serious drawback of the method limiting measurements in isothermic regime).

The study of macroobject movement and its inversion under the influence of application of the direct pulse current was carried out in correspondence to generally accepted methodics. Oxide melts (by existing concept - electrolytes[6,7]), Table 1, oxi-sulphide melts (combination electrolytes and nonelectrolytes[23]), Table 2, were used as a main subject of research. Water solutions of nonorganic compounds (classical electrolytes[23]) were used for control experiments.

Oxi-sulphide melts are slags of nonferrous metallurgy with low concentration of dissolved sulphides.

The melts were chosen according to the next criteria:

- a possibility to determine the transition of microheterogeneouty into macroheterogeneouty

Table 1. Chemical composition of synthetic oxide melts

Melts	SiO_2	Al_2O_3	Fe tot.	CaO	Fe met	T° C
1	24.73	8.02	52.20	14.80	0.24	1160
2	38.70	10.38	35.92	14.55	0.02	1120
3	41.44	10.48	17.04	32.37	0.32	1250
4	46.38	18.18	10.15	25.26	-	1120
5	44.18	20.23	5.37	29.83	-	1200
6	42.08	18.65	-	39.25	-	1220
7	41.10	14.10	4.78	39.50	-	1175
8	37.70	13.55	12.08	36.80	-	1200
9	31.40	16.70	23.56	27.45	-	1230

Table 2. Chemical composition of industrial melts (slags)

NN	Slag type	SiO_2	Al_2O_3	Fe tot.	CaO	Cu	S
1	Vanyukov	29.60	8.60	51.35	8.40	0.80	0.48
2	Electrical 1	48.57	8.48	11.96	16.20	0.46	0.18
3	Reverberatory 1	42.62	10.27	22.14	8.70	0.55	0.45
4	Reverberatory 2	31.42	7.76	35.28	5.10	0.42	no dt
5	Electrical 2	45.50	11.05	2.60	31.20	0.12	0.12
6	Shaft	31.80	3.60	47.70	7.40	0.45	1.20

Figure 1. Dependence of oxi-sulfide melt viscosity, electrical smelting slag 2, on the time of vibration for diferent temperatures.

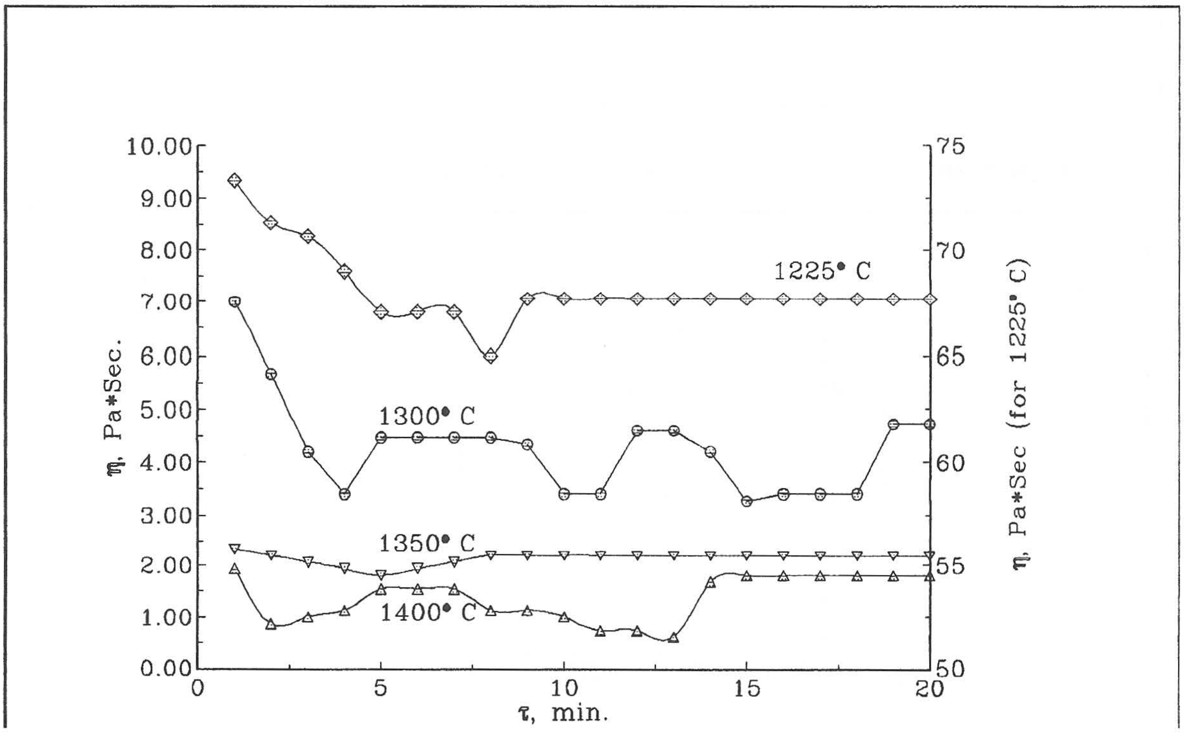


Table 3 Copper content shots and in matrix melts

Slags N (Tab.2)	5	4	3	2	1
C (shots), %	95.2	72.8	64.1	93.1	92.0
C (matrix) %	45-50	35-45	35-45	45-50	45-50

Table 4 Composition of layers of melt 9 obtained under mechanical oscillations at the temperature 1800°C

Crucible cut	SiO_2	CaO	Al_2O_3	Fe
Upper layer	27.00	22.96	22.35	15.20
Middle layer	29.08	24.00	20.25	16.83
Bottom layer	28.84	22.40	22.41	16.40

Figure 2a Thermogravitogramm of slag 6

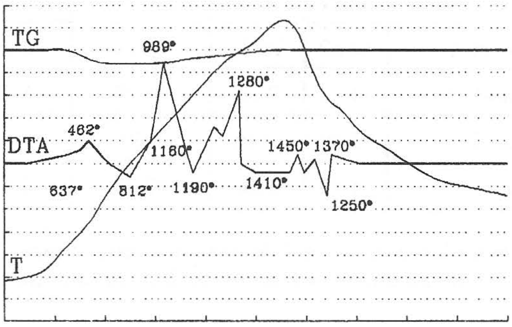
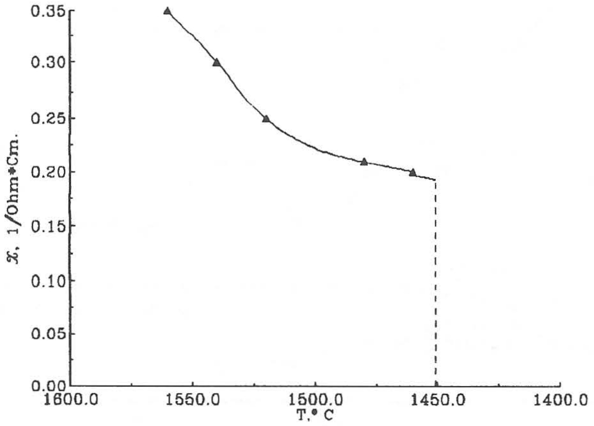


Figure 2b Dependence of electroconductivity of slag 6 on temperature



- a possibility (despite the structural changes during phase transitions) to determine with a certain degree of validity phase composition in the liquid by the solid sample;
- a possibility to compare the behaviour of electrolytes (oxide melts) and nonelectrolytes (sulphide melts).

Measurement of the viscosity and the influence of mechanical oscillations on the structural changes in a melt were carried out in polythermal and isothermal regimes, Figure 1. It is obvious that viscosity measurements became stable with the connection to structural changes in the melt, Figure 2, with various influence of temperature on alignment viscosity values. This may be attributed to the structural changes in accordance with the phase diagram. It is clear that the viscosity change depends on enrichment of the upper layer of melt with sulphides or with oxides, which have a low melting point and that slag 3 has the most stable structure. The influence of mechanical oscillations on copper content depending on section position in a crucible (the cooled melt was divided into three equal parts perpendicular to the height of the crucible) is shown on Figure 3 for slags 1 and 2. It appears that the structural properties of slag have a strong influence on the impoverishment of slags under superposition of mechanical oscillations to the melt, which explains the difficulties discovered by Dergachev[24] during the addition of reductant to the melt.

It was found that mechanical oscillations applied directly to the melt cause separation by liquation of the slag itself, and also separation of the sulphide components dissolved in slag. A part of sulphides floated on the melt surface for a long time despite the fact that diameter of the shots was 6-8 mm and copper content in them up to 93.1%. The other part of sulphides settled on the bottom of the crucible, Table 3.

Most of the obtained data show that the nature and the degree of oxide-sulphide melt liquation are correlated with the changes of the molecular composition of melts depending on temperature.

All the melts were subjected to the influence of combined electro-magnetic fields. The results of this experiments were evaluated by the melt conductivity and the analysis of the solid slag structure.

It is shown[21,22] that the change of alternating electromagnetic fields was leading to the change in conductivity of synthetic oxide melts, Figure 1. It can be seen that for the slag 9 the variations in conductivity under the influence of magnetic field are connected to structural transition under the temperature above 1450°C that also shows under normal conditions. The most interesting anomalies of conductivity of oxide melts were discovered at the moments of solenoid disconnection and cooling the melts. Thus for slag 7, Table 1, under the influence of magnetic field and temperature 1526°C conductivity was 0.031 $Ohm^{-1}\times cm^{-1}$. When the current is switched off the conductivity increases abruptly up to 3.42 $Ohm^{-1}\times cm^{-1}$. For slag 8 the similar change under 1570°C was from 0.048 to 0.132 $Ohm^{-1}\times cm^{-1}$; for the slag 9 from 0.07 to 0.095 $Ohm^{-1}\times cm^{-1}$ under 1459°C.

We observed subsequent decrease and increase of conductivity for slag 8 - after conductivity decreased it began to increase again at the proximity of slag melting point and continued till 1148°C (i.e. 50°C below melting temperature), Table 5.

After the superposition of combined electromagnetic fields on the melts, the first-kind phase transition did not change the monotony decrease of conductivity during temperature decrease for slags 1,7-9. A similar phenomenon was observed for the high ferrous nontreated melts. The measurements for slag 6 under usual conditions showed that melting does not lead to conductivity appearance and the beginning of conductivity coincided with the thermal effect under 1450°C, Figure 2, during cooling. Similar pattern was obtained for the sulphide component of slag 3, Table 2, when the retrograde dissociation with formation of liquid metallic copper was accompanied with a conductivity jump of already cooled slag , Table 6.

Table 5. Electroconductivity of slag 8 depends on temperature under cooling

T , °C	1570	1500	1410	1293	1231	1210	1182	1164
χ, $Ohm^{-1}\times cm^{-1}$	0.13	0.11	0.10	0.095	0.095	0.11	0.17	0.26
T, °C	-	1148	1133	1120	1110	1095	1085	1062
χ, $Ohm^{-1}\times cm^{-1}$	-	0.860	0.29	0.11	0.05	0.03	0.02	0.0

Table 6. Behaviour of conductivity and temperature of slag 3 in time under cooling

τ,min	30	45	0	75	90	105	120	135
T,°C	1075	1055	1050	1050	1025	1010	1000	980
χ, $Ohm^{-1}.cm^{-1}$	0.2	0.21	0.23	0.33	0.48	0.48	1.7	0

Figure 3. Dependence of conductivity of slag 2 on temperature.

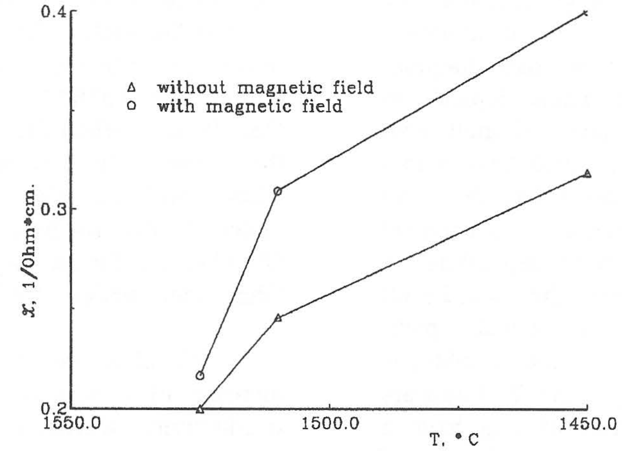


Figure 4. The strength of the current through slag 3, Table 1, during the movement of sulphidedroplet depending on duration of the process.

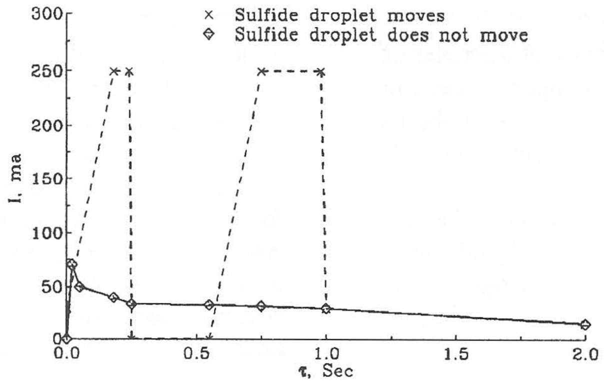


Table 7 gives the changes in conductivity of slag 6 under the influence of magnetic field and cooling during 81 minutes with the following heating during 20 minutes. A similar pattern was observed for all the slags, as an example slag 2 is shown on Figure 3.

Combined variable magnetic fields caused the transition of the melt microinhomogeneities into macroinhomogeneities with following coacervation of the liquid, Table 8.

The investigations of transition of miroinhomogeneities of the liquid into macroinhomogeneities showed that the movement of micro- and macroparticles in a liquid is of the similar nature. This was confirmed by our experiments on movement of sulphide inclusions in an oxide melt under the influence of direct current, Figure 4. Significant increase of current strength at the moment of switching on is explained by the triboelectric effect during movement of a sulphide droplet in an oxide melt (sedimentation effect) and interaction of the gaseous phase with the oxide melt. If sulphide melt was not present in a liquid the reaction of carbon oxide with the oxide melt led to the increase of current strength from 180 mA to 1.5 A, vacuum formation in the system and dissociation of the melt into less complicated oxide components with a loss of the slag melting capacity. Substituting the sulphide droplet with a graphite disk we got similar results which gives the right for revision of theoretical postulates on the nature of movement of liquid in liquid under the influence of direct current[24]. It was found that direct current may dissociate a liquid into less complicated components, and the pulse current is more effective than the constant one.

Table 7Variations in slag conductivity for slag 6, Table 2, depending on the duration and temperature of the process.

τ, min.	1	3	4	6	9	81	99	100
T, °C	1475	1325	1200	1050	900	825	1325	1400
χ,Ohm^{-1} ×cm^{-1}	1	1.14	1.14	0.43	0	0	0	0.11

Table 8.Composition of the melt (%) in interelectrode space (IS) and in the total mass of the melt (TM).

Slag and place of sampling	SiO_2	Al_2O_3	Fe tot.	CaO
Slag 2 (IS)	35.00	23.20	22.27	11.30
Slag 2 (TM)	28.64	33.15	19.80	10.20
Slag 1 (IS)	22.78	13.74	36.20	14.17
Slag 1 (TM)	22.70	15.07	35.70	12.90
Slag 9 (IS)	30.30	20.70	17.30	25.80
Slag 9 (TM)	22.96	36.30	13.00	20.80

DISCUSSION

Superposition of mechanical oscillations and variable electromagnetic fields on oxide and oxi-sulphide melts makes possible, under certain conditions, to detect microinhomogeneities in liquids and transfer them into macroinhomogeneities. Adequacy of the influence of varies types of energy on liquids as well as melts allows to consider the nature of liquids as molecular. A possibility to control conductivity of liquid with the help of combined electromagnetic fields speaks in favour of electron type of conductivity in liquid systems.

There is no need to use spontaneous electrolytic dissociation for explanation of electric current transport through liquid and explanation of principles of liquid formation. The anomalies in separation of oxi-sulphide systems with application of mechanical oscillations, Figure 2, Tables 3 and 4, are explained by formation of molecular combinations in a liquid (including copper oxi-sulphides) in correspondence with a phase diagrams of chemical systems.

Anomalies in a conductivity values for oxide melts and cooled slags are explained with molecular movement in liquids (sedimentation and electrophoretic effects) and electrical phenomena accompanying crystallisation - retrograde dissociation of solid compounds and recrystallisation, Tables 7 and 8. The conclusion concerning the absence of spontaneous electrolytic dissociation in transition of solids into liquid state is confirmed by monotones decrease of conductivity with the temperature decrease in first-kind phase transition which means a similar nature of conductivity in solid and liquid media, and also by a capacity of liquids to conduct electric current during structural changes in the melt, Figure 2.

Constant and pulse current cause movement of solid and liquid inclusions in oxide melts. The movement of the objects causing in its turn an increase of the strength of the current through the liquid, Figure 4. This makes it necessary to take into account molecular movement when accumulators and chemical sources of power are developed.

Recognition of the molecular nature of liquids (absence of spontaneous electrolytical dissociation and electron type of conductivity in liquids) and discovery of anomaly strong current appearing in chalcogenide systems during chemical and phase transitions call for a new approach in understanding of electrolyte formation and development of chemical and thermochemical sources of power. The investigation of transport properties of liquids and a better understanding of the mechanism and thermodynamical properties of interatomic and intermolecular chemical reactions are becoming the matter of special importance.

CONCLUSIONS

It was found that:

- coacervation of melts is promoted with the help of combined electromagnetic fields and mechanical vibrations;
- the structure of the melts depends not only on the chemical composition and temperature but also on any other energy factors actively influencing the melts;
- the law introduced by N.I.Usanovich on anomality of electric conductivity in water solutions may be applied to melts;
- spontaneous electric dissociation can not be considered as a principle of formation of structural elements of liquids;
- slags from various processes have a strictly individual structure and properties determined by the structure;
- the behaviour and properties of melts can be described from the point of view of the molecular structure of slags;
- melts have the electron type of conductivity.

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