Viscosity and Constitution of Slags Associated With Metallorthermic Extraction of Some Less Common Metals

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CONTENTS

	Page		Page
ABSTRACT	58	2. VISCOSITY MEASUREMENT OF	
INTRODUCTION	58	SOME INDUSTRIAL SLAGS	68
1. STRUCTURE AND VISCOSITY OF		2.1. Blast Furnace Slags	68
SILICATE MELTS	58	2.2. Blast Furnace Slags with	
1.1. Flow in Molten Silica	59	Titanium Oxides	68
1.2. Flow in Binary Melts	59	2.3. High Titania Slags	69
1.3. Interrelation between		3. THERMOPHYSICAL PROPERTIES	
Conductance and Viscosity	62	OF ALUMINO-THERMIC SLAGS	69
1.4. Polycomponent Melts	62	3.1. Liquidus Temperature of	
1.5. Role of Ionic Interaction on		Alumina Based Melts	69
Viscosity	62	3.2. Role of CaF ₂ in Alumino-	
1.6. Complex Melts	63	thermic Slags	70
1.7. Calcium Fluoride Addition to		3.3. Viscosity of Aluminothermic	
Silicate Melts	66	Slags	70
1.8. Role of Other Constituents	67	3.3.1. Ferrotitanium Slag	71
1.8.1. Slags with Iron Oxides	67	3.3.2. Low Carbon Ferrochrome Slag	72
1.8.2. Slags with Barium Oxide	67	3.3.3. Ferrosilicozirconium Slag	72
1.8.3. Minor Constituents	67	3.3.4. Ferroniobium Slag	72
1.9. Effect of Temperature on		CONCLUSIONS	73
Viscosity	68	REFERENCES	73

ABSTRACT

Slags resulting from aluminothermic reduction of oxides for production of less common metals and their ferroalloys contain a high percentage of alumina and have a high melting point as well as being highly viscous. Alumina exhibits both covalent and ionic bonding under different conditions. It is expected that high alumina slags may behave like silicate melts that contain silica having a covalent bond. Consequently, an exhaustive review on structural aspects of silicate melts, their viscosity, activation energy of viscous flow, conductance, etc., has first been made. The role of fluorides and other constituents on the viscosity of silicate melts has also been discussed. Some investigation results on viscosity measurement of some industrial blast furnace slags with and without titanium oxides and high titania slags have been presented to appreciate the structure of silicate melts. Review of relevant literature on the liquidus temperature and role of calcium fluoride on the thermo-physical properties of alumina-based melts has been made. Finally, the meagre information available on slag viscosity of some aluminothermic slags such as those of FeTi, FeCr, FeSiZr, and FeNb has been furnished.

INTRODUCTION

The viscosity of metallurgical slags has an important influence on furnace operation. Viscosity helps to govern the reaction rates by its effect on diffusion of ions through the liquid slag to and from the metal/slag interface. Where the metal droplets have to trickle through the slag, a high viscosity slag would increase their residence time in the slag bath. The useful effect of this action is that it provides a longer time for chemical exchanges to occur between the two media, but where slag-metal separation is the sole aim, a slag of high viscosity has to be avoided. Especially in metallothermic processes, viscosity has a substantial effect on the speed and completeness of reduction reactions and also on the rate at which the metal droplets sink through the liquid slag layer. The transfer of heat between the slag and metal is also affected by the viscosity of the slag. For example, in a liquid of low viscosity, heat transfer by convection is rapid. Further, a low viscosity slag facilitates the escape of gases from the solidified metal in the case of electroslag refining processes.

On the other hand, the refractory is not damaged very much by a high viscosity slag.

Apart from the above, knowledge of variation of viscosity with composition and temperature helps in predicting the structure of liquid slags.

Many investigations have been carried out over the past 50 years on the viscosity of silicate slags with varying composition, and the structure of the melts have been predicted from these studies. Similarly, viscosity studies of blast furnace slag, steelmaking slag, high titania slag, etc. have provided useful information on the compositional adjustments of the respective slags needed to obtain the best metallurgical results. Relatively little has been done on the viscosity of high alumina slags resulting from aluminothermic reduction of metal oxides. The authors, before commencing with a detailed study of the viscosity and liquidus temperature of aluminothermic slags, thoroughly reviewed the literature on viscosity of slags in general and the liquidus temperature of the relevant melts. Some of the related literature is summarized here.

1. STRUCTURE AND VISCOSITY OF SILICATE MELTS

Adequate literature is available on viscosity studies of binary, ternary, and quaternary oxide systems with silica and lime as the main components and alumina and magnesia as additional constituents. Determination of viscosity (μ) and activation energy of viscous flow (E_μ) through these investigations has helped in predicting the structure of the slags. Hence we first present a brief discussion on the nature of viscous flow.

Experimental determinations of electrical conductivity /1/, electron transport /2/, viscosity /3/, and expansivity /4/ have established that molten oxide slags are ionic in nature like halide melts but have very high viscosity and high activation energy of viscous flow in comparison to halides. (The μ and E_μ of halides range from 0.5-5 cps and 6-10 kcal/mole at temperatures much above the liquidus /5/.) The type, size, and structure of the various ions present in the slag melt have a direct effect on slag viscosity because viscosity is determined by the more slowly moving anions (i.e., large ions). On the other hand, the structure and size of these ions depend on the type of constituents present in the slag. In general, covalent oxides when molten are very viscous, unlike molten ionic oxides, and hence the relative

proportion of these two types of oxides will decide the value of viscosity.

1.1. Flow in Molten Silica

In the case of pure molten silica the building units are SiO_4 tetrahedra where each silicon ion is tetrahedrally coordinated with four oxygen ions while each oxygen ion is linked to two Si^{4+} ions leading to a three-dimensional network. Much of the three-dimensional bonding present in the solid silica is retained, although there may be a change from long- to short-range ordering during melting. This gives low conductance, high viscosity, and high value for activation energy of viscous flow. The high value of E_μ of molten silica (135 kcal/mole /6/) suggests that the movement of flow units involves the breaking of Si-O bonds.

1.2. Flow in Binary Melts

When a basic metal oxide is added, each added oxygen ion enters the network and separates the corners of the two tetrahedra while the added cation remains adjacent to the negative charges, as shown in eqs. 1(a) and 1(b).

Thus the oxygen bridges between the groups are broken, the driving force for this breakdown process being the attraction between the cation and the unshared oxygen (or singly bonded oxygen). The degree of breakdown depends on the type and amount of metal oxide added. It is observed that while bivalent metal cations tend to link the network by bridging two oxygens, monovalent ones do not /3/. It is generally agreed that breaking down the structure results in smaller and smaller silicate groups and that viscosity is lowered. It is believed that the cations are randomly distributed throughout the lattice, their presence giving rise to two general effects /3/: (1) weak points are introduced into the silica network by the rupture of Si-O bonds; and (2) the Si-O bonds near the metal ion are weakened due to the polarizing effect of the cation, so that a general loosening effect in the lattice occurs. This is

illustrated in the simplified two-dimensional representation in Fig. 1.

Fig. 1: Mechanism of collapse of silicate lattice.

The viscosity of silicates decreases with rising temperature and is represented by

$$\mu = A e^{E_\mu/RT} \quad (2)$$

Hence the plots of $\log \mu$ vs $1/T$ are reasonably linear with some minor exceptions. For example, in silicates with more than 41% CaO, the slope decreases with rising temperature and is less above 1700°C than below it. It may be mentioned here that a linear relationship of $\log \mu$ vs $1/T$ means E_μ is constant, i.e., degree of polymerization is constant over the range of temperature. If the degree of polymerization changes, there will be a continuous change of liquid structure with temperature and the plot will give a curved line. When a sudden change of liquid structure occurs, a break in the straight line relationship is obtained.

Viscosity measurement of binary silicate melts /3,6/ have yielded the values of E_μ , and a plot of this E_μ against percentage of metal oxide shows that E_μ falls rapidly from 135 kcal/mole for pure silica to 20-40 kcal/mole as the network is broken down. The activation energy of viscous flow is related to the energy required to move one silicate group, or a major part thereof, with respect to the other. When the silicate groups become smaller, the number of associated negative charges become less. Thus the number of ionic bonds which have to be broken or distorted to enable the group to move becomes less and, therefore, one expects the value of E_μ to decrease. In the case of silicates, it is seen that some

10-12 mole percent of alkali metal oxide and 15-20 mole percent of alkaline earth oxide are sufficient to bring down the value of E_μ from 135 to 40 kcal/mole, and, thereafter, the rate of decrease becomes much smaller.

The effects of monovalent and divalent metal oxides are different because at equimolar compositions there will be twice as many monovalent cations as divalent ones, and the divalent cations tend to maintain the continuous bonding of the lattice by bridging oxygen atoms, as mentioned earlier. Hence, by addition of group II metal oxides, the decrease of E_μ will be more gradual, i.e., the collapse of the silica framework will only occur when comparatively more metal oxides have been added. In the case of Group II metal oxide systems, E_μ is independent of the cationic species at all compositions up to 55 mole percent of metal oxide, whereas for Group I systems, this is only true up to about 35 mole percent. This smaller composition range is attributed to steric effects due to the larger number of monovalent cations present at higher concentrations of metal oxide. Moreover, E_μ for alkali silicates is lower than those of alkaline earth silicates.

From an expansivity study of alkali metal silicates, Bockris *et al.* /4/ calculated the number of broken bridges and inferred that an addition of up to 12 mole percent of alkali metal oxide results in a random breakdown of this silicate network so that three-dimensional bonding still exists almost throughout the melt. It is proposed that, within this composition, the cations are held in cages as shown in Fig. 2. The abrupt change of expansivity (an increase by approximately a factor of 83) and activation energy of viscous flow at 12 mole percent alkali metal oxide addition indicates that there is a change in silicate structure in this region. At higher concentrations the network breaks down more or less completely to give discrete globular anions of the type shown in Fig. 3.

Fig. 2: The two dimensional silicate cages

Fig. 3: Globular anions existing in silicate melts

From the measurement of various physical properties of silicate melts, different structural models have been proposed to explain the change of properties with change of composition. The chain formation concept and the discrete anion model proposed by Bockris and coworkers /3,4,6/ is the most successful structural model for the silicate melts. According to this model, at the orthosilicate composition (66 mole percent of CaO), the melt is considered to consist of SiO_4^{4-} tetrahedra. Addition of silica to this composition results in polymerization of these tetrahedra to give chains, the lengths of which increase with rising silica content. The empirical formulae of the anions in the range of Si/O ratio of 0.25:0.333 are presented in Table 1. The chain formation concept holds satisfactory from 66 mole percent of molar oxide (MO) to 50 mole percent.

TABLE 1
EMPIRICAL FORMULAE OF ANIONS /6/

Si/O	Percent molar oxide	Empirical formulae
0.250	66	SiO_4^{4-}
0.286	60	$\text{Si}_2\text{O}_7^{6-}$
0.300	57	$\text{Si}_3\text{O}_{10}^{8-}$
0.307	55	$\text{Si}_4\text{O}_{13}^{10-}$
0.312	54	$\text{Si}_5\text{O}_{16}^{12-}$
0.322	52	$\text{Si}_{10}\text{O}_{31}^{22-}$
0.333	50	$\text{Si}_n\text{O}_{2n}^{2n-}$

However, from the activation energy measurement at 50 mole percent CaO, it was established that the planar rings of the type $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_4\text{O}_{12}^{8-}$ (Fig. 3) are present at this composition. Further increase in silica causes polymerization of these rings and bigger anions of the general formula $\text{Si}_n\text{O}_{n+3}^{6-}$ or $\text{Si}_n\text{O}_{2n+4}^{8-}$ may result. Out of these, $\text{Si}_n\text{O}_{2n+3}^{6-}$ is preferable /3/, as the Si-O-Si bond angle at this ionic species is constantly 135° . The discrete anions, which increase gradually in size and do not change in type, are formed by further addition of SiO_2 such as

and so on.

The idealized $\text{Si}_6\text{O}_{15}^{6-}$ ion present at 33 mole percent MO and essentially formed by the linking of two $\text{Si}_3\text{O}_9^{6-}$ rings is shown in Fig. 4 /7/. The ions postulated at compositions between 10-50 mole percent of MO are given in Table 2.

Fig. 4: Idealised Si_6O_{15} ion of 33 mole percent metal oxide.

TABLE 2
ANIONS PRESENT BETWEEN 10-50 MOLE
PERCENT METAL OXIDE /3/

Composition	Molar percent MO	Discrete Ion	Chain length A°
$\text{SiO}_2 + \text{MO}$	50	$\text{Si}_3\text{O}_9^{6-}$	-
$2\text{SiO}_2 + \text{MO}$	33	$\text{Si}_6\text{O}_{15}^{6-}$	6
$3\text{SiO}_2 + \text{MO}$	25	$\text{Si}_9\text{O}_{21}^{6-}$	9
$4\text{SiO}_2 + \text{MO}$	20	$\text{Si}_{12}\text{O}_{27}^{6-}$	12
$5\text{SiO}_2 + \text{MO}$	16.7	$\text{Si}_{15}\text{O}_{33}^{6-}$	15
$6\text{SiO}_2 + \text{MO}$	14.3	$\text{Si}_{18}\text{O}_{39}^{6-}$	18
$7\text{SiO}_2 + \text{MO}$	12.5	$\text{Si}_{21}\text{O}_{45}^{6-}$	21
$8\text{SiO}_2 + \text{MO}$	11.1	$\text{Si}_{24}\text{O}_{51}^{6-}$	23

Thus, addition of SiO_2 to 50 mole percent MO- SiO_2 permits the formation of discrete flow units without severing Si-O bonds, as evidenced from the small increase of E_μ up to 88 mole percent SiO_2 ; thereafter, there is a sudden increase of E_μ due to the instability of the discrete anions. It is suggested by Callow /8/ that cations of the first 12% MO are accommodated within the interstices of the three-dimensional silica network, any further addition producing a break-up into complex anions.

In an actual melt an equilibrium mixture of two or more discrete anions may be present. Toop and Samis /9,10/ have suggested methods to find out the most probable number of silicate anions and also O^{2-} ions. According to their theory, whenever two silicate anions polymerize, the resultant reaction is:

where O^- is the singly bonded oxygen, O° is the doubly bonded ion, and O^{2-} is the free oxygen ion. On the other hand, whenever there is a breakdown into simple anions, the resultant reaction is:

The equilibrium constant K for eq. (4) is given by

$$K = \frac{(\text{O}^\circ)(\text{O}^{2-})}{(\text{O}^-)^2} \quad (6)$$

and is a function of temperature and composition of the melt. Considering various factors such as valency of silicate anions and their stability with respect to size, they have given a curve which describes a relationship between the number of silicon ions per

average anionic species and proportion of singly bonded oxygens ($O^{\cdot}/O^{\circ} + O^{\cdot} + Si^{4+}$). With the help of this plot the probable number of silicate anions can be established, and consequently the structure of the melt can be defined.

1.3. Interrelation between Conductance and Viscosity

The binary liquid silicate structure has also been predicted from conductance measurements of melts /1/. The Rasch-Hinrichsen law

$$K = A_e^{-E_k}/RT \quad (7)$$

is obeyed for the system. The conductance is found to rise, and the energy of activation for conductance (E_k) is found to fall with increasing metal oxide content. The electrical conductance is ionic, the current being carried predominantly by metal cations. This is in agreement with the fact that conductance increases with an increase in metal oxide content and reaches a peak with oxides of monovalent metals of small ionic radius. A comparison of E_k and E_μ for the binary systems of both alkali and alkaline earth oxides shows that E_μ is always much greater than E_k , demonstrating that μ is determined by the movement of the large anionic silicate groups whereas conductance is related to the motion of the cations. Addition of metal oxide has a network breaking effect and, consequently, there is an increase in mobility of cations through the broken structure. Bockris *et al.* /1/ used the ion-oxygen attraction model to interpret their results. They found that cations with a high ion oxygen attraction ($I > 1.6$) tend to seize oxygen ions and hold them in a particular type of packing dependent upon cation size; hence such cations, for example, Si^{4+} , Al^{3+} , Ti^{4+} , are termed 'network formers'. Ions of low ion-oxygen attraction ($I < 0.7$) are unable to build a network and are called 'network modifiers'. These include the alkali and the alkaline earth metal cations, with the exception of Mg^{2+} , which has a partial network forming tendency.

1.4. Polycomponent Melts

Mackenzie /11/ took viscosity measurements on ternary liquid silicate systems with silica and two metallic oxides (two alkali oxide or one alkali and one alkaline earth oxide) over the temperature range 900-1400°C and reported that the linear relationship between $\log \mu$ and $1/T$ still holds. The activation energy of viscous flow was found to vary between

36-43 kcal/mole. It was inferred that the mechanism of flow in binary melt containing one cation of a particular group should be identical to any polycomponent liquid silicate with two or more cations of the same group, provided that the total molar concentrations of metal oxides are equal. Similarly, a ternary melt containing cations of different groups may be viewed as an ideal mixture of two binary melts. On this basis the activation energy of viscous flow can be determined from the relationship

$$E_\mu = n_A (E_A)_x + n_B (E_B)_x \quad (8)$$

where n_A and n_B are the mole fractions of the two metal oxides, and $(E_A)_x$ and $(E_B)_x$ are activation energies for the two groups at the total metal oxide concentrations, respectively. He found good agreement between the calculated values according to eq. (8) and the observed values of the polycomponent systems considered. From this he concluded that the discrete ion theory based on binary systems is applicable to polycomponent melts and that the mechanism of flow is identical at the same molar concentrations of silica. He also suggested an empirical relationship to calculate the viscosity for each group,

$$\log \mu = (\alpha + \beta C) + \frac{\gamma + \delta C}{2.303 RT} \quad (9)$$

where α , β , γ and δ are constants and C is the total molar concentration of metal oxides. The values of these constants for Group I and Group II metal oxides were determined. Eq. (10) was then used to calculate the viscosity of the polycomponent system:

$$\mu = n_A (\mu_A)_C + n_B (\mu_B)_C \quad (10)$$

Here also he found good agreement between calculated and experimental values.

1.5. Role of Ionic Interaction on Viscosity

Based on a reaction rate phenomenon, the expression for viscosity is given as /6,12/:

$$\mu = \frac{Nh}{V} e^{\frac{-\Delta S^*}{R}} e^{\frac{\Delta H^*}{RT}} \quad (11)$$

where N is Avogadro's number, V is molar volume of flow units (chains or discrete anions), h is Planck's constant, ΔS^* is the entropy of activation, and ΔH^* is the heat of activation (same as activation energy for viscous flow).

ΔH^* depends on the size of the average flow unit and the strength and number of various coulombic interactions between the flow unit and its surrounding species.

ΔH^* rises with an increase in flow unit size. The importance of coulombic interactions in binary silicate melts may be the attraction between the singly bonded oxygens of the flow units and free metallic ions ($M^{++} - O^-$ interaction) and the repulsion between two singly bonded oxygens of different flow units ($O^- - O^-$ interaction). ΔH^* increases with a higher number of attractions and a lower number of repulsions. These interactions also affect the values of ΔS^* which rises with an increasing number of attractions and decreasing number of repulsions.

As the metal oxide percentage is increased, smaller flow units form, and therefore the molar volume decreases. Calculations based on actual viscosity measurement have shown that ΔH^* and S^* also decrease with an increase in metal oxide contents. A decrease in ΔS^* suggests that $O^- - O^-$ interactions tend to be more dominating than $M^{++} - O^-$ interactions. A decrease in ΔH^* is probably caused by the joint effect of a decrease in flow unit size and increased effectiveness of $O^- - O^-$ interaction. From eq. (11) it is apparent that variation in ΔS^* and V tend to counteract the effect due to variation in ΔH^* . However, since the viscosity continuously falls with increasing addition of metal oxide, it is obvious that the latter effect is always more dominant than the other two. It is important to note here that, because of relatively higher and higher oxygen requirements of the smaller flow units, the progressive additions of metal oxide are increasingly less effective in reducing the flow unit size. This explains why with increasing metal oxide percent, viscosity is lowered at an ever-decreasing rate.

The contribution of different oxides in reducing the viscosity can be discussed in light of the above phenomenon. Due to the bridging effect of alkaline earth cations, the $O^- - O^-$ interaction is not as effective as in alkali metal cations. Hence, addition of a given amount of alkali metal oxide results in a greater reduction in viscosity than occurs for an alkaline earth addition of the same amount.

1.6. Complex Melts

Most industrial silicate slags contain alumina, magnesia, and calcium fluoride as well as lime and silica. Hence the way in which these substances enter into silicate melts is of interest.

When alumina is present in the melt, it is considered that Al^{3+} adopts a four-fold coordination with oxygen and substitutes for silicon in the linked tetrahedral structure /13,14/, provided that the cation/anion ratio is also adjusted in order to preserve electroneutrality. This is possible when the molar ratio of Al_2O_3/CaO is less than one, i.e., sufficient basic oxide is present in the melt. In such cases the melt contains SiO_4^{4-} and AlO_4^{5-} ions. When this ratio exceeds one, there will not be sufficient oxygen for the formation of AlO_4^{5-} tetrahedra together with the tetrahedral silicate anionic units, and hence aluminium in these melts will have six-fold coordination with oxygen and will enter the interstices in the structure /15/. This will contribute to the disintegration of complex aluminosilicate anions. Machin and Hanna /14/ have suggested that when the basic oxides present are less than enough to furnish the required oxygen, polymeric ions such as those given below are formed:

The probability of a high percentage of these polymeric ions would be raised by increasing percentage of alumina and/or silica and lowered by increasing percentage of lime and/or magnesia. They have given a relationship to calculate the degree of polymerization or the ratio of shared to unshared oxygen atoms, R . This is expressed as:

$$R = (4-N) / 2(N-2) \quad (12)$$

where N is the oxygen/silicon ratio (O/Si ratio is the number of oxygen atoms/the number of silicon or aluminium atoms present in the flow unit; Al atoms can be counted as equivalent to silicon atoms).

From the viscosity study of the system $CaO-SiO_2-Al_2O_3$ within the temperature range of $1450-2000^\circ C$, Kozakevitch /13/ found that some of the isokoms (lines of equal viscosity) for the above melts reach minima when the molar ratio Al_2O_3/CaO is about 1; i.e., for a given silica concentration viscosity increases as CaO is replaced by Al_2O_3 until the molar ratio Al_2O_3/CaO is about 1. Above this ratio an increase in alumina content decreases the viscosity. So when the molar ratio $Al_2O_3/CaO < 1$, i.e., in neutral and basic slags, alumina and silica behave similarly. In other words under such conditions the tetrahedral $Al-O$ coordination is isomorphous to that of $Si-O$ coordination.

Fig. 5: Discrete anions in liquid alumina silicates

dination, i.e., Al and Si will occupy similar sites in the lattice so that the total network forming ions will be Al + Si. However, at high molar Al_2O_3/CaO ratios and high silica concentrations, Al_2O_3 behaves as a network modifier and hence decreases the viscosity. This is consistent with the generally accepted view that alumina is amphoteric, acting as a base in acid melts and as an acid in basic melts.

Seshadri and Gupta /16/ have, however, proposed an alternative model for aluminosilicates. By comparing the viscosity data for the binary $CaO-SiO_2$ system and the ternary $CaO-SiO_2-Al_2O_3$ system on the basis of average anion size and charge, they have demonstrated that the four-fold coordination model for Al^{3+} does not satisfactorily explain the viscosity results. In the new model proposed, aluminium, having a valency of three, is considered to be bonded to only three oxygens, as illustrated in Fig. 5. This predicts a variable coordination number of Al^{3+} in the melt because a high level of disorder persists in the liquid state (i.e., different Al^{3+} ions may have different coordination numbers depending on the neighbours present). This is strongly supported by Al-nuclear resonance studies made on $CaO-SiO_2-Al_2O_3$ glasses /17/ which indicate that the oxygen coordination sphere of the aluminium is more or less statistically distorted. This should not have been the case in four-fold coordination of aluminium where it is completely shielded by four surrounding oxygens. Based on this it is suggested by Gupta and Seshadri /12/ that in aluminosilicate melts $Al^{3+}-O^-$ type of

interactions are also present besides $Ca^{++}-O^-$ and $O^- - O^-$ interactions. This interaction will increase the activation energy of viscous flow. Depending on the Al_2O_3/SiO_2 ratio, i.e., the Al/Al + Si ratio, the proportion of $Al^{3+}-O^-$ interaction will vary from melt to melt; hence flow unit size alone cannot be taken as a measure of viscosity. It follows that the variation of viscosity in aluminosilicate melts may be described as: (1) for constant average flow unit mass, viscosity should rise with the increase in Al/Al+Si ratio, and, consequently, (2) for the same Al/Al+Si ratio, viscosity should rise with the increase in average flow unit mass.

Turkdogan and Bills /18/ have suggested an empirical formula to find the silica equivalence of alumina at high Al_2O_3/CaO ratios and high silica concentrations from the viscosity data of $CaO-SiO_2$ and $CaO-SiO_2-Al_2O_3$ melts. For a given temperature and viscosity the silica equivalence of alumina(Na) is given by the difference between silica concentration of binary and ternary melts:

$$Na = N_{SiO_2} \text{ (binary)} - N_{SiO_2} \text{ (ternary)} \quad (13)$$

The calculated values of Na from the viscosity data of Bockris and Lowe /6/ and Kozakevitch /13/ were plotted and are reproduced in Fig. 6. It can be seen from the figure that Na is related to the molar ratio Al_2O_3/CaO and alumina concentration within the composition range studied by Kozakevitch. It should

Fig. 6: Silica equivalence of alumina, Na, related to molar Al_2O_3/CaO ratio and molar alumina concentration in $CaO-SiO_2-Al_2O_3$ melts.

be further noted that the relationship is independent of temperature within the range 1500-1800°C. The curve shown by the dotted line corresponds to the binary $\text{CaO-Al}_2\text{O}_3$ system. A more usable form of this diagram is shown in Fig. 7, where mole fraction of alumina is plotted against N_a for several molar $\text{Al}_2\text{O}_3/\text{CaO}$ ratios.

The slags of more practical interest are $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ type quaternary slags. Machin, Hanna, and Yee were the pioneer workers to systematically measure the viscosity of these systems over a wide range of compositions in platinum crucibles /14,19-21/. They plotted the isokoms at temperatures of 1350, 1400, 1450 and 1500°C and observed that some of the isokoms were approximately parallel to the lines along which the acid/base ratios (moles of SiO_2 + moles of Al_2O_3 / moles of CaO + moles of MgO) are constant, especially so in the

Fig. 7: Silica equivalence of alumina related to molar alumina concentrations and molar $\text{Al}_2\text{O}_3/\text{CaO}$ ratio in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ melts.

system with 40% SiO_2 . The S-shaped isokoms show minimum change of viscosity with variation of alumina content near the ends. In the region of 60% or more silica, alumina appears to be less effective in increasing the viscosity. This is also the case in slags with 40% or less silica content. In the area between these limits the effect of alumina on the viscosity of the melt is nearly as great as that of silica. It was also observed by them that the viscosity at constant lime content decreases with increasing magnesia content at constant silica content. When both silica and

alumina remain constant, the rise of magnesia decreases viscosity only to a slight degree for quantities of magnesia up to 10 wt%. As magnesia is increased to 20 wt%, the decrease in viscosity for the same silica and alumina value is more marked. Similar findings have been reported by Yakushev *et al.* /22/ in a synthetic slag of 40-48% CaO , 17.5-40% Al_2O_3 , 15-30% SiO_2 , and 4-12% MgO .

The rate of change of viscosity with respect to variation of lime and alumina content is less as the magnesia content increases. Advantage may be taken of this fact to minimize viscosity variation of slag in iron blast furnace operation.

In this connection it may be seen from the results of Bockris *et al.* /3/ and Mackenzie /11/ that alkaline earth oxides are interchangeable in their effects on the viscosity of binary melts, and similar behaviour is therefore expected to hold for the quaternary melts. This has been illustrated graphically by Turkdogan and Bills /18/ (Fig. 8). It can be observed from the figure that lime and magnesia are replaceable on the molar basis and that the derivation of silica equivalence of alumina (N_a) from Fig. 7 is not affected by the presence of magnesia. The plot of Fig. 8 demonstrates that the data on binary, ternary, and quaternary melts could be represented by a

Fig. 8: Variation of viscosity with composition of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ melts at 1500°C.

single curve with only a small scatter. However, the viscosity values of the slags may differ by as much as 20% even for the same $\text{Na} + \text{N SiO}_2$ value so that the usefulness of this curve may be limited.

Kawahara *et al.* /23/ have suggested, however, that MgO is amphoteric in nature, e.g., in the $\text{CaO-SiO}_2\text{-MgO}$ system, MgO behaves similarly to CaO , but in the $\text{Na}_2\text{O-SiO}_2\text{-MgO}$ system, it acts as an acidic oxide. Like all amphoteric oxides, the strength of MgO as a basic oxide increases with decreasing basicity of the melt and as a function of its content in the melt.

1.7. Calcium Fluoride Addition to Silicate Melts

The discrete anion model still holds good for reduction of viscosity caused by adding calcium fluoride to silicate melts. In binary silicates incorporation of fluoride is only possible at compositions containing more than about 12% M_xO_y (otherwise separation of a pure fluoride phase occurs /6/). It is suggested that the F^- ions replace the divalent O^{2-} ions in the silicate structure /24/. The depolymerization action of the fluoride is explained by the reactions of the type shown in Fig. 9.

Fig. 9: Depolymerisation of silicate structure by addition of fluorides.

Kozakevitch /25/ also found that calcium fluoride was much more effective on a molar basis than lime in lowering the viscosity of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts. He postulated that if calcium fluoride enters the silicon-oxygen lattice of the slag by breaking silicon-oxygen bonds in a manner similar to calcium oxide, then one mole of CaF_2 should be equivalent to two moles of lime in its effect on viscosity (Fig. 10). However, the effect of calcium fluoride was found to be much greater than that expected from the above theory. In a viscosity measurement investigation, Bills /26/ took two $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags (40:40:20 and 35:50:15) and added 2% and 9.5% CaF_2 to the first slag and 5% and 15% CaF_2 to the second one. It was discovered that addition of CaF_2 decreased the viscosity of the melts considerably and that this effect

Fig. 10: Comparison of the effect of calcium oxide with hypothetical effect of calcium fluoride on silicate network.

was much greater at lower temperatures. From the viscosity observation he suggested that it was unlikely that CaF_2 breaks the Si-O bonds with consequent reduction in the size of the silicate flow unit. However, he agreed with Baak's postulation /27/ that CaF_2 ionizes in such a way as to act as a solvating agent for the large silicate anions which are bound together by electrostatic forces. When CaF_2 is added, it reacts with Ca^{++} ions to form two CaF^+ ions which attach themselves to singly bonded oxygens of the flow units, hence decreasing the attractive interaction between the singly bonded oxygens (O^-) and calcium ions. This action is known as the *solvating effect* of unstable CaF^+ ions on the silicate anions as shown in Fig. 11. This results in a considerable lowering of the viscosity.

If this theory is correct, the magnitude of the effect of CaF_2 on the decrease in viscosity, especially at low temperature, indicates that, normally, the flow resistance due to ionic interactions is just as important as the size of the silicate flow units themselves. It is due to this interaction effect that viscosity in binary alkaline earth silicates is so much higher in value than in corresponding alkali silicates where this electrostatic binding of silicate anions cannot take

Fig. 11: Hypothetical solvating effect of addition of CaF_2 to silicate melt.

place due to the absence of multivalent cations. The above mechanism suggested by Baak is supported by activity coefficient curves of $\text{CaSiO}_3\text{-CaF}_2$ systems /28/ and conductivity measurements on $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$ melts /29/. The mechanism was also supported by Gupta and Seshadri /30/ who determined viscosity measurements of aluminosilicate slags containing 20%, 25%, and 30% Al_2O_3 , each with 5%, 10%, and 15% CaF_2 additions. They observed that, for the same weight percent of CaF_2 addition, the percentage reduction in viscosity at a given temperature is almost independent of alumina content of the melt and that between 5 and 10 wt% CaF_2 , the ability of alumina to reduce viscosity is comparatively low over the entire range investigated. They explained their observations assuming a three-fold coordination for aluminium and calculating the number of flow units per 10^5 g of slag.

Kato and Minowa /31/ added different fluorides to aluminosilicate melts and observed that the effect of the fluorides in reducing the viscosity is ranked as $\text{CaF}_2 > \text{MgF}_2 > \text{AlF}_3 > \text{NaF}$. For the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system, it is also reported that 6 wt% addition of CaF_2 approximately halves the viscosity of the quaternary slag without calcium fluoride /5/.

1.8. Role of Other Constituents

1.8.1. Slags with iron oxides. From a viscosity study of the $\text{CaO-SiO}_2\text{-FeO}$ system, Kozakevitch /32,33/ found that above 35 mole percent SiO_2 viscosity depends on SiO_2 content and is virtually independent of FeO and CaO contents due to the predominance of silicate anions above this composition. In another study Bills /26/ inferred that a gradual addition of FeO up to 15 wt% decreases the viscosity of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ quaternary slags and that the effect of larger additions of FeO is more pronounced at high temperatures. At lower FeO contents than 15 wt%, the effect of addition of more FeO is equivalent on a molar basis to the addition of MgO , but at higher FeO content it is not valid. He suggested that the reason might be due to the difference in electrostatic binding forces which bind Fe^{2+} and Mg^{2+} cations to silicate anions. He measured the energy of activation of viscous flow, which was found to decrease slightly with an increase in temperature but was fairly constant for all slags (45 kcal/mole).

The iron oxide, when added to silicate melts, can break up the silicate anions by providing free oxygen

ions according to the equations /34/:

In acid slags the addition of iron oxide decreases the viscosity more than in basic slags, as iron oxide in acid slag can break up the silicate anions more effectively than in basic slags. In basic slags, however, the trivalent iron ion exists to a larger extent in the form of ferrite anions which are not able to provide free oxygen ions. Moreover, in basic slags, even if iron oxide content is low, the silicate anion is of smaller size and hence viscosity is low. Consequently, the addition of iron oxide has little effect in lowering the viscosity in basic slags. Just as the smallest structural unit of the silicate anion is SiO_4^{4-} , like $\text{Fe}_2\text{O}_4^{2-}$ ions are in the ferrite anion, they are hardly liable to thermal dissociation without complete structural change. Hence viscosity of acid slag is strongly dependent on temperature at low iron oxide content and weakly so at high iron oxide content, whereas viscosity of basic slag is weakly dependent on temperature at all iron oxide contents.

1.8.2. Slags with barium oxide. Bills /26/ replaced part of the lime in the $\text{CaO-SiO}_2\text{-FeO}$ system with BaO and observed that, for a given temperature, the effect of this substitution on a weight percent basis is to raise the viscosity of the melt, as a result of the replacement of CaO by BaO , which leads to a lower mole fraction of alkaline earth oxide and, consequently, to a higher mole fraction of silica (mol wts of CaO and BaO are 56.1 and 153.4, respectively).

A comparison of binary data of CaO-SiO_2 , FeO-SiO_2 , BaO-SiO_2 , and MgO-SiO_2 systems reveals that at 1450°C FeO-SiO_2 melts have very low viscosity compared to corresponding ones in the CaO-SiO_2 system. This may be due to the existence of a stronger bond between the metal cation and silicate anion in the latter system. However, at 1600°C there is less difference in viscosity of the CaO-SiO_2 , BaO-SiO_2 , and MgO-SiO_2 systems, because at higher temperatures the bonding effect is less.

1.8.3. Minor constituents. Nesterenko *et al.* /35/ measured the viscosity of the $\text{CaO-MgO-SiO}_2\text{-5% Al}_2\text{O}_3$ system with additions of 2% sulphur, 1% MnO , 1% FeO , and 0.5% K_2O and found lower viscosities due to these additions. They also established that, at a given temperature, the range of slags with a mini-

imum viscosity corresponds to the slags of maximum conductivity.

1.9. Effect of Temperature on Viscosity

From eq. (2) it is clear that the viscosity of silicate melts decreases exponentially with rise in temperature. However, the plot of $\log \mu$ vs $1/T$ may or may not be linear, as discussed earlier, taking structural effect into consideration. When the temperature of the melt is increased, one or both of the following two phenomena may take place: (1) weakening of the ionic bonds between cations and discrete anions, (2) gradual breakdown of the discrete anions to smaller flow units. If the first occurs, the activation energy of viscous flow remains constant within the temperature range. If the second occurs, there is a change of activation energy with a change in temperature.

2. VISCOSITY MEASUREMENT OF SOME INDUSTRIAL SLAGS

A large volume of literature is available on the viscosity measurement of industrial slags such as blast furnace, steel making, high titania, etc. Salient features of these studies will be presented here appropriate to the above discussions on melt structure.

2.1. Blast Furnace Slags

Blast furnace slag contains CaO , SiO_2 , Al_2O_3 , and MgO as major constituents, with MnO , FeO , CaS , and sometimes TiO_2 as minor constituents. The amount of basic oxides in the blast furnace slag is expressed as CaO/SiO_2 or the amount of basic oxides divided by the amount of acid oxides. Alumina, depending on the slag composition, may behave as an amphoteric oxide in these slags, as discussed earlier.

From the viscosity measurement of industrial blast furnace slags with a wide composition range, it has been observed /36-41/ that the viscosity variation with change of composition is complicated. Nevertheless, all the investigators agree that viscosity variation with a CaO/SiO_2 ratio depends on the MgO level in the slag; the higher the MgO content, the lower the desired CaO/SiO_2 ratio for optimum viscosity. Further, they agree that a high CaO/SiO_2 ratio combined with a high MgO content in the slag results in "short" slags. It has also been reported that high alumina blast furnace slags (20-34% Al_2O_3) show erratic viscosity variation due to the change of the

Al/Si ratio because, when the Al_2O_3 content is constant, the higher CaO/SiO_2 ratio increases the Al/Si ratio; and, as discussed earlier, the former decreases the viscosity whilst the latter increases it.

Some investigations have been carried out on the liquidus temperature of blast furnace slags /42-44/ because the low liquidus temperature of a slag of given composition results in a high degree of superheat and hence low viscosity at the operating temperature. Fine and Arac /42/ utilized a statistical relationship to determine the variation of liquidus temperature of the synthetic slag with 10% Al_2O_3 and the ratio, $\text{wt}\%(\text{CaO} + \text{MgO})/\text{wt}\%(\text{SiO}_2 + \text{Al}_2\text{O}_3)$, ranging from 0.94-1.13, with the addition of MnO , FeO , Na_2O , and TiO_2 . The change of liquidus temperature is given by

$$\Delta T = -19(\text{wt}\% \text{Na}_2\text{O}) - 8(\text{wt}\% \text{FeO} + \text{wt}\% \text{MnO}) + b(\text{wt}\% \text{TiO}_2) \pm 3^\circ\text{K} \quad (15)$$

where b has two values, 10 and 20, for the two slag compositions investigated. As the liquidus temperature depends on the basicity ratio, Al_2O_3 and MgO contents, in a complicated way, Singh *et al.* /43/ plotted the liquidus temperature vs MgO wt percent in the slag for various basicities and Al_2O_3 contents. From their plots it is observed that for a high basicity ratio (1.5), there is only one value of MgO giving the lowest liquidus temperature, but for low basicity ratios, the liquidus temperature remains constant for a wide range of MgO contents.

2.2. Blast Furnace Slags with Titanium Oxides

Titaniferous ores are also sometimes smelted in the blast furnace and are said to cause problems such as accretions, scaffolds, hearth cloggings, and high fuel consumption /45/. A few investigations have been carried out to discover the role of TiO_2 , Ti_2O_3 , and TiO on the liquidus temperature and viscosity of slags /46-54/. It is commonly agreed that all oxides of titanium up to a total amount of 10 wt% are effective in reducing the viscosity when the slag is slightly acidic, so long as titanium carbide is not formed. It is suggested that thickening of slag in graphite containers may be due to a reduction of TiO_2 by carbon leading to a consequent depletion of oxygen ions. Hence, to that end, adding TiO_2 decreases viscosity by furnishing additional oxygen. From the relationship of E_a vs weight percent of added titanium oxide, Handfield *et al.* /53/ suggested that Ti_2O_3 is much more effective as a network modifier

than TiO_2 . The property of "shortness" of the slag is also observed /54/ in titania bearing slags when Al_2O_3 exceeds 23 wt% and MgO exceeds 16 wt%, with $\text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3$ exceeding 0.95.

2.3. High Titania Slags

Viscosity measurement of industrial titania slags (68-80% TiO_2 and 3-15% FeO) indicate that once the slags are completely molten, they are characterized by a viscosity of only 30 cps, which remains fairly constant with further increase in temperature /52,55/. Hence it was suggested that these melts are structurally different from polymerizing melts and, in the main, are semiconductors. This supposition is supported by electrical resistivity measurements of these slags, which show that they have much lower electrical resistivity than siliceous slags /56/. The specific conductivity of these melts is so high /57,58/ (30-200 $\text{ohm}^{-1}\text{cm}^{-1}$ in comparison to 5 $\text{ohm}^{-1}\text{cm}^{-1}$ for ionic melts) that the melt may be ionic-electronic rather than purely ionic. Reznichenko /57/ has postulated that molten high TiO_2 slags consist mainly of anions of the type TiO_6^{8-} based on the fact that the TiO_6 octahedron is the basic structural unit with solid anosovite. His hypothesis that the same basic structural unit is found in both solid and molten slags can account for the ease of crystallization of the melt, supported by the fact that nonpolymerized ionic melts are very fluid. However, his suggestion is not compatible with the high electrical conductivity of the sample and its strong dependence on composition. For this reason it is unlikely that TiO_6^{8-} anions are the basic structural units of molten titania based slags. Hence the structure can only be clearly predicted after a theory of semiconducting properties of the slag is developed.

In another investigation of thermophysical properties of slag composed of 36-62 wt% TiO_2 , 0-25 wt% Al_2O_3 , 0-25 wt% FeO , 19.5 wt% Ti_2O_3 , 10 wt% SiO_2 , 1.5 wt% CaO , 1.0 wt% MgO , and 1 wt% MnO , which resulted from the smelting of titanomagnetite /59/, it was observed that the fusibility temperature rose with an increase in TiO_2 and Al_2O_3 contents and fell with an increase in FeO content. This conclusion was reached based on phase composition. The viscosity of this slag, over a wide range of composition, never exceeded 500 cps at 1500°C , rising with an increase in Al_2O_3 content above 20% and a decrease in FeO content.

3. THERMOPHYSICAL PROPERTIES OF ALUMINOTHERMIC SLAGS

Many low carbon ferroalloys such as ferrotitanium, ferrochromium, ferrovanadium, ferroniobium, ferromolybdenum, ferrozirconium, and ferrotungsten, as well as pure metals such as niobium, zirconium, molybdenum, and tungsten, are produced by aluminothermic reduction, for which aluminium is usually used as the reductant (although calcium, magnesium, and zirconium have been used in some cases). Niobium production by aluminothermic reduction of niobium pentoxide has been attempted by various authors /60-65/, as has ferroniobium production /66/. Similarly, other metals such as vanadium from vanadium pentoxide /67-70/; molybdenum from molybdenite /71-73/, molybdenum disulphide /74/, molybdenum trioxide /75/, and calcium molybdate /76/; tungsten from wolframite /77/ and calcium tungstate /78/; and tantalum from tantalum oxide /79-81/ have also been produced by aluminothermic reduction. Likewise, ferrotitanium is produced by aluminothermic reduction of ilmenite /82-89/, perovskite /90/, and also by aluminosilicothermic reduction of ilmenite /91-92/. The resultant slag in all these cases contains a high percentage of alumina (60-70%) and unreduced oxides along with some gangue oxides. These slags have a high melting point. Therefore, a study of liquidus temperature of slags approximating aluminothermic slags, with the addition of certain basic oxides and halides, is very important because the lower the liquidus temperature, the higher the superheat available to make the slag sufficiently fluid at the working temperature.

3.1. Liquidus Temperature of Alumina-Based Melts

In this connection it is appropriate to quote the work of Nityanand and Fine /93/. They determined the liquidus temperature of $\text{CaO-Al}_2\text{O}_3$ melts with 0-10 wt% TiO_2 . The percentage of Al_2O_3 taken in the binary mixture was 49.0-51.5 wt%, the balance being CaO . The liquidus lines for $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ melts in air, as presented by the above authors, are reproduced in Fig. 12. It is observed that without TiO_2 addition, the minimum liquidus temperature of 1647°K is obtained for 51% Al_2O_3 and 49% CaO . The addition of 0-1% TiO_2 decreases the liquidus temperature with $\text{Al}_2\text{O}_3/\text{CaO}$ ratio of 49/51 to 51.5/48.5, whereas greater TiO_2 addition raises it.

Fig. 12: The effect of additions of titania on the liquidus line of $\text{CaO-Al}_2\text{O}_3$ system under oxidising conditions ($\text{PO}_2 = 0.21$).

For 10% wt% TiO_2 , the liquidus temperature is as high as 1943°K at $\text{Al}_2\text{O}_3/\text{CaO}$ of 51/49, i.e., about 300°K higher than that without the addition of TiO_2 . Measurement at low oxygen potential ($p_{\text{O}_2} = 10^{-16}$ atm) shows that an increase in the liquidus temperature of as much as 350°K results due to the addition of 10 wt% TiO_2 . Thermodynamic calculations indicate that Ti^{3+} and Ti^{2+} ions may exist at low oxygen potential. Thus, to maintain electrical neutrality, some oxygen must be evolved from the melt. The aluminothermic slag for production of ferrotitanium contains Al_2O_3 and TiO_2 , and also CaO when lime is added as a flux; therefore, this knowledge of liquidus temperature will be helpful for the study of ferrotitanium slags of varying composition.

3.2. Role of CaF_2 in Aluminothermic Slags

Calcium fluoride is said to reduce the liquidus temperature and viscosity of slags. The role of calcium fluoride in silicate slags has been discussed earlier. In the absence of CaF_2 , acid and high alumina slag melts exhibit high viscosity resulting from the large

dimensions and low mobilities of the aggregates of complex ions such as Al_3O_7^- , AlO_3^- , etc. in the melts. Adding fluorine ions results in the breakdown and consequent reduction in size of these complex structures, with the result that the melt exhibits high fluidity.

While carrying out a viscosity study of the slags, the container as well as conditions must be such that there will not be any reaction with the crucible or any compositional changes. In graphite crucibles $\text{CaF}_2\text{-Al}_2\text{O}_3$ melts form CaC_2 , Al_4C_3 , and graphite in the melt /94/. Similarly, CaF_2 will react with water and some metal oxides such as SiO_2 , TiO_2 , and V_2O_5 to produce CaO and gaseous fluorides as exemplified by the reactions:

These compositional changes can be minimized if the sample is dry and the measurement is carried out in a sealed container /95/. In practice, however, these compositional changes may not be as large as anticipated since the CaO formed will react to form calcium aluminates, silicates, etc., thus reducing the activities of these oxides.

It is reported that in an $\text{Al}_2\text{O}_3\text{-CaO-CaF}_2$ ternary, Al-O complexes predominate at low CaF_2 contents due to the existence of a considerable amount of covalent bonding; further, additions of CaF_2 cause a gradual breakdown of the complexes /95/.

Evseev /96/ has proposed that at low CaF_2 levels the molecules of Al_3O_7^- are bound by Ca^{2+} ions and that any addition of fluoride ions tends to break the chains at these positions and then fill the vacant sites. Mitchell and Cameron /97/ speculated that at higher CaF_2 contents networks based on AlO_2F_2^- and AlOF_2^- are formed and that the addition of CaO to these melts tends to release F^- ions from the networks and produce AlO_3^- and AlO_2^- structures. Nakamura and Yanagase /98/ have suggested that CaF_2 has little effect on the structure of aluminate anions for a CaO rich composition but does influence the structure of other compositions.

Viscosity determination of $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ melts has been performed by several authors /99-103/. Although the reported data exhibit considerable discrepancies, they do show that viscosity is decreased by CaF_2 additions and increased by Al_2O_3 additions. An increase in CaO content increases the viscosity slightly, as this results in slightly tighter bonding in the melt /95/.

In a recent investigation Yanagase *et al.* /104/ studied the viscosity, liquidus temperature, electrical conductivity and two-liquid regions of $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ melts and suggested that the behaviour of CaF_2 is similar to that of CaO . The isoviscosity curves as determined are shown in Fig. 13. For the compositions where the molar ratio of $\text{Al}_2\text{O}_3/\text{CaO} = 1$, the isoviscosity and isoconductivity lines show abrupt changes, indicating that Al_2O_3 may be behaving as an amphoteric oxide as in silicate melts. In the composition range of mole $\text{Al}_2\text{O}_3/\text{mole CaO} < 1$, Al_2O_3 is likely to yield complex anions such as AlO_2^- and AlOF_2^- resulting in an increase in viscosity and a decrease in electrical conductivity with increasing alumina. In the melts where mole $\text{Al}_2\text{O}_3/\text{mole CaO} > 1$, behaviour of Al_2O_3 is similar to that of CaO in that the isoviscosity and isoconductivity lines appear to be parallel to the lines of constant CaF_2 .

Viscosity determinations of $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-Nb}_2\text{O}_5$ and $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5$ melts show that an addition of up to 20% Nb_2O_5 to a mixture of 70% $\text{CaF}_2 + 30\%$ Al_2O_3 or of up to 20% V_2O_5 to a mixture of 70% $\text{CaF}_2 + 30\%$ Al_2O_3 decreases the viscosity at 1600°C /105,106/. However, in the case of $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ melts, viscosity decreases with an additional 5% TiO_2 but then increases with further addition /105/.

Fig. 13: I₁ - Viscosity lines of $\text{CaO} - \text{Al}_2\text{O}_3 - \text{CaF}_2$ melt at 1580°C under dried argon.

3.3. Viscosity of Aluminothermic Slags

3.3.1. Ferrotitanium slag. Suchilinkov and Pliner /107/ studied the effect of CaO , BaO , and SrO on the viscosity of industrial ferrotitanium slags. The analysis of the industrial slag that they selected was 75.23% Al_2O_3 , 14.25% TiO_2 , 5.31% CaO , 3.29% FeO , 0.75% SiO_2 , and 1.16% MgO . To two slag samples they added CaO in order to form a slag of 9.0% and 14% CaO . To the other two slag samples, 4.0% and 9.0% BaO and to a fifth slag sample, 5% SrO were added. The effects of these additions on viscosity at various temperatures are shown in Fig. 14. As seen in the figure, CaO exerts a greater effect than SrO and BaO in reducing the viscosity. The nature of viscosity and temperature relationship shows that the temperature has little effect on viscosity when the slags are overheated well above the liquidus (1550-1650°C). The viscosity value of the slag with 14% CaO was about 130 cps at a temperature above 1550°C.

In another investigation Pliner *et al.* /108/ measured viscosity in the slags obtained during industrial production of ferrotitanium (A), special purpose low-carbon ferrochrome (B), ferrosilicozirconium (C), and ferroniobium (D_1 and D_2). The chemical analyses of these slags are contained in Table 3. Because a certain amount of metal remains in industrial slags in the form of beads and very small metallic inclusions arising as a result of decomposition of lower

Fig. 14: Effect of CaO , SrO and BaO additions on viscosity of industrial ferrotitanium slags. I - No addition, II & III - CaO addition (9 and 14 wt%), IV - SrO addition 5 wt%, V & VI - BaO addition (4 and 9 wt%).

TABLE 3
CHEMICAL COMPOSITION OF INVESTIGATED SLAGS

Alloy	Al ₂ O ₃	CaO	MgO	FeO	SiO ₂	TiO ₂	ZrO ₂	ΣMe
Ferrotitanium (A)	60.6	12.8	4.74	1.67	2.96	10.11	-	6.70
Low-carbon ferrochrome (B)	54.0	22.2	12.20	1.38	0.97	-	-	0.93 (C _F)
Ferrosilicozirconium (C ₁)	54.6	30.8	5.12	0.91	2.66	-	5.57	-
Ferrosilicozirconium (C ₂)	19.9	32.5	6.21	0.35	25.84	-	15.20	-
Ferroniobium (D ₁)	55.0	20.2	2.07	1.30	5.78	7.78	2.92	4.21 (Nb)
Ferroniobium (D ₂)	73.5	16.0	7.30	1.75	0.44	0.29	0.43	0.01 (Nb)

oxides may also be found, the composition of metallic content was also determined in each slag.

As shown in Fig. 15A, the ferrotitanium slag is a short slag for which viscosity drops steeply within a range of only 50°C. This slag, however, has very low viscosity values, ranging from 150 cps at 1830°C to 180 cps at 1760°C. The curve illustrated in Fig. 15A can be used as a basis for selecting the temperature for industrial production of ferrotitanium. According to the published data /109/, the temperature of the melt at the moment when the reducing reactions finish should exceed by 250°C the minimum temperature at which deposition of the metal droplets through the molten slag is possible. This minimum temperature from the figure can be taken as 1750°C, i.e., the temperature at which there is a steep viscosity rise.

3.3.2. Low carbon ferrochrome slag. In the case of this slag /108/, it can be seen from Fig. 15B that viscosity variation with respect to temperature is gradual. The uniform increase in viscosity of the slag as it cools down over a wide temperature range helps in a complete separation of slag from metal, allowing the alloy to be obtained without much metal loss in the form of beads in the slag.

3.3.3. Ferrosilicozirconium slag. The viscosity of this slag obtained /108/ by two different methods is shown in Fig. 15C. Here also there is a gradual change of viscosity with temperature, as with ferrochrome slag. The presence of a high quantity of zirconium dioxide in the slag, however, does not bring about any essential change in the viscosity in comparison to that of lime-alumina slag with a Al₂O₃/CaO ratio of 60:40, as reported by Kozakevitch /110/.

3.3.4. Ferroniobium slag. Viscosity of ferroniobium slag produced from pyrochlore concentrate (D₁) and niobium pentoxide (D₂) /108/ in the high temperature region (around 1700°C) is almost the same, as shown Fig. 15D, but in the former, a sudden change of viscosity takes place at lower temperatures (1420-1540°C). Accordingly, producing ferroniobium from pyrochlore concentrate (D₁) under industrial temperature conditions should enable better separation of slag from metal and hence less metallic beads should appear in the slag. However, as is apparent from considering Table 3, slag D₂ has better separation than slag D₁. It has been pointed out /108/ that this may be due to a decrease in interphase tension between the slag and the metal in the case of slag D₁.

Fig. 15: Viscosity of slags investigated in the production of ferroalloys as a function of temperature (nomenclature as in Table III).

CONCLUSIONS

The review of literature shows that there is a wide scope for a thorough and systematic investigation of the liquidus temperature, conductance, and viscosity of slag-melts resulting from metallothermic production of various less common metals and their ferroalloys such as Fe-Ti, Fe-V, Fe-Mo, Fe-W, Fe-Nb, etc. A detailed study with additions of various fluxing constituents such as CaO, MgO, and CaF₂, would throw some light on the structural aspects of aluminothermic slags. Such an investigation would also help in selecting an appropriate slag composition for better slag-metal separation. Determination of the relationship between viscosity and temperature would help in selecting the optimum temperature conditions for a heat, ensuring the most effective separation of the metal from the slag and thus increasing the recovery of the important metal and the yield of the ferroalloy.

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