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HEATS OF FORMATION OF REFRACTORY SILICIDES

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Leo Brewer and Oscar Krikorian

March 1956

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ABSTRACT

Heat-of-formation data of silicides are reviewed.

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Brewer and Krikorian[2] have determined the equilibrium composition triangles of a number of ternary systems. From the equilibrium conditions, they have set limits to the heats of formation of the silicides. Recently some calorimetric data have become available. Robbins and Jenkins[1] have taken advantage of the rapid rate of reaction of metals with silicon to determine the heats of formation of a number of silicides. They initiated each reaction by a thermite charge which evolved a known amount of heat. Thus the difference between the calorimetrically determined heat evolution and the heat due to the thermite charge gave them the heat of reaction. It is possible to compare their results with those given by Brewer and Krikorian.[2]

The heats of formation of the silicides listed by Robbins and Jenkins fall in or close to the ranges given by Brewer and Krikorian except for the zirconium silicides. The excess of silicon observed in the final samples of Robbins and Jenkins indicates that their zirconium silicide heats should be somewhat more negative due to incomplete reaction. On the other hand, the zirconium silicide heats given by Brewer and Krikorian are much too negative due to a misinterpretation of their results for the Zr-O-Si phase diagram. From the observation that silicon reacted with ZrO_2 to form $ZrSi_2$, they concluded that silicon and ZrO_2 could not co-exist and thus they drew joins between $ZrSi_2$ and SiO_2. However, calculation of the SiO partial pressure under their conditions shows that a partial pressure of over 10^{-3} atm SiO can be expected. This is large enough to cause loss of SiO even with an inert atmosphere blanket. Thus the reaction observed between ZrO_2 and Si must be $1/2\ ZrO_2(s) + 2Si(l) = SiO(g) + 1/2\ ZrSi_2$, and Si and the ZrO_2 phase can remain in equilibrium with one another without reaction if loss of gas can be prevented. Thus the phase diagram given in Fig. 1 of Brewer and Krikorian's paper must be modified as indicated in Fig. 1 of this report.

By combination of the phase diagrams of Brewer and Krikorian with the calorimetric determinations of Robbins and Jenkins, it is possible to present a rather complete table of heats of formation of the refractory silicides. These are presented in Table I of this report.

Table I

ΔH^{o}_{298} of formation in kcal/gram atom Si			
1/2 $TiSi_2$	-16.1	1/2 $TaSi_2$	-13.9
TiSi	-31.0	5/3 $TaSi_{0.6}$	-25.3
1/3 Ti_5Si_3	-46.2	Ta_2Si	-25 to -30
1/2 $ZrSi_2$	-19	5 $TaSi_{0.2}$	< -25
ZrSi	-37	1/3 $Ta_{4.8}Si_3C_{0.5}$	-25 to -38
1/5 Zr_6Si_5	-41	1/2 $MoSi_2$	-15.7
1/2 Zr_3Si_2	-46	10/6.5 $MoSi_{0.65}$	-23.4
1/3 Zr_5Si_3	-46	Mo_3Si	-24 ± 3
Zr_2Si	-50	1/3 Mo_4CSi_3	-24 ± 3
Zr_4Si	-52	1/2 WSi_2	-11.2
1/2 $CeSi_2$	-16.6 to -34.4	10/7 $WSi_{0.7}$	-11 to -20
1/x $CeSi_x$	< -16.6	1/2 $ReSi_2$	-12.5*
1/2 $NbSi_2$	- 8.5 to -21	ReSi	-11.6*
1/3 Nb_5Si_3	-21 ± 10	Re_3Si	- 6.2*
20/11 $NbSi_{0.55}$	-21 ± 10		

*Values for the Re silicides have been recalculated using ΔH^{o}_{298} = 105 kcal for the heat of sublimation of Si.

These new values allow a more precise examination of the variation of bonding energy. In the discussion of bonding energy, the energy required to form two gram atoms of atomic vapor is used as the bonding energy for all the compounds as well as the elements. Thus the bonding energies are the ΔH values for the following reactions:

$$2M(s) = 2M(g)$$
$$MSi(s) = M(g) + Si(g)$$
$$1/4\ M_5Si_3(s) = 5/4\ M(g) + 3/4\ Si(g)$$
$$2/3\ M_2Si(s) = 4/3\ M(g) + 2/3\ Si(g)$$
$$2/5\ M_3Si_2(s) = 6/5\ M(g) + 4/5\ Si(g)$$
etc.

The results for some of the silicides are given in Fig. 2. These may be compared with Fig. 9 given in the paper by Brewer and Krikorian[2] and with Figs. 9, 10, 11, 13, 14, 15, and 16, given in UCRL-2888.[3] The similarities between the curves suggest that the bonding must be similar in the metals and in the refractory borides, silicides, carbides, and nitrides. A striking indication of the similarities of the bonds in the elemental phases and in the silicide phases is shown by the virtually constant values for the heats of formation of the MSi_2 phases ranging from the third to the seventh group of the periodic table. Another illustration of this is given in Fig. 3, where the ratio of the bonding energies of some carbides and silicides to those of the corresponding metal is given, and in Fig. 4, where a similar plot is given for nitrides.

Perhaps an even better way of predicting trends in the bonding energies is to compare bonding energies for compounds of a group in the periodic table. Thus the ratio of the bonding energies of MoN to WN is 1.090. The same ratio for the silicides Mo_5Si_3 and $WSi_{0.7}$ is 1.087. For the carbides MoC and WC the ratio is 1.091.

There are now enough data and sufficient indication of trends across the periodic table to allow rather good predictions of the heats of formation of refractory compounds.

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References

(1) Robbins, D. A., and Jenkins, I., Acta Met., 3, 598-604 (1955).

(2) Brewer, L., and Krikorian, O. H., J. Electrochem. Soc., 103, 38-51 (1956).

(3) Krikorian, O. H. High-Temperature Studies: I. Reactions of the Refractory Silicides with Carbon and with Nitrogen. II. Thermodynamic Properties of the Carbides. III. Heat of Formation of the $^3\pi_u$ State of C_2 from Graphite. University of California Radiation Laboratory Report UCRL-2888. April, 1955.

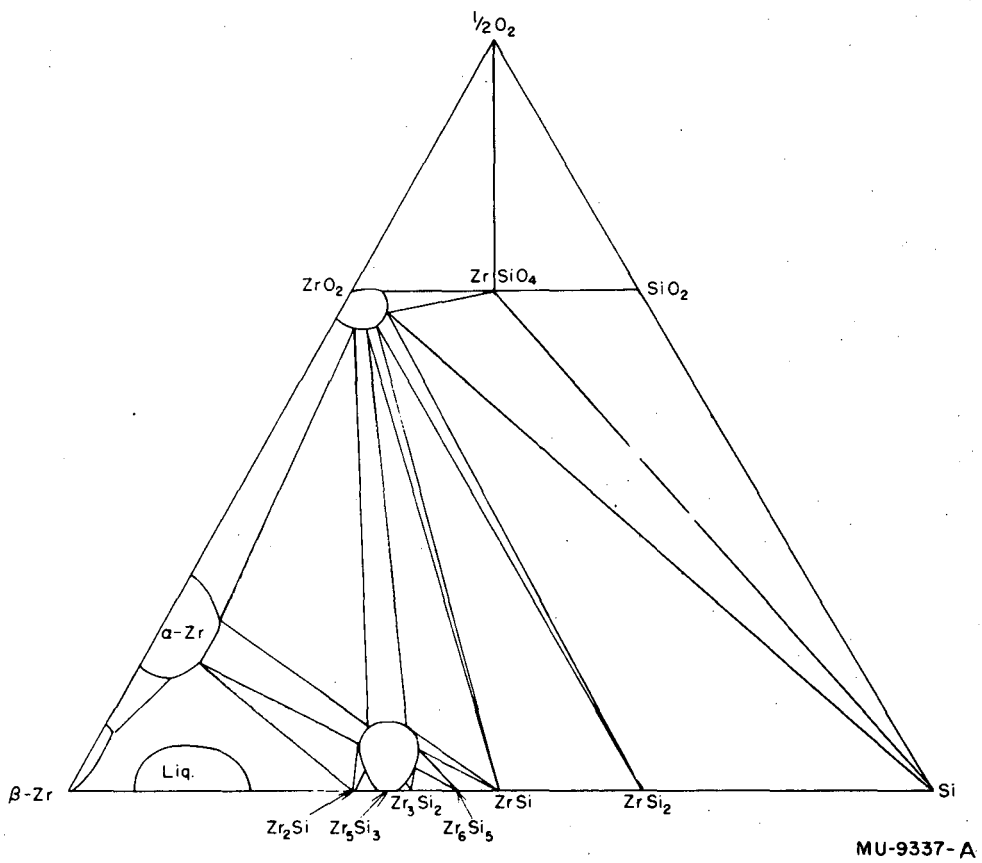

Fig. 1. Provisional diagram of the Zr - Si - O system at 1950° K.

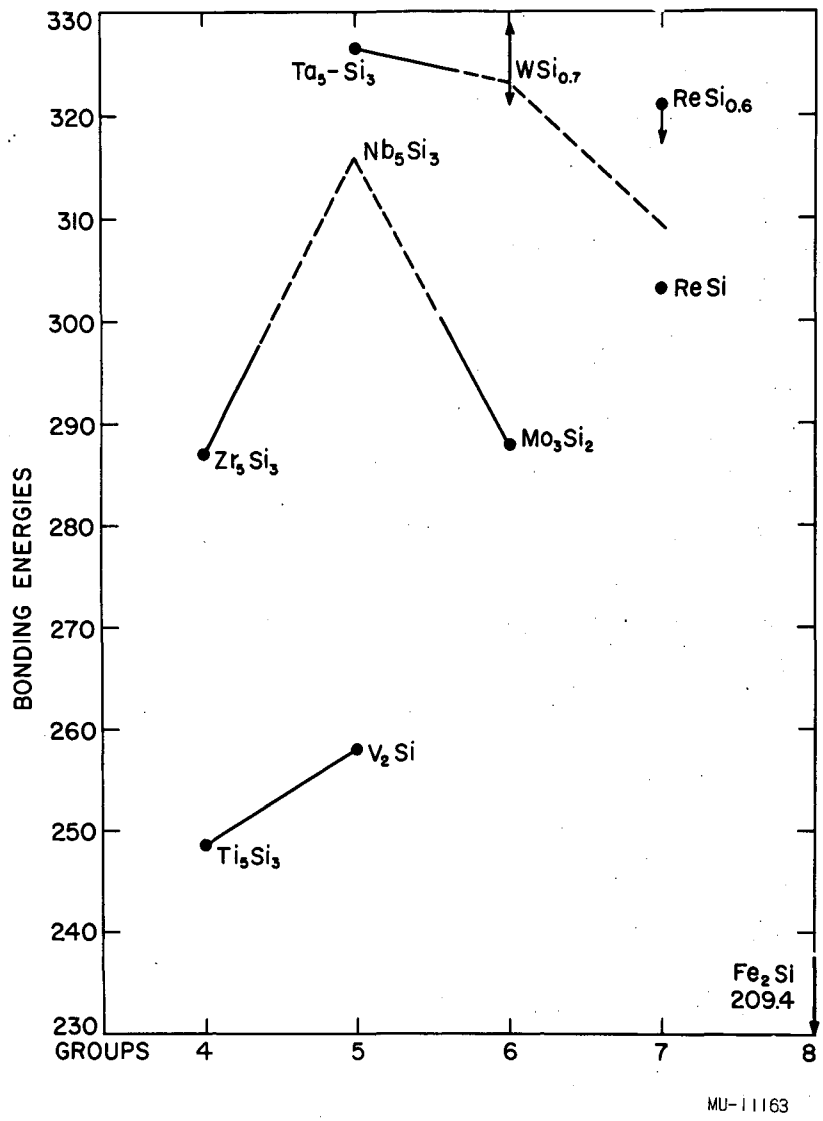

Fig. 2. Bonding energies versus group of periodic table.

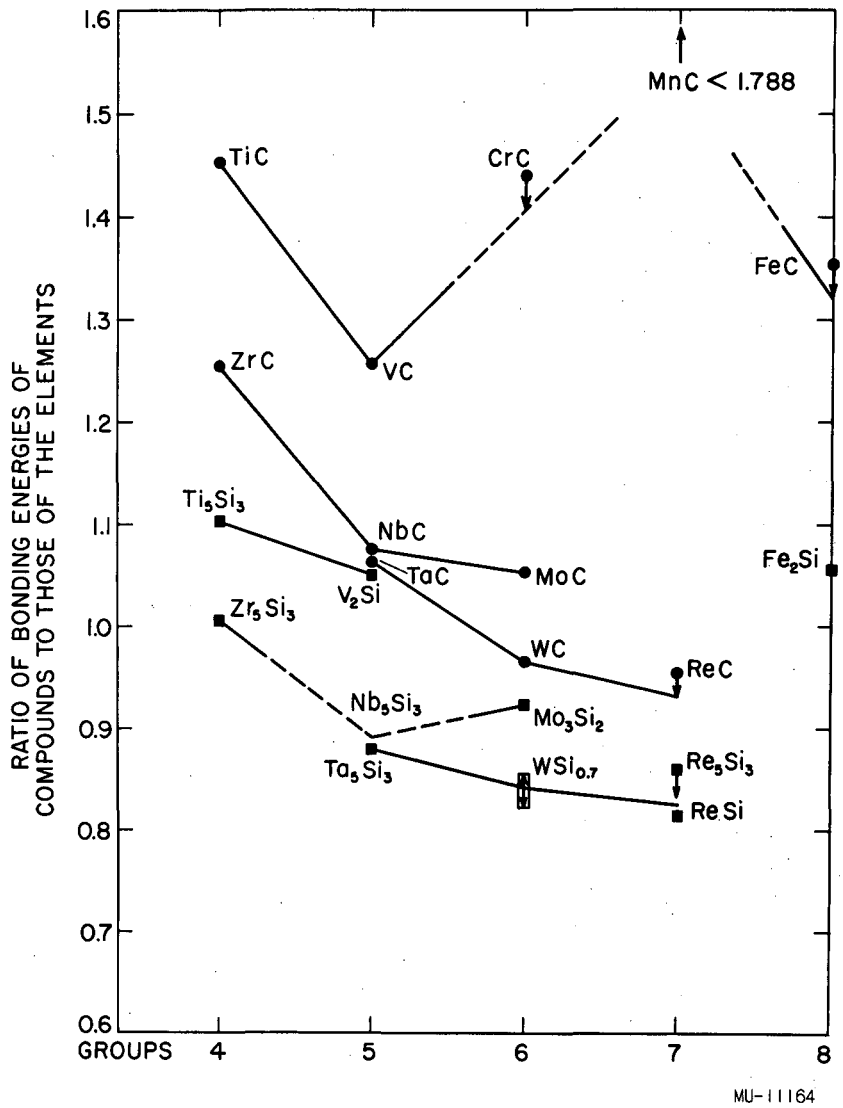

Fig. 3. Ratio of bonding energies of carbides and silicides versus group of periodic table.

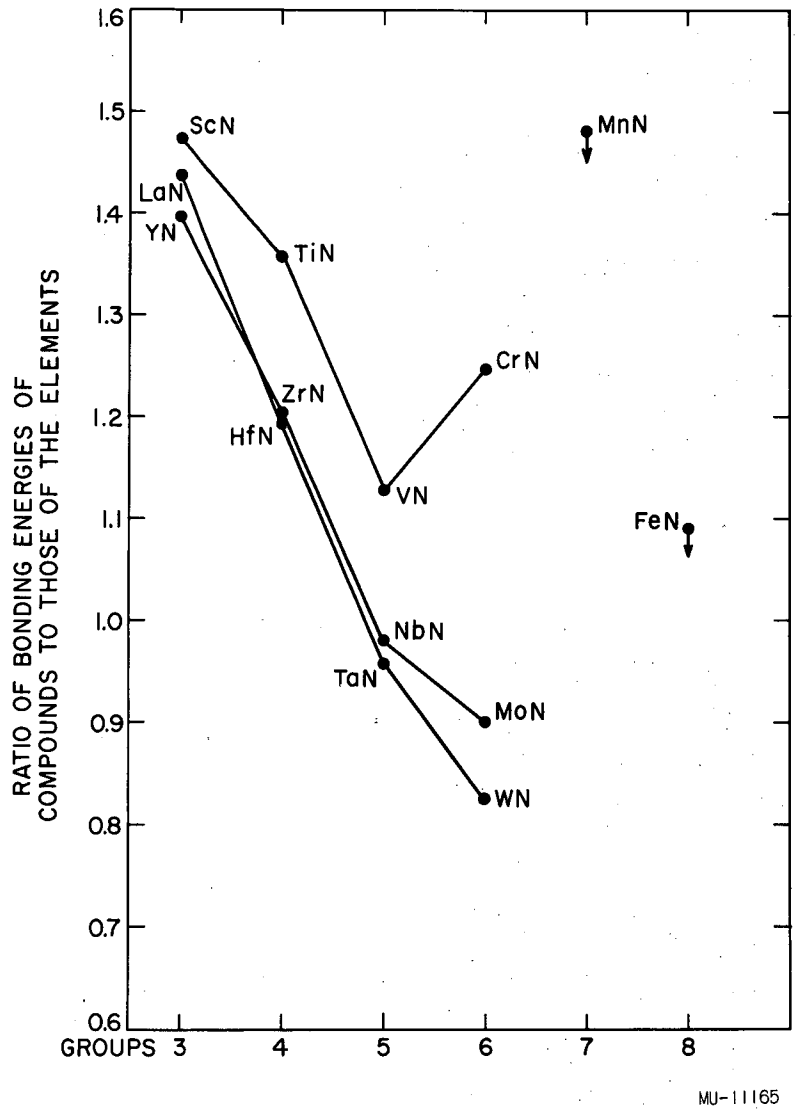

Fig. 4. Ratio of bonding energies of nitrides versus group of periodic table.