Thermodynamic Analysis on Interactions of Silicon Dioxide with Iridium during Module Reduction and Monitoring Treatment

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Abstract

The goal of this work was to understand the possible reactions between Ir and SiO_2 contaminants in the presence of C (graphite insulation) and a cover gas for conditions representative of those for a Module Reduction and Monitoring (MRM) treatment at 1410 K. This treatment is for reduction of $^{238}PuO_2$ fuel used in isotopic heat sources for space missions. A thermodynamic analysis has been performed for the relevant portions of the Ir-Si-C-O phase diagram using the CALPHAD method.

The results show that over the range of relevant pressures of CO and CO_2 in the argon cover gas, SiO_2 is not stable in the presence of Ir. Levels of Si impurity dissolved in the iridium solid solution are expected to be up to 875 μg/g at or near the surface.

Introduction

An iridium alloy, containing 3000μg/g W, 60 μg/g Th, and 50μg/g Al, is as used as a cladding to encapsulate $^{238}PuO_2$ fuel pellets used in isotopic heat sources for space missions. The alloy is produced at Oak Ridge National Laboratory with typical elemental impurity contents of 10 μ/g/g. Some fueled capsules have been found to contain small silicon containing particles, presumed to be SiO_2, on the outer surface of the capsule. An analysis was conducted to understand the possible reactions between the Ir alloy cladding material and a SiO_2 impurity during subsequent processing at elevated temperature in a Module Reduction and Monitoring (MRM) treatment [1]. In this treatment the iridium-alloy fueled clad, surrounded by a carbon fiber insulation material and other carbon components, is placed in a stainless-steel container, which is periodically evacuated and backfilled with high purity argon. Over the course of the treatment oxygen outgasses from the fuel, flows out of the clad through the frit vent, and reacts with the carbon insulation material to produce reaction products of CO and CO_2 gas. The purpose of this is to reduce the oxygen stoichiometry of the plutonia fuel and minimize further oxygen outgassing during storage of the heat source. All heat is provided by the nuclear decay of the fuel material and large temperature gradients exist in the system. A fuel clad temperature of 1410 ± 25 K was calculated from thermal properties of the materials due to experimental limitations on temperature measurement within the system [2]. Typical measured argon gas composition at the completion of the treatment is 0.0016 atm CO and 0.0001 atm CO_2, values consistent with the calculated temperature of the outermost carbon components of 860 ± 25 K. Knowledge of the quaternary Ir-Si-C-O phase diagram is an essential first step to understand the

reaction at elevated temperature of SiO_2 on an iridium surface in the MRM treatment environment of graphitic materials and an argon cover gas with specific low levels of CO and CO_2 gases.

Methodology

There is no phase diagram or thermodynamic information about this quaternary in the literature. Therefore, the CALPHAD (CALculation of PHAse Diagram) methodology [3-8] was used in this work to develop a thermodynamic database of Ir-Si-O-C. The essence of the CALPHAD approach is to simultaneously evaluate all available thermochemical and constitutional data for the system and then obtain one set of model equations for the Gibbs free energies of all phases as functions of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams of interest can be calculated. The alloying elements of W, Th, and Al in the iridium cladding were assumed to have negligible effect on this analysis because their levels are too low.

The data for all chemical reactions between the elements Ir, Si, C, and O used in the phase diagram calculations were taken from standard commercially available databases with the exception of the reactions between Ir and Si since these are not present in any of the available databases. The Ir-Si-C-O quaternary database was developed from thermodynamic descriptions of the constituent unaries, binaries and ternaries as follows:

- Thermodynamic properties of all pure elements were taken from the SGTE pure element database [9].
- Thermodynamic properties of the various solution and compound phases of Ir-O, Ir-C, Si-C, Si-O and C-O were adopted from the SGTE SSOL4 and SSUB3 databases [10].
- The Ir-Si binary model was developed in this study.

- Thermodynamic properties of ternary and quaternary systems were obtained by extrapolation from the lower order systems, assuming no ternary compounds and negligible higher-order interactions.

Thermodynamic properties of the Ir-Si binary were modeled for this study, either from published data on the iridium silicides, or were estimated using generally accepted methods used in database generation based on published phase diagram information and/or published data for the analogous Pt-Si system. The binary phase diagram, based on available experimental data [11], is shown in Fig. 1. The thermodynamic model of the Ir-Si binary used in this study includes three phases: (a) the iridium-silicon solid solution with the face centered cubic (FCC) structure, (b) the iridium-rich intermetallic compound of composition Ir_3Si, and (c) the intermetallic phase of composition IrSi. The other Ir-Si metallic phases were not included due to lack of any available data. This is not expected to have any important effect since the compositions of interest are those that are rich in Ir relative to the Si content.

The enthalpy of formation of the IrSi compound has been experimentally measured and is reported as -63.8±3.7 and -64.4±2.6 (KJ/mol·atoms) in [12]. An average value of 64.1 was used for IrSi in this work. The enthalpy of formation of Ir_3Si was estimated based on the similarity between the Pt-Si and Ir-Si systems, similar crystal structures, and the availability of thermodynamic data for Pt-Si [13], as shown in Table 1. The entropy of formation of IrSi and Ir_3Si is assumed to be the same as that of PtSi and Pt_3Si compounds. The estimated enthalpies and entropies for IrSi and Ir_3Si are consistent with the relationship found in other transitional metal silicides suggested by Chart [14].

Table 1. Thermodynamic Properties Used in the Estimation of the Enthalpy of Formation of Ir_3Si

	PtSi	IrSi	Pt_3Si	Ir_3Si
Crystal structure	(orth)MnP	(orth)MnP	(tetr)U_3Si	(tetr)U_3Si
Enthalpy of formation (KJ/mol atom)	-65.8 [12]	-63.8±3.7 -64.4±2.6[11]	-45.0 [12]	-44.0[13]

The thermodynamics of Si solubility in iridium are of particular interest in this study. This solubility is constrained by the stability of the neighboring compound Ir_3Si. In this study, the solid solution of Si in Ir is represented as (Ir). The mixing energy of Si with Ir is optimized based on the experimental solvus of (Ir) shown in the Ir-Si binary phase diagram in Fig. 1. The equation for the Gibbs free energy of the Ir solid solution is written below:

$$G_{Ir,Si}^{Fcc} = x_{Ir}G_{Ir}^{Fcc} + x_{Si}G_{Si}^{Fcc} + RT(x_{Ir}\ln(x_{Ir}) + x_{Si}\ln(x_{Si})) + L(x_{Ir}x_{Si}) \quad (1)$$

Where G is the Gibbs free energy, x is the mole fraction, R is the universal gas constant, T is the absolute temperature and L is the fitting parameter. An optimized value for the "L" parameter is obtained when the Gibbs energy can best reproduce the (Ir) solvus.

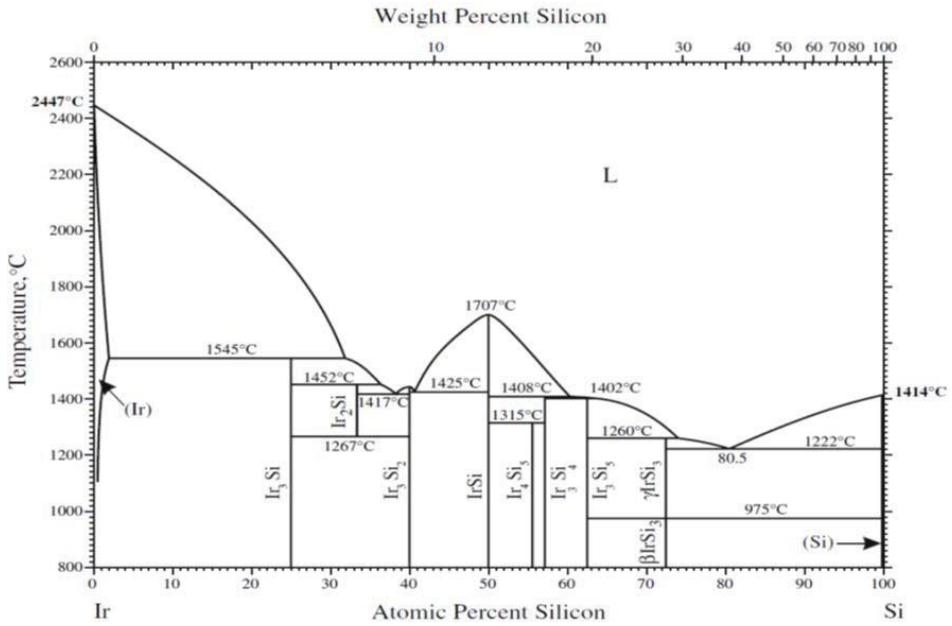

Fig. 1. Assessed phase diagram of Ir-Si [4]

Phase diagram calculations were made using the Pandat thermodynamic software [15]. Calculations were made for the region of the Ir-Si-O-C quaternary phase diagram relevant to the local equilibrium at the surface of the iridium in contact with varying amounts of SiO_2 and surrounded by a large quantity of carbon as graphite. Since the iridium alloy is either in contact with carbon or is in equilibrium with the cover gas, which is also in equilibrium with carbon, only the portion of the phase diagram in which graphite is a stable phase was considered relevant to the MRM treatment conditions.

The composition of the cover gas in the MRM treatment can have an important effect on the calculation of the phases present and phase compositions. Although the cover gas is introduced as purified argon, the composition changes with time and temperature as the oxygen outgases and the stoichiometry of the plutonia fuel is reduced by periodic replacement with fresh purified argon. The pressures selected for evaluation in this study were based on the measured tap partial pressures reported for the MRM cycle in literature [2]. As the argon is inert it does not affect the thermodynamics and is not directly included in the system model. Therefore, the gas phase is modeled as a low-pressure environment in which the total pressures of the gases, primarily CO and CO_2, are simulated based on the measured partial pressures of these gases in the argon gas samples. This methodology has no significant effect on the predicted phase stability or equilibrium compositions. The presence of argon gas can have effects on kinetics of mass transfer in the gas as well as effects on heat transfer, which is a subject beyond the scope of this study. The phase equilibria were calculated for total gas pressure values in the range of 0.001 to 1.0 atm. The details of the relationship of this total gas pressure at the iridium surface in this thermodynamic model to the measured gas partial pressures in reference [2] are discussed in a subsequent section of this report.

Results

The relevant isothermal section of the Ir-Si-C-O phase diagram at 1410 K calculated using the developed thermodynamic database is shown in Fig. 2. The calculation was done at 1410K and fixed x(C) at 0.5. The y-axis is the total pressure change and the x-axis is from 0.5 mole of Ir to 0.5 mole of SiO_2. This temperature is selected based on the calculated value of the iridium surface during MRM treatment. The weight fraction of Si, defined as the overall weight fraction of Si divided by the sum of the overall weight fraction of Si and Ir, varies over five orders of magnitude in Fig. 2. The equilibrium phases were calculated for total pressures of the non-inert gases of 0.001, 0.01, 0.1, and 1 atm. In all cases the gas phase is essentially CO, that is 99.8% or greater of the total pressure in atm. The calculated partial pressure of CO_2 gas is 0.0015 atm when the CO pressure is 1 atm and decreases as the square of the CO pressure to a value of 1.5 x 10^{-9} atm for a CO pressure of 0.001 atm. At 1410 K the only other gas species present at levels greater than 10^{-10} atm is SiO. A pressure of SiO of 1.2 x 10^{-6} atm is calculated for a metal mole fraction of silicon of 0.57 at a total (or CO) pressure of 0.001 atm and is less than 10^{-7} atm for other conditions calculated.

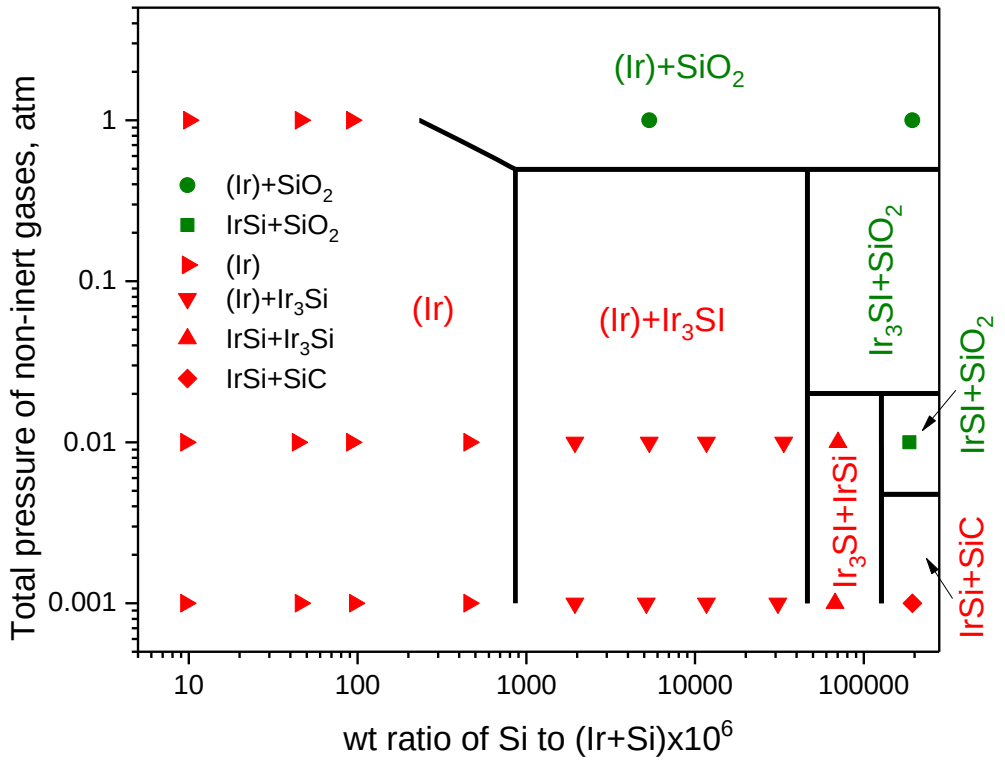

Fig. 2. Calculated isothermal section at 1410 K of Ir-Si-C-O phase diagram for phases in equilibrium with graphite and gas.

The calculated silicon content in the Ir solid solution is shown as function of the overall Silicon to (Iridium+Silicon) ratio at the various gas pressures. At a total gas pressure of 1 atm the Si dissolved in Ir increases with initial Si content up to 260 µg/g. At higher Si content SiO_2 is in equilibrium with iridium solid solution. At 0.01 atm and all lower total pressures SiO_2 is not stable and the Si dissolved in Ir increases with initial Si content up to 875 µg/g. At higher Si content Ir_3Si is in equilibrium with iridium solid solution with this same Si level. Both horizontal lines extend to higher silicon contents up to the respective phase boundaries shown in Fig. 2.

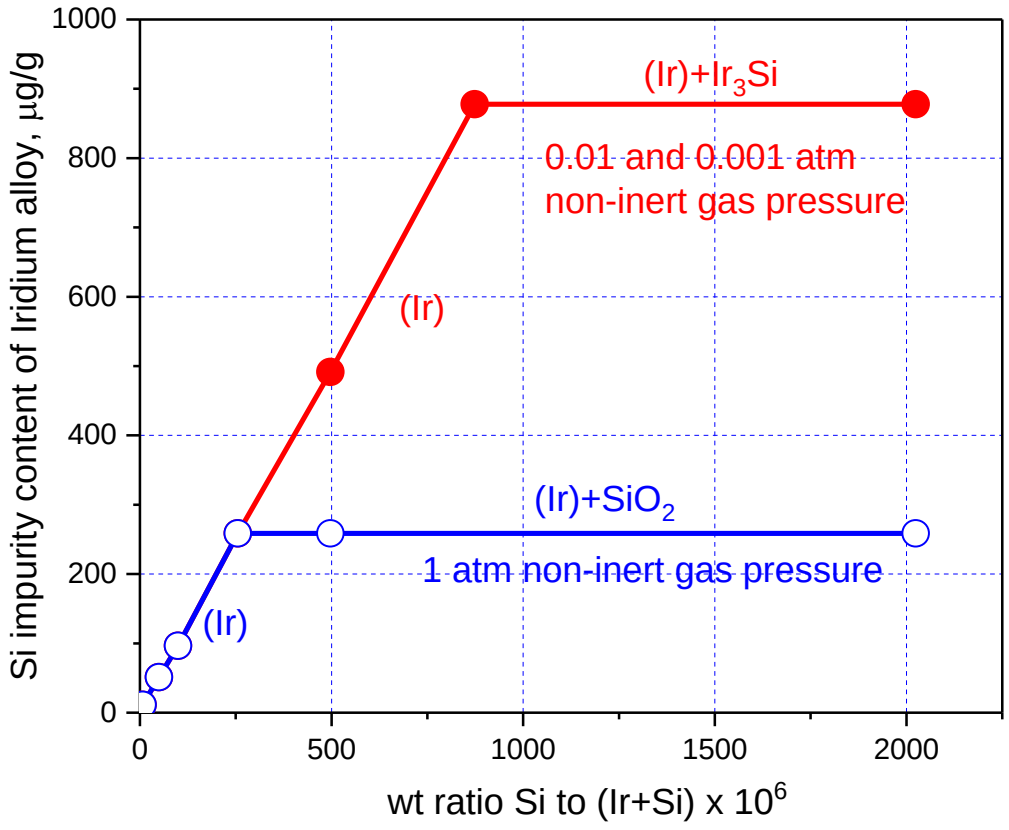

Fig. 3. Dependence of Si impurity content of iridium alloy on overall Si content in equilibrium with graphite and gas at 1410 K.

Discussion

These results are applicable to conditions at the surface of the iridium alloy fuel clad with SiO_2 surface contamination during exposure in the MRM treatment. The measured compositions of the gas as it exits the stainless steel can and the O to Pu ratio of the fuel reported in ref. [2] are reproduced in Table 2. Early in the treatment outgassing of oxygen from the fuel produces similar and relatively high pressures of CO and CO_2, indicative of a relatively oxidizing environment. By the end of the cycle outgassing of oxygen from the fuel is greatly diminished, the CO pressure is much reduced (by a factor of approximately 20), and the pressure of CO_2 is dramatically decreased (by a factor of approximately 300). This is indicative of a relatively reducing environment.

The gas was assumed to be in equilibrium with graphite at the temperature of the insulation just before the gas exited the can. This temperature was estimated in reference [2] to be 860 K based on the ratio of the pressures of CO to CO_2. But the iridium surface temperature is higher (1410 K). In order to estimate the gas composition at this higher temperature, it is assumed that there is a quasi-equilibrium of this gas with the measured gas at an estimated temperature of 860 K. This quasi-equilibrium assumes that the gas circulates within the can and that the gas composition changes such that it is in local equilibrium with carbon. The CO_2 present in the gas at lower temperatures reacts with the insulation to form CO at the higher temperatures. The total gas pressure at the iridium surface at 1410 K is equivalent to the CO pressure because calculated gas compositions are all 0.998 mole fraction CO or greater for all conditions of this study. The total gas pressure is then estimated using Equation 2 with the resulting values shown in the last column of Table 2.

$$p(\text{total, 1410 K}) = p(\text{CO, 1410 K C}) = p(\text{CO, meas}) + 2 \times p(CO_2, \text{meas}) \quad (2)$$

Table 2. Estimation of Gas Pressure at the Iridium Surface During MRM Treatment from Data of ref. [2]

		Measured Pressure, atm			Estimated Pressure, atm
Gas tap no.	0/Pu ratio	CO	CO_2	$CO+CO_2$	CO at 1410 K
1	1.99973	0.0326	0.031	0.064	0.095
2	1.99953	0.0396	0.0159	0.056	0.071
3	1.99945	0.0197	0.0037	0.023	0.027
4	1.99942	0.0075	0.0008	0.0083	0.0091
5	1.99941	0.0016	0.0001	0.0017	0.0018

The results of this study indicate that SiO_2 will not be stable on the surface of iridium during the MRM treatment. At pressures of 0.005 atm or less, characteristic of the end stage of the MRM treatment, SiO_2 will react to form SiC even in the absence of Ir. At higher pressures up to 0.1 atm, characteristic of the early and middle stages of the MRM treatment, SiO_2 may exist on the surface initially in equilibrium with the Ir_3Si or IrSi intermetallic phase as indicated by the Si- rich side of the phase diagram in Fig 2. However, the intermetallic phase will be in contact with the (Ir) phase with Si contents calculated to be 875 μg/g. Diffusion of Si into the iridium subsurface over the course of time will lower the Si content at the surface and consume the SiO_2. The phases present with increasing depth will follow those shown on a horizontal line extending from the right to the left of Fig 2 for any given pressure. As an example, at a total pressure of 0.01atm initially the surface is SiO_2 transitioning to IrSi, Ir_3Si, and (Ir) with increasing depth. As the exposure continues diffusion of Si into the Ir subsurface moves the location on the diagram to the left indicating dissolution of SiO_2 until the stable phase at the surface becomes IrSi. Further diffusion may deplete the intermetallic phase until the

surface contains only (Ir) with a Si impurity content that follows the plot in Fig 3. With additional time the Si content at the surface will continue to decrease.

The uncertainties in the results of this study are primarily attributable to uncertainties in the thermodynamic and phase diagram data used in the model. The most important of these is the solubility data for Si in (Ir) as a function of temperature obtained from the published phase diagram. The omission of the intermediate Ir-Si intermetallic compound Ir_3Si_2 from this analysis results in some error in the phase stability in the region of Figure 3 labeled as "IrSi + Ir_3Si". Including Ir_3Si_2 will likely introduce new phase equilibria of Ir_3Si+Ir_3Si_2 and Ir_3Si_2+IrSi . The new phase equilibrium will not affect the phase equilibrium between (Ir)+Ir_3Si, For the currently relevant problem where the Si solubility in (Ir) is limited by the phase equilibrium of (Ir)+SiO_2 at high non-inert gas pressure and (Ir)+Ir_3Si at low pressure, therefore, the missing of Ir3Si2 won't change the overall conclusions of this analysis.

Conclusions

1. A thermodynamic analysis using the CALPHAD method of phase equilibria of the portions of the Ir-Si-C-O phase diagram relevant to conditions of an MRM treatment indicates that SiO_2 on the surface of iridium is expected to be unstable.
2. The pressures and concentrations of CO and CO_2 in the argon cover gas vary during the course of the MRM treatment. Based on reported tap measurements of CO and CO_2 concentrations in the gas at the end of the cycle, the gas is sufficiently reducing that any SiO_2 on the surface will react with Ir to form an Ir-Si intermetallic phase.
3. At earlier times in the MRM treatment the gas atmosphere is less reducing and SiO_2 can exist for a limited time on the surface in equilibrium with Ir-Si intermetallic compounds. However, diffusion of Si into the subsurface regions will result in dissolution of SiO_2 over time.

4. At the gas compositions relevant to the MRM treatment the Si impurity dissolved in the iridium solid solution at or near the surface is calculated as 875 μg/g. This value has the greatest uncertainty associated with it due to uncertainty in the published Ir-Si phase diagram.
5. The uncertainties in this analysis, including the omission of an intermediate compound of Ir with Si due to a lack of thermodynamic data, may affect some details of the analysis but have no impact on the overall results or conclusions.
6. In the absence of Ir, the thermodynamic model shows that SiO_2 is reduced to SiC at CO and CO_2 pressures corresponding to the end of an MRM cycle at 1410 K.

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