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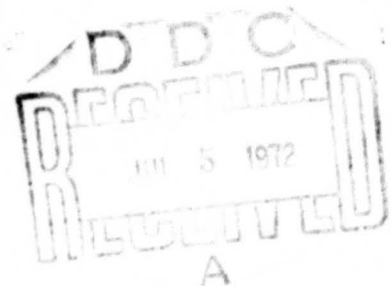
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VISCOSITY, DENSITY AND SURFACE ENERGY
OF MOLTEN ALLOYS OF IRON AND SILICON

by

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Ye. S. Levin, B. A. Baum



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13. ABSTRACT <p>To get a better insight into phys. properties of the Fe-Si system the kinematic viscosity and the surface energy were calcd. for alloys with variable amts. of Si. From the slope of log given vs 1/T curves the activation energy was calcd. and the change in the isobar-isothermal potential given. By plotting the given potential vs T it was possible to obtain the energy of activation of viscous flow. The dependence given and given potential on the alloy compn., which deviates from the rule of additivity, shows that the Fe-Si melts do not behave as ideal solns. The energy of activation of viscous flow should be related to the bonding energy in the melts and to the dimensions of at. assocns. representing the units of viscous flow. A higher energy of activation of Fe-Si permits concluding that in this case the units of viscous flow are the quasimols. of Fe-Si. In other melts together with quasimol. complexes particular atoms of the component in excess appear, their influence on the viscous flow being essential. At higher temps. the no. of these particular atoms is slightly increased which contributes to a decrease in the activation energy.</p>			

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VISCOSITY, DENSITY AND SURFACE ENERGY OF MOLTEN ALLOYS OF IRON AND SILICON

/Article by P.V. Gel'd, P. V. Kocherov, Ye. S. Levin and B. A. Baum; Physical-Chemical Basis of Steel Production, Russian, 1968, pp 9-13/

Investigations of heats and volume effects in mixing, heats of fusion and a number of other characteristics of molten alloys of silicon with fourth period transition metals indicates a high energy of interaction of dissimilar atoms and their severe micro-heterogeneity /1, 2/.

Results of determining viscosity, surface energy and density of Fe-Si alloys are presented below.

Kinematic viscosity was calculated according to the decrement of damping of a cylindrical crucible with the melt /3/. Surface energy and density were determined by the "large drop" method /4, 5, 6/.

On the basis of data on the relationship of kinematic viscosity of the melts to temperature, represented in Fig. 1, it is possible to calculate the activation energy in a straight-line slope in coordinates $\lg v \sim T^{-1}$, the change of isobaric-isothermal potential $\Delta Z = RT \ln(v \cdot M / \eta \cdot N)$ and the energy of activation of viscous flow by the tangent of the straight line in coordinates $\Delta Z \sim T$ /7/.

The non-idealness of the examined system can be confirmed by the relationship of v and ΔZ to composition as shown in Fig. 2, which does not conform to the additive rule.

From data presented in Figs. 1 and 2 it follows that the activation energy of viscous flow (E) of all the melts (with the exception of Fe-Si and Si) is very close and depends very little on temperature. The change of action entropy of viscous flow is distinguished by this.

The magnitude of E can be determined basically by the bonding energies in the melt and by the dimensions of the atom groupings which are units of viscous flow. The higher activation energy for Fe-Si permits one to suggest that the units of viscous flow in the melt of monosilicide are evidently "quasimolecules" of Fe-Si /1, 2/. In melts of other compositions (Fe_3Si , $Fe_{21}Si_{11}$, Fe_5Si_3 ,

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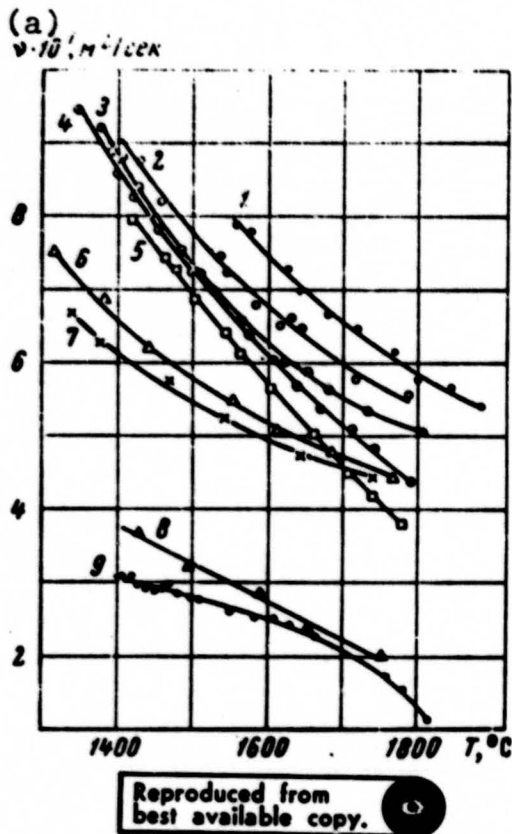


Fig. 1. Relationship of kinematic viscosity of Fe-Si alloys to temperature: 1--Iron; 2--25 At.% Si (Fe_3Si); 3--34% ($\text{Fe}_{21}\text{Si}_{11}$); 4--37.5% (Fe_5Si_3); 5--50% (FeSi); 6--67% (FeSi_2); 7--62%; 8--85% Si; 9--Silicon; a-- $v \cdot 10^7$, m^2/sec .

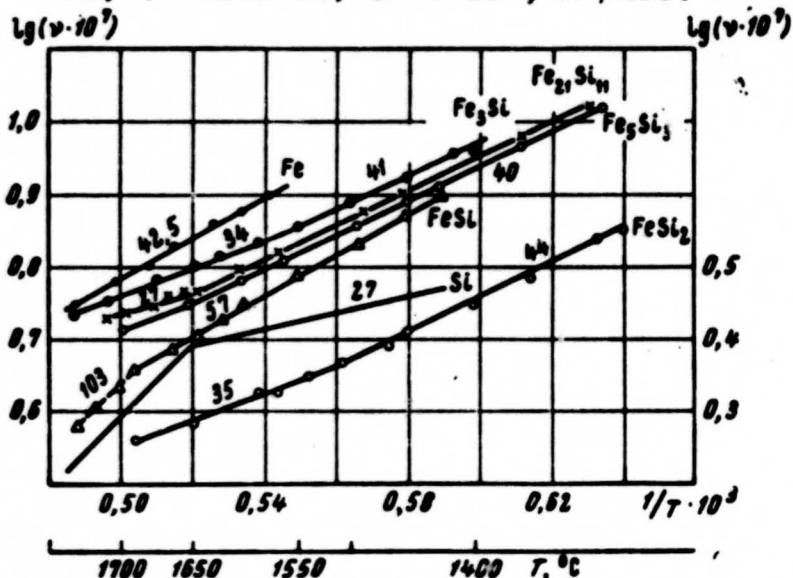


Fig. 2. Relationship of $\lg v$ of Fe-Si alloys to magnitude of T^{-1} : Numbers near the straight lines are the activation energies in the given temperature interval $E \cdot 10^{-3}$ kJoules/kg-atom.

FeSi₂, etc.) along with the quasimolecular complexes, in which strong homopolar bonds prevail, individual atoms of the excess component /Fe-up to 50 at.% Si and Si-above 50 at.% Si/ have substantial significance in viscous flow. Sizes and energies of interaction between them is approximately the same which leads to closeness in the activation energies of viscous flow. Certain differences in magnitudes were probably caused by the fact that the structure and composition of the quasimolecular groupings are basically determined by the structure and composition of the solid phase and varies with growth of N_{Si}. With increased temperature the energy of thermal movement of the particles grows which leads to a decrease in the sizes of the cybotactic groupings in the melts and an increase in the number of "free" atoms. This develops with some decrease in the activation energy (see Figs. 1 and 2).

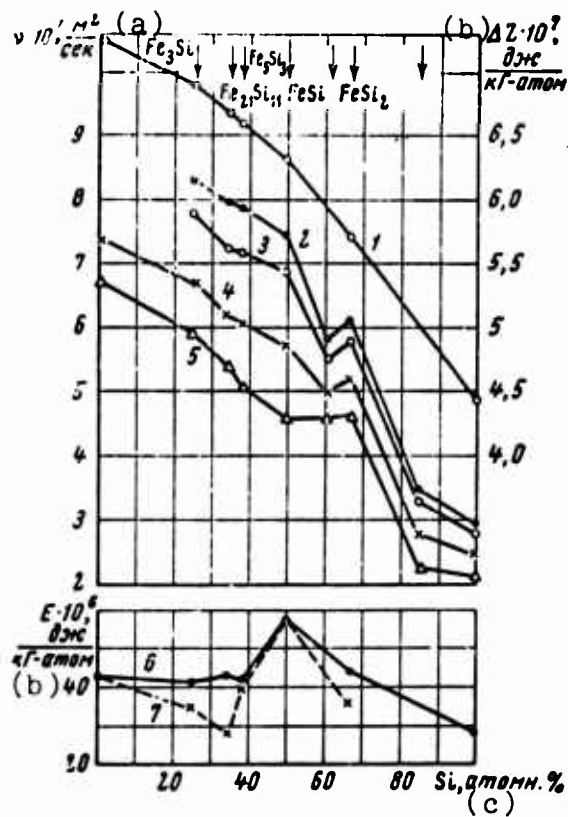
For iron monosilicide at temperatures above 1700 C the activation energy turns out to be higher than at low temperatures which was caused by a change in the mechanism of viscous flow.

Apparently the dissociation of "quasimolecules", starting at almost 1700 C, initially leads to a decrease in the energy of interaction between units of viscous flow which become not only "quasimolecules" but also individual atoms of iron and silicon.

The self-forming structure of the monosilicide can be confirmed, as shown in Figs. 3 and 4, also by the shape of the surface tension isotherms and density of Fe-Si alloys.

With the addition of silicon to iron, as a result of a strong interaction of the dissimilar atoms ($\epsilon_{\text{Fe-Fe}} < \epsilon_{\text{FeSi}} < \epsilon_{\text{Si-Si}}$), quasimolecular complexes are formed and the melt acquires a micro-heterogeneous structure /1, 2/. Here single cybotactic groupings are enriched with these complexes and the others with iron atoms. Inasmuch as the interaction of atoms in the indicated complexes takes place primarily in the directed homopolar bonds, then they turn out to be relatively weak bonds with the melt and with each other and flow into the surface layer thus lowering σ . According to the degree of increased silicon content the composition of the alloy approximates being equiatomic. "Quasimolecules of FeSi are in the composition with structural units and the bonding energy between them is quite large which allows one to talk about the relatively high surface tension of the melt (almost 1210 ergs/cm²). With a further increase of silicon concentration the microheterogeneity of the melt is again increased and forms micro-groupings respectively enriched with Fe₂Si₃-complexes as well as excess atoms. Since bonding of the latter with the melt is weaker they flow into the surface layer causing a lowering of its surface energy. This finds confirmation in the concentration relationship of silicon adsorption (see Fig. 4).

Accuracy of the presented concepts can also be confirmed by the value of compression observed in the formation of melts



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Fig. 3. Relationship of kinematic viscosity v , change in isobaric-isothermal potential ΔZ and activation energy of viscous flow E to composition of the alloys: 1-- ΔZ , 1600 C; 2-- v , 1450 C; 3-- v , 1500 C; 4-- v , 1600 C; 5-- v , 1700 C; 6-- $T < 1570$ C; 7-- $T = 1570-1700$ C; a-- $v \cdot 10^7, \frac{m^2}{sec}$; b-- $\Delta Z \cdot 10^7, \frac{kJ}{atom}$; c--Si, atomic %.

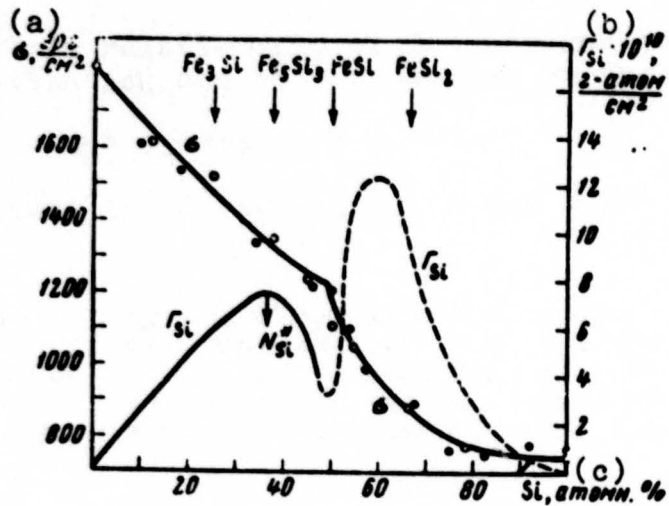


Fig. 4. Isotherms (1550 C) of surface tension and adsorption of silicon (G_{Si}) of molten Fe-Si alloys, black dots--data from Bork β /, white dots--data of the authors: a-- σ , ergs/cm²; b-- $G_{Si} \cdot 10^{10}$, g-atom/cm².

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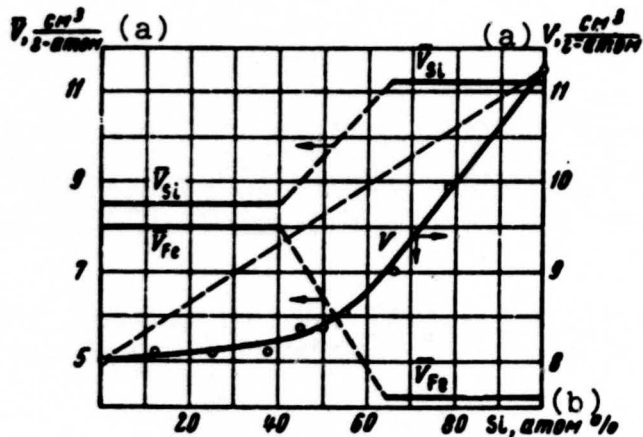


Fig. 5. Relationship of molar (V) and partially molar (\bar{V}) volumes of the components of the Fe-Si alloys to composition at 1550 C: a-- V , cm³/g-atom; b--Si, atomic %.

of the pure molten components (Fig. 5). The maximum values of compression ($\Delta V = [(9.68-8.34)/8.34] \times 100 = 16\%$) corresponds to alloys close in composition to equiatomic which speaks about the high energy of inter-particle interaction in them.

The temperature relationship of density and surface energy in the first approximation can be represented by the equations:

$$\rho = \rho_0 - at; \quad \sigma = \sigma_0 - bt$$

where t is temperature in $^{\circ}\text{C}$ and ρ_0 , σ_0 , a and b are constants presented below:

(a) Bcc. % Si	7,0	14,36	23,18	28,50	33,46	37,50	50,31	66,50	100,00
(b) ρ_0 , g/cm ³	7,64	8,99	6,66	6,67	6,57	6,22	5,32	4,78	3,11
(c) $a \cdot 10^4$ g/cm ³ -deg	7,74	6,40	7,01	10,0	10,4	9,6	8,0	9,2	4,0
(d) σ_0 , ergs/cm ²	19,85	18,79	1815	1665	1620	1450	1210	1025	884
(e) b , ergs/cm-deg	0,250	0,233	0,300	0,284	0,333	0,267	0,217	0,167	0,104

Key: a--Weight % Si
 b-- ρ_0 , g/cm³
 c-- $a \cdot 10^4$ g/cm³-deg
 d-- σ_0 , ergs/cm²
 e-- b , ergs/cm-deg



Thus, analysis of the isotherms of the studied characteristics of molten ferrosilicide (v , ΔZ , E , ρ , σ , G_{Si} , V , \bar{V}) indicate the change with increased silicon concentration with a structure of close order of melts and the possibility of forming micro-groupings in them, close in composition and structure to the monosilicide.

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