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# Computer calculations of heterogeneous equilibria in the system C-O-H-N-Si-Ar

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crystal height increased rapidly in the first 5 min of crystallization time, then proceeded more slowly. Approximately 40% of the height attained in 10 min was reached in 1 min; 75% of this height was reached in 5 min. The width of the lamellae did not vary with crystallization time. These results are in accordance with previous data obtained for epitaxial crystallization of polyethylene [1], and seem to be generally characteristic of solution epitaxial crystallization of polymers.

Selected-area electron diffraction clearly shows the presence of two chain orientations  $90^\circ$  apart (Figs. 1b and 2b). All diffraction patterns obtained indexed as form I, as shown in Fig. 3. All reflections in Fig. 2b index as  $0kl$ , indicating that the  $bc$  plane and thus the chain axis are both parallel to the substrate surface. "Extra" reflections, which do not index as  $0kl$  were occasionally observed (e.g. in Fig. 1b), and probably result from "toppled over" epitaxial crystals which are still more or less oriented with respect to the substrate directions. Patterns containing these "extra" reflections in addition to the usual  $0kl$  reflections were occasionally observed on KCl also. Similar electron diffraction patterns from thinner films (1 and 5 min crystallization times) showed that the same crystal structure (form I) persisted to within 30 Å of the substrate surface.

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C. M. BALIK  
R. FARMER  
ERIC BAER

Department of Macromolecular Science,  
Case Western Reserve University,  
Cleveland, Ohio 44106  
USA

## Computer calculations of heterogeneous equilibria in the system $C-O-H-N-Si-Ar$

In the development of ceramic materials for high-temperature applications there is a great need to establish phase equilibria in order to produce, process, and understand the properties in the service conditions. The understanding of the gas-phase reactions is more important than in the usual metallic systems since:

(1) the materials are usually made in a high surface area, fine powdered form by way of gas-phase reactions;

(2) the successful fabrication by hot-pressing or sintering is often made possible by the presence of a small amount of liquid that may be formed or consumed by gas-phase reactions;

(3) the materials are usually intended to be single phase but the service behaviour is dramatically influenced by the presence of minor amounts of residual grain-boundary phases;

(4) the service conditions are at high temperature and often in chemical environments much different with respect to temperature, pressure, and composition than those of fabrication;

(5) minor changes in the amounts of gas-phase species such as  $O_2$ ,  $H_2$ ,  $N_2$ ,  $SiO$ , etc., can result in dramatic changes in the protective films responsible for high-temperature protection since the materials have many stable gas-phase molecular species and do not react only by evaporation.

In summary it is seldom instructive to deal only with the condensed phase equilibria as in the case of most metallic systems. In fabrication and service conditions there is always a chemically active

TABLE I All species for which data are available in system C—O—H—N—Si—Ar

C	O	H	N	Si	Ar
⟨C⟩ ref.	O <sub>2</sub> ref.	H <sub>2</sub> ref.	N <sub>2</sub> ref.	[Si] ref.	Ar ref.
C	O	H	N	Si	
C <sub>2</sub>	O <sub>3</sub>	H <sup>+</sup>		Si <sub>2</sub>	
C <sub>3</sub>	O <sup>-</sup>	H <sup>-</sup>		Si <sub>3</sub>	
C <sub>4</sub>	O <sub>2</sub> <sup>-</sup>				
C <sub>5</sub>					
C <sup>-</sup>					
C <sub>2</sub> <sup>-</sup>	CO	CH <sub>4</sub>	CN	⟨SiC⟩ β	
	CO <sub>2</sub>	CH <sub>3</sub>	CNN	⟨SiC⟩ α	
	CCO	CH <sub>2</sub>	HCN	SiC	
	C <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CNC	Si <sub>2</sub> C	
	CO <sub>2</sub>	CH	C <sub>2</sub> N <sub>2</sub>	SiC <sub>2</sub>	
		C <sub>2</sub> H <sub>2</sub>	C <sub>4</sub> N <sub>2</sub>		
		C <sub>2</sub> H	CN <sup>-</sup>		
			CN <sup>+</sup>		
CHO	H <sub>2</sub> O	NH	NO	SiO <sub>2</sub>	
CH <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	NH <sub>2</sub>	NO <sub>2</sub>	SiO	
C <sub>2</sub> H <sub>4</sub> O	HO <sub>2</sub>	NH <sub>3</sub>	NO <sub>3</sub>	SiO <sub>2</sub>	
CHN	OH	N <sub>2</sub> H <sub>2</sub> (c)	N <sub>2</sub> O		
C <sub>4</sub> H <sub>12</sub> Si	OH <sup>+</sup>	N <sub>2</sub> H <sub>2</sub> (t)	N <sub>2</sub> O <sub>3</sub>		
	OH <sup>-</sup>	N <sub>2</sub> H <sub>4</sub>	N <sub>2</sub> O <sub>4</sub>	SiH	
	H <sub>3</sub> O <sup>+</sup>		N <sub>2</sub> O <sub>5</sub>	SiH <sub>4</sub>	
CHNO			NO <sub>2</sub> <sup>-</sup>		
	HNO		NO <sup>+</sup>		
	HNO <sub>2</sub> (t)			⟨Si <sub>3</sub> N <sub>4</sub> ⟩ β	
	HNO <sub>2</sub> (c)			⟨Si <sub>3</sub> N <sub>4</sub> ⟩ α	
	HNO <sub>3</sub>			SiN	
[Si—C]	[Si <sub>2</sub> N <sub>2</sub> O—SiO <sub>2</sub> ]				

Elements — 6

⟨ ⟩ = solid

[ ] = liquid

gas phase present. When one considers the usual available high-temperature furnaces and the impurities introduced from the furnace hardware, atmospheres and surface contaminants, the minimum system of interest involves a range of pressure from vacuum to near 1 atm, a range of temperature from 1000 to 2000 K, and at least the chemical constituents C, O, H and N. It is usually desirable to include an inert species such as argon to provide the possibility of an additional degree of freedom which is always present in real systems of interest. Of course, beside this minimum set of important environmental elements, one must consider other major elements which for the current materials include at least Si and usually others such as Al and Zr. Obviously, such systems are very complicated and this complication explains much of the difficulty in reproducibly making materials and understanding their service behaviour. This letter attempts to present a method of calculation and presentation of equilibrium data

in one system of interest, namely C—O—H—N—Si—Ar.

Fortunately, the temperatures of interest are high enough that gas-phase equilibrium can usually be presumed. However, due to the inherent complexity, little is learned from the treatment of individual chemical equilibria. For example, considering only Si—O—C there are twelve independent reactions that can be written between the known important gas and condensed phase species [1]. Even so, this treatment does not include possible solution phases or many of the now well-known gas species. Another method of attack has been made possible by the high-speed computer coupled with the growing availability of thermochemical data for species of interest. Several calculation schemes have been employed but all are basically minimizations of the overall free energy of a system constrained by temperature, pressure, and the masses of the components. The method used here is essentially that of Eriksson [2] with

modifications to fit the local computer system. In order to proceed, free-energy data are required at the temperatures of interest for all species. The amounts of the components are specified and the program then finds the amounts of each species that gives the lowest free-energy for the total system with the chosen constraints. Equilibrium between all species and phases is presumed.

While the computer program is quite effective in performing the free-energy minimization, it is not yet coupled with a data base and, therefore, the necessary data must be located, assessed, prepared, and inserted manually.

As with all thermodynamic calculations, the location and selection of data constitutes a major problem. In this case it is even more severe due to the large number of potentially important species. The following procedure was adopted: for the six elements considered, the JANAF tables [3] were consulted for all species known. This, together with more recent data from Hendry [4] and phase-diagram studies by Gauckler *et al.* [5], indicated that 70 gas species, 14 ion, 6 condensed phases of fixed stoichiometry, and 2 condensed solutions should be considered. Table I gives a summary of these species.

Considerable attention was given to formulating a simple method to eliminate from consideration species that ultimately would not be of interest in the final result. Such a rule would be of obvious utility in the later coupling of this method to computerized data bases. Unfortunately, all general attempts failed. For example even if a species will be present at equilibrium at a stoichiometrically negligible level, e.g.  $O_2$  or  $Si_2C$ , it is still not desirable to eliminate it from consideration. The amount may be small but the changes in one minor species relative to other minor species may be important. A positive  $\Delta G_F^0$  is also not a safe method for elimination of a species. In short there is always some range of conditions in the system where every species can be important. If a total range of conditions of interest can be specified, some species may, however, be safely eliminated.

In defining a total range of interest, it is necessary to establish bounds on the range of composition or element activities and the temperature and pressure ranges that will ever be encountered in situations of fabrication or service. Full attention should be given to the fact that most situ-

ations of interest are not isothermal or isobaric with respect to the gas phase. For example, the gas phase may be in equilibrium with the sample and furnace hardware in the hot zone but also react with other parts of the system at different temperatures, such as in cold wall furnaces. Also, the pressure conditions within the fine pores of a sintered compact will be very different to those in the furnace, particularly in vacuum furnaces where the total pressures are low and, therefore, the mean free paths of gas species are comparable or larger than the specimen pores.

In the system mentioned, the ranges of interest were chosen as listed in Table II. Also given in Table II are indications of the basis for fixing each range.

With these ranges it is possible to eliminate some, but perhaps not all of the unimportant species. For the condensed phases the most stable form was included except that both  $\alpha$  and  $\beta$  forms of  $SiC$  and  $Si_3N_4$  were retained since their stability difference is quite small. In the case of  $SiO_2$ , only the glass phase was included since it is known to be of primary importance relative to the crystal forms for kinetic reasons. The liquid solution of  $Si$  was treated as pure  $Si$  since the solubilities in it are known to be small and the thermodynamic data are unknown. The solution of  $Si_3N_4$  in  $SiO_2$  was included since it is known to exist [5]. It was assumed ideal due to lack of other data. For the gas phase, the most stable gas species for each element was included as well as the most stable gas species with a given set of elements. A species was excluded if consideration of a single equilibrium reaction showed that nowhere in the total range of interest can the species be present at equilibrium in an amount equal to at least 1% of another included species with the same elements. For example, the individual carbon gas species were calculated for the case of unit activity carbon where each achieves its maximum level. In this way  $C_4$  and  $C_5$  can be ruled out since they can never be as much as 1% of the most prevalent carbon species. This procedure undoubtedly includes more species ( $C$ ,  $C_2$ ,  $C_3$ ) than may be necessary, but none the less is able to cut the total appreciably.

Several preliminary calculations were run to show that all the ions were completely negligible with respect to species of the same elements when

TABLE II Range of interest for the system C–O–H–N–Si–Ar

Temperature	1700–2800 K	Usual processing or service temperature
Gas total pressure	$10^{-8}$ to 1 bar	Vacuum to normal Furnace limits
<i>Activities</i>		
Carbon $a_C = 1$ (graphite)	$10^{-8}$ to 1 bar	From hydrocarbon impurity to graphite furnace parts
Oxygen	$10^{-30}$ to 1 bar	From vacuum–carbon furnace to air environment
Hydrogen	$10^{-8}$ to 1 bar	From residual pump down in vacuum furnace to $H_2$ sintering
Nitrogen	$10^{-6}$ to 1 bar	From nitrogen gas impurity on pump down to $N_2$ atmospheres
Silicon $a_{Si} = 1$ (liquid)	$10^{-8}$ to 1 bar	From decomposition of SiC or $Si_3N_4$ to liquid-phase reaction
Argon	$10^{-8}$ to 1 bar	From impurity or pump down to inert sintering
Charge	Assume no voltages present and no total charge	

TABLE III Species of interest in system C–O–H–N–Si–Ar

C	O	H	N	Si	Ar
(C) ref.	O <sub>2</sub> ref.	H <sub>2</sub> ref.	N <sub>2</sub> ref.	[Si] ref.	Ar ref.
C	O	H	N	Si	
C <sub>2</sub>				Si <sub>2</sub>	
C <sub>3</sub>	CO	CH <sub>4</sub>	CN	(SiC) $\beta$	
	CO <sub>2</sub>	CH <sub>3</sub>	C <sub>2</sub> N <sub>2</sub>	(SiC) $\alpha$	
		CH <sub>2</sub>		SiC	
	H <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub>	NO	Si <sub>2</sub> C	
	HO	CH		SiC <sub>2</sub>	
		C <sub>2</sub> H <sub>2</sub>			
		C <sub>2</sub> H		SiO	
				SiO <sub>2</sub>	
		NH <sub>2</sub>			
CHO	HNO	NH <sub>3</sub>		SiH	
CH <sub>2</sub> O	HNO <sub>2</sub> (t)			SiH <sub>4</sub>	
CHN				(Si <sub>3</sub> N <sub>4</sub> ) $\beta$	
CHNO				(Si <sub>3</sub> N <sub>4</sub> ) $\alpha$	
	[Si <sub>2</sub> N <sub>2</sub> ]-SiO <sub>2</sub> ]			SiN	
				Si <sub>2</sub> N	
Elements	6	Condensed 6	( ) = solid	[ ] = liquid	
Gas phase	43	Condensed sol. 1			

the system is uncharged. Therefore, all ions were neglected. Table III shows the final system considered which has been narrowed to 6 elements, 1 condensed solution phase, 6 condensed phases of fixed stoichiometry and 43 gas species. The tabular free-energy data were fitted by least squares to a two-term equation which reproduces the data for all species to within 1% over the temperature range of interest.

The confines of tri-space are a great restriction on the talents of the thermodynamicist. The lengthy tables of free-energy data with the help of the computer can relatively easily be transformed into more lengthy tables of equilibrium results, but little is gained until these results can be summarized into an easily digested presentation that

allows the materials scientist to assess results over whole ranges of related conditions. In simple systems this presentation is quite well handled by the conventional phase diagrams. For a six component system a new approach must be sought. In short, present day equilibria calculations are far ahead of the ability to present the results in a coherent way.

One possible approach is that of "phase stability diagrams" (PSD), outlined by Williams [6]. These diagrams can, by restricting attention to a single composition, give the amount of the various phases present as a function of temperature or pressure. While this is not completely satisfactory

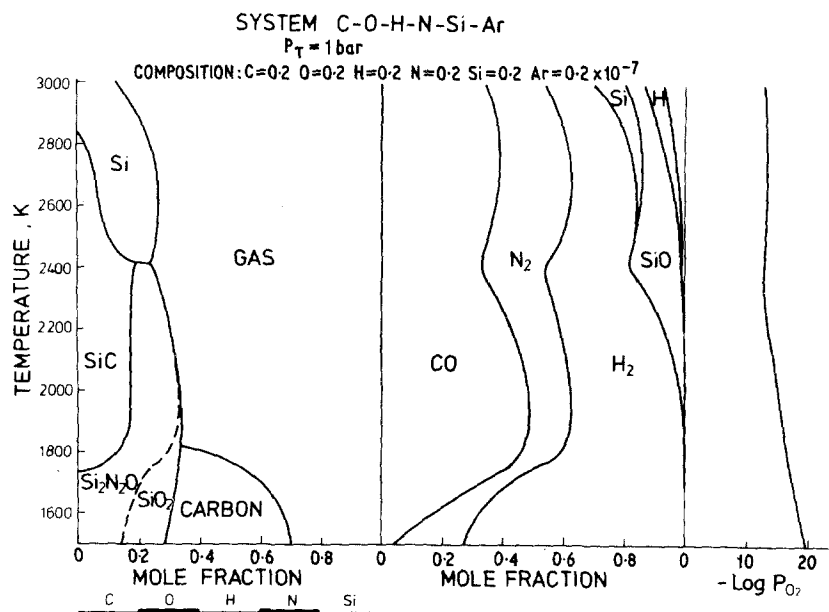


Figure 1 Calculated phase equilibria in the system C-O-H-N-Si-Ar at  $P_T = 1$  bar, composition: C = 0.2, O = 0.2, H = 0.2, N = 0.2, Si = 0.2, Ar =  $0.2 \times 10^{-7}$ .

it is very useful, particularly when the phases are of fixed composition as is usually true in ceramic systems. In this way many pages of computer output can be condensed to one page. An example of such a diagram is shown in Fig. 1.

In this diagram the total pressure is fixed at 1 atm and the composition is chosen to be equal amounts of C, O, H, N, Si and a small ( $0.2 \times 10^{-7}$  mole fraction) of Ar. At the lower left the starting composition in terms of atom fraction is shown. Of course the starting form of the element is unimportant to the calculated result.

The fraction of each phase present at a given temperature can be seen directly as the horizontal length of each field. In the case of the solution phase  $\text{Si}_2\text{N}_2\text{O}-\text{SiO}_2$  the fraction  $\text{Si}_2\text{N}_2\text{O}$  is given by the dashed line within the phase field. For the gas phase, two additional plots are convenient. First, the mole fraction of major constituents ( $> 1$  mol %) are given in a supplementary diagram immediately to the right, while any minor species of interest may be represented on a log scale in yet another region to the right. This has been illustrated with  $P_{\text{O}_2}$ .

Since the potential reactions are significantly influenced by total pressure, a more complete three-dimensional diagram may be useful, where  $P_T$  is plotted in a third dimension. The more complete diagram has not yet been calculated, but

several results at  $2000^\circ\text{C}$  show that at  $P_T = 10^{-2}$  bar the oxynitride phase disappears and below  $P_T = 10^{-5}$  atm bar, the system is all gas.

It also should be noted that from about 1725 to 1825 K this system shows three condensed phases as well as the gas phase. This in no way violates the Gibbs phase rule due to the many degrees of freedom present in a six-component system. Also the exact shape of the fields in the region at about 2425 K has not been established.

Several somewhat surprising results are found through examination of the minor species present. First, at all temperatures the atomic oxygen exceeds the molecular oxygen by 4 to 5 orders of magnitude. Also, in some ranges there are many constituents present in amounts of about 1%. Examples are  $\text{Si}_2\text{C}$ ,  $\text{SiC}_2$ ,  $\text{HCN}$ . These have not been shown in the diagrams but may, in some cases, be of particular interest when one or more minor constituents is suspected of being kinetically important to a phase change.

The greatest problem in application of complex phase equilibria calculations is the translation of the experimental conditions into the most appropriate thermodynamic constraints. A continued study will attempt to solve several problems relevant to ceramic processing by considering system compositions approximating those in the laboratory.

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L. GAUCKLER\*

E. HUCKE†

H. L. LUKAS

G. PETZOW

Max-Planck-Institut für Metallforschung,  
Institut für Werkstoffwissenschaften,  
Heisenbergstrasse 5,  
D-7000 Stuttgart-80, Germany

\*Now with Swiss Aluminium Ltd. Research and Development, CH-8212 Neuhausen, Switzerland.

†University of Michigan, Materials and Metallurgical Engineering, Ann Arbor, Mich 48109, USA.

### High-temperature compatibility of pyrolytic carbon with nickel-copper alloys

Compatibilities of carbon fibres and pyrolytic carbon with pure nickel at elevated temperatures were discussed in detail in our previous papers [1–3]. A migrating nickel layer was observed in each sample of carbon. Graphitization was caused by the catalytic reaction of the nickel layer. Degradation of carbon fibres by the graphitization was observed. The rate determining step of the graphitization was the diffusion of carbon atoms in nickel. A carbon fibre–nickel composite material with higher stability at elevated temperatures could be obtained if the diffusion could be prevented.

In the present work, the effect of adding copper to nickel on the migration rate of the metal layer was examined. As carbon does not diffuse through solid copper, its solubility in copper must be exceedingly small [4]. Therefore solubility and diffusivity of carbon should be affected and should be decreased by the alloying, when copper is added to nickel.

Pyrolytic carbon ( $c_0 = 6.85 \text{ \AA}$ ), which was obtained by pyrolysis of methane, was used as a sample. Copper was electro-plated on the polished surface of the pyrolytic carbon and afterward nickel was electro-plated. An ordinary copper bath based on copper sulphate and an ordinary hard nickel bath based on nickel sulphate were used for the electro-platings. Both the electro-platings were

carried out at room temperature with a current density of  $0.2 \text{ A dm}^{-2}$ . The total thickness of the double electro-plated layer was  $0.8 \mu\text{m}$  for all samples. The plated thickness of each metal was controlled by varying the electroplating time according to the required copper concentration (5, 10, 20 at %, respectively) in the alloy.

The double plated carbon samples were kept at  $450^\circ \text{C}$  for 1 h in a vacuum of  $2 \times 10^{-5} \text{ mm Hg}$  to allow tight adherence at the carbon–copper and copper–nickel interfaces. No reaction or inter-diffusion was observed at either of the interfaces during heat treatment.

A heat treatment temperature of  $1000^\circ \text{C}$  was found to be appropriate for observing the

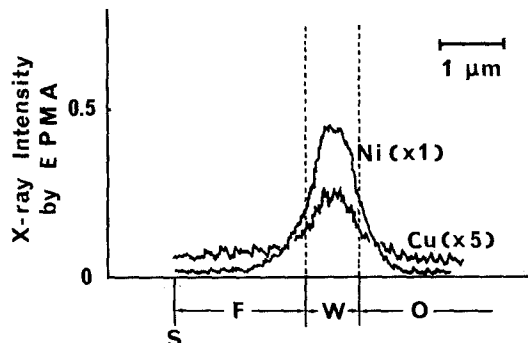


Figure 1 X-ray intensities of nickel and copper by EPMA. The carbon with Ni–Cu(10 at %) was held by  $1000^\circ \text{C}$  for 16 h. S: surface of the pyrolytic carbon; F: flakey area; W: white layer, i.e. alloy layer; O: original pyrolytic carbon.