INTEREST OF THERMOCHEMICAL DATA BASES LINKED TO COMPLEX EQUILIBRIA CALCULATION CODES FOR PRACTICAL APPLICATIONS

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ABSTRACT

Since 1974, Thermodata has been working on developing an Integrated Information System in Inorganic Chemistry. A major effort was carried on the thermochemical data assessment of both pure substances and multicomponent solution phases. The available data bases are connected to powerful calculation codes (*GEMINI* = *Gibbs* *Energy* *Mini*mizer), which allow to determine the thermodynamical equilibrium state in multicomponent systems. The high interest of such an approach is illustrated by recent applications in as various fields as semi-conductors, chemical vapor deposition, hard alloys and nuclear safety.

RESUME

Depuis 1974, Thermodata développe un Système Intégré d'Informations dans le domaine de la Chimie Inorganique. Un effort trés important a été apporté à la critique et validation des données thermochimiques des substances pures ainsi que des phases solutions polyconstituées. Les bases de données disponibles sont connectées à des codes de calcul puissants (*GEMINI* = *Gibbs* *Energy* *Mini*mizer), qui permettent de déterminer l'état d'équilibre thermodynamique dans un système polyconstitué. Le grand intérêt d'une telle approche est illustré par des applications récentes dans des domaines aussi variés que les semi-conducteurs, le dépôt chimique en phase vapeur, les alliages durs et la sureté nucléaire.

I. FROM THEORETICAL PRINCIPLES TO PRACTICAL APPLICATIONS

In nature, all events are bound by the two principles of Thermodynamics, which are of great interest for practical applications. The first principle states that the energy of an isolate system is constant, the second one that the entropy of an isolate system tends to a maximum [1]. These two principles have been acquired towards the middle of nineteenth century (Sadi Carnot, 1824, Jules Robert Mayer, 1842, Clausius, 1850, W. Thomson - Lord Kelvin -, 1853) [2].

The combination of these two principles and the mathematical theory "On the Equilibrium of Heterogeneous Substances" are the most important contribution to Physical Science brought by Professor Josiah Willard Gibbs in 1876 and 1878 [3]. As major theoretical result, the Gibbs energy (at constant pressure) or the Helmoltz energy (at constant volume) of an isolate system is minimum at thermodynamical equilibrium.

A very important step for practical applications of the now universally recognized works of Gibbs was the advent of Computer Science with Electronics towards the middle of the twentieth century, Thermochemical Equilibrium Calculation being part of it. Consequently, there is nowadays no more theoretical or computer limitations to calculate the equilibrium state in complex systems containing a high number of components and phases. The remaining criterion for choosing an equilibrium calculation code among all those existing is its easiness to use, and it is for that main reason that *GEMINI* (*G*ibbs *E*nergy *Mini*mizer) type codes have been recently developed by THERMODATA/CNRS/INPG in Grenoble (France).

However, even if theoretical tools are commonly available, there still exists a strong limitation to extensive applications. It is evidently the lack of reliable and self-consistent thermodynamic data for most of multicomponent phases of interest. Dealing with pure substances or one single phase is indeed inadequate for practical applications. Applied Research is much more interested in complex chemical systems, including together a lot of gaseous or condensed stoichiometric species, and also multicomponent solution phases. Such problems cannot be resolved by isolate searchers, without a large effort of synthesis at a wide level. Thus first thermodynamical data bases have been created to answer that need near 1970. The On-line Integrated *THERMODATA* system [4] was a precursor in Europe and was the origin of the *S*cientific *G*roup *T*hermodata *E*urope (*SGTE*) data bases [5].

This coherent predictive approach including both thermochemical data bases and calculation code has soon given promising results in as various fields as semi-conductors, hard alloys, chemical vapor deposition and nuclear safety.

II. USER ASPECTS OF THERMOCHEMICAL EQUILIBRIUM CALCULATION

1. Semi-conductors

The *MnTe* compound has semi-conductor properties at *room* [6] and high temperature [7]. Its practical interest consists in its capacity for making "blende" structure pseudo-binary solid solutions with IIB (II_B = Cd, Hg, Zn) metal telurides : the

paramagnetic cation Mn^{++} brings into the low temperature lattice spin glass properties when Mn content is low, and antiferromagnetic properties at higher concentration.

These alloys have magneto-optical properties (Faraday rotation) interesting for electronics (preventing laser beam retro-diffusion in its own cavity, current censors).

On a metallurgical point of view, the addition of Mn to II-VI compounds allows the realization of electronical devices, among which are suitable substrates or plug coatings in infra-red detectors replacing Cd-Te [8-9].

The *Mn-Te* binary phase diagram (figure 1) has been critically assessed by using the Lukas et al.'s program [10], because the thermodynamic properties are needed for simulating the elaboration process of multicomponent solid solutions.

2. Solidification microstructure calculations

Most industrially important engineering alloys contain more than two components, but with respect to the equilibrium phase diagrams of such systems, only a limited amount of data are available in the literature. In this respect, the use of calculated equilibrium phase diagrams opens new possibilities to control the microstructure and therefore the properties of complex alloys. Combined with recent microstructural growth and microsegregation models for multicomponent systems, the size, type and fraction of phases as a function of the solidification conditions (i.e. solidification speed and thermal gradient) can be predicted.

We were interested here in the solidification behaviour of a laser cladded hypoeutectic Co-based alloy (Stellite 6). Stellite-type cobalt-based hardfacing alloys are well known and widely used due to their wear and corrosion resistance, both of which are maintained to high temperatures, and are used primarily for unlubricated or elevated-temperatures wear applications. Most of these alloys consist of 30 wt% Chromium with varying amounts of tungsten (4 to 17 wt%) and carbon (1 to 3.2 wt%).

For the microstructural calculations, the quaternary phase diagram *C-Co-Cr-W* was calculated using both *GEMINI* code and *SGTE* solution data base. The *dendritic growth* of the primary fcc cobalt phase was described using a recent growth model [16] modified for multicomponent systems [17-18]. The calculated phase diagram was used to determine the liquidus temperature of the alloy, the liquidus slope and partition coefficient with respect to every solute.

Because of microsegregation caused by the difference in solubility of components in the liquid and solid phases, solidification of metals usually leads to solid fractions of phases which are not predicted by the equilibrium phase diagram. The determination of the *solidification path* (i.e. the locus of the points representing the composition of the residual liquid when solidification proceeds) is therefore of prime importance to calculate the microsegregation. Different microsegregation models can be used in multicomponent systems (see for example [19], provided the phase diagram is known. In particular, it is very important to know the evolution of the tie-lines with both the temperature and composition, as well as the description of the two-fold saturation surfaces, i.e. equilibria between a liquid and two solids. The solidification path of the alloy investigated was determined using Scheil's model [20] for

multicomponent systems [19] linked with the calculated quaternary phase diagram (figure 2).

3. Chemical Vapor Deposition (CVD)

Chemical vapor deposition (*CVD*) is one of the methods used for elaboration of thin films of different solid materials. It consists of depositing one or more solid phases on the surface of a heaten substrate by means of heterogeneous chemical reactions between the substrate and the feed gas phase, while the gaseous reaction by-products are evacuated from the deposition area. The chemistry and the deposition mechanisms of the *CVD* are not always easy to control so, a great number of preliminary experiments is often necessary in order to determine the optimum conditions i.e. deposition temperature, total and partial pressures or nature and composition of the precursor gases. Many times the result still remains unsatisfactory. This is the case of WSi_2 thin films elaborated from a gas phase composed of a mixture of tungsten hexafluoride, WF_6, silane, SiH_4 and hydrogen, H_2. The choice of this gas phase, which is up to now the most frequently used one, is rather based on the physical properties or the availability of the constituent precursors than on the advantages they present from a thermodynamic point of view. In the following it will be illustrated that a thermodynamic investigation of the integral chemical system involved in the process is the far most appropriate method to understand the mechanism of the WSi_2 deposition and to improve the process, by evidencing in a systematic way the influence of the experimental parameters on the characteristics of the deposited films.

The thermodynamic data for the phases which participate in the chemical reactions, i.e. all the species formed by combining the elements of the basic chemical system, Si, W, F (or Cl), H, were taken when available from different international notoriety bases [5], or critically selected from the literature. Especially the data of the silicon compounds resulted from a consistent assessment of the $M-Si$ binary systems ($M = Mo$, Ta, Ti, W) [21] by using the Lukas et al.'s program [10].

The thermodynamic investigation was made by using the *GEMINI* code. The results were presented by means of *CVD* phase diagrams, in which the deposition fields of the silicon compounds from WF_6, SiH_4 and H_2 are plotted as a function of the Si and W precursor initial partial pressures.

From the study of these diagrams (figure 3) it is easy to realize why the deposition of WSi_2 is such a delicate task under the conditions described : the pure WSi_2 deposition domain is almost reduced to a line. The width of this domain increases when the metal gas vector WF_6 is replaced by WCl_4. Consequently, a small fluctuation of the input gas composition will not necessarily result in the codeposition of the W_5Si_3 or Si phase. It thus seems a priori interesting to consider the use of chlorides instead of fluorides as tungsten precursors for the *CVD* of WSi_2.

The influence of the other parameters of the process was in this way optimized [22]. It appeared for example that if SiH_4 is replaced by $Si_2H_2Cl_2$ as silicon precursor, the WSi_2 single phase deposition domain grows even further thus providing very comfortable deposition conditions. It is also true for $TaSi_2$, which presents a larger deposition domain than WSi_2 (figure 4). The two first figures prove the advantage for using

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chlorides instead of fluorides as metal gaz vector, and $Si_2H_2Cl_2$ instead of SiH_4 as silicon gas vector. By comparison of several silicides, $TiSi_2$ was found to be the most suitable material for *CVD* (figure 5). It was in this way evidenced that the thermodynamic simulation of a *CVD* process which is based on a complex equilibria calculation code linked to a thermochemical data base, can help to avoid a number of errors in principle, to save considerable time in finalizing the experimental setup and to interpret certain phenomena observed during the experimental procedure. This approach was successfully applied to the elaboration of different materials thin films, such as tantalum, molybdenum and titanium disilicides or hard coatings of titanium nitride and diboride [21, 23].

4. Nuclear safety (Molten Core-Concrete Interaction)

In the unlikely event of a severe accident in a nuclear power plant, the core may melt through the vessel and slump into the concrete reactor cavity. The hot mixture of core material would interact thermally with the concrete basemat, and the corium which results from the *Molten Core-Concrete Interaction (MCCI)* would therefore be composed of molten fuel, control rods, stainless steel structures, part of the bottom of the vessel and molten concrete. Thus, the chemical analysis of *MCCI* phenomena leads to take into account very complex systems, containing simultaneously a lot of gaseous and condensed stoichiometric species, and also solution phases.

Since 1988, on request from the Institut de Protection et de Sureté Nucléaire (IPSN), THERMODATA has developed in collaboration with the United Kingdom Atomic Energy Agency (UKAEA) and National Physical Laboratory (NPL) an oxide data base containing as major constituents UO_2, ZrO_2, SiO_2, Ca_O, Al_2O_3, FeO, MgO, BaO, SrO and La_2O_3.

The two first very important practical applications of this oxide data base linked to the *GEMINI* code have been on the one hand, the calculation of liquidus, solidus and isopleths sections for different core (UO_2-ZrO_2) - concrete $(Al_2O_3-CaO-SiO_2)$ mixtures [24-26] (figure 6), and on the other hand the calculation of three selected fission products (*BaO, SrO* and La_2O_3) release by vaporization from the corium in conditions of existing experiments [26].

III. CONCLUSION

The high interest of thermochemical data bases linked to a complex equilibria calculation code (*GEMINI*) has been illustrated by recent practical applications in various fields. A critical assessment of the *Mn-Te* system has been useful for the metallurgical elaboration of ternary semi-conductors. The equilibrium state calculation of the *C-Co-Cr-W* system has been linked to hard alloys solidification microstructures calculations. Assessed thermochemical properties of *Mo-Si*, *Si-W*, *Si-Ta*, *Si-Ti* and *Ti-N* systems have been applied to the elaboration of different materials thin films by chemical vapor deposition. In the nuclear safety field, an oxide thermochemical data base ($Al_2O_3-CaO-SiO_2-UO_2-ZrO_2-BaO-SrO-La_2O_3$ system) has been

developed thanks to an international collaboration between France and United Kingdom for the thermochemical modelling of molten core concrete interaction (MCCI) phenomena .

Future success of such a thermodynamical approach remains closely subordinate to the extent of standardization of modelling concepts and methods, which is the only way for treating complex practical problems in a reasonable time.

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FIGURE 1 : THE MN-TE CALCULATED PHASE DIAGRAM COMPARED WITH THE
           AVAILABLE EXPERIMENTAL INFORMATION.

FIGURE 2 : EVOLUTION OF THE COMPOSITION IN THE RESIDUAL LIQUID AS
           SOLIDIFICATION PROCEEDS, ACCORDING TO SCHEIL'S MODEL
           [20].

           Note : The content of each solute element in the
                  liquid is normalised with   respect to the
                  initial alloy composition. At a solid fraction
                  of 0.65, the composition of the liquid reaches
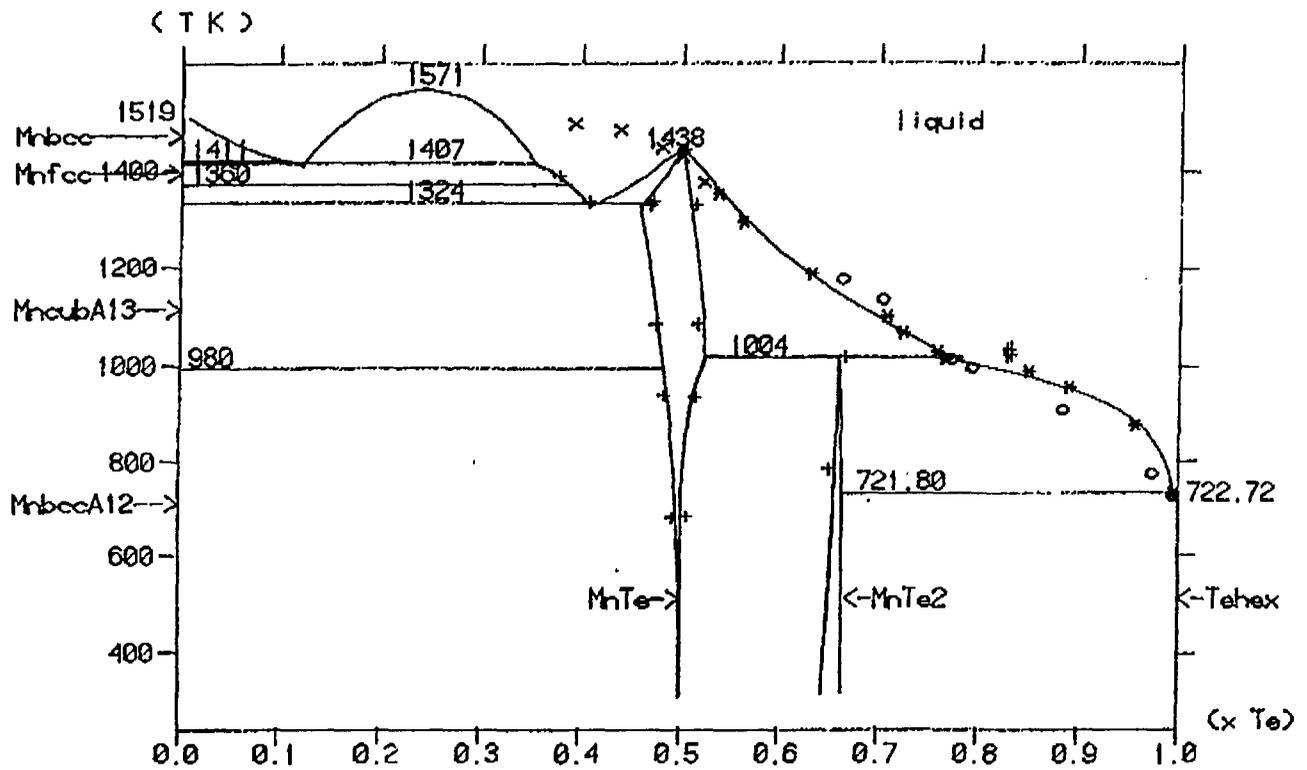   the eutectic valley.

FIGURE 3 : METAL GAS VECTOR INFLUENCE IN CVD OF W-SILICIDES.
           T=1000K, P(AR)=0.9 ATM, $P(WF_6 + SIH_4 + H_2)$=0.1 ATM.

FIGURE 4 : SILICON GAS VECTOR INFLUENCE IN CVD OF TA-SILICIDES.
           T=1000K, P(AR)=0.9 ATM, $P(TACL_5 + SIH_4 + H_2)$=0.1 ATM.

FIGURE 5 : SELECTED METAL (TI) INFLUENCE IN CVD OF SILICIDES.
           T=1000K, P(AR)=0.9 ATM, $P(TICL_4 + SIH_4 + H_2)$=0.1 ATM.

FIGURE 6 : CALCULATED LATTICE OF LIQUIDUS AND SOLIDUS CURVES FOR
           DIFFERENT CORE (UO_2-ZRO_2) - CONCRETE $(AL_2O_3-CAO-SIO_2)$
           MIXTURES.

FIGURE 1 : THE MN-TE CALCULATED   PHASE DIAGRAM COMPARED   WITH THE AVAILABLE EXPERIMENTAL INFORMATION.

Abrikosov&al.,(11)
Vanyarko&al.(12)
Pajaczkowska,(13)
Matelka,(14)
Kasal&al.,(15)

Mn-Te : THERMODATA 19/11/92

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FIGURE 2 : EVOLUTION OF THE COMPOSITION IN THE RESIDUAL LIQUID AS
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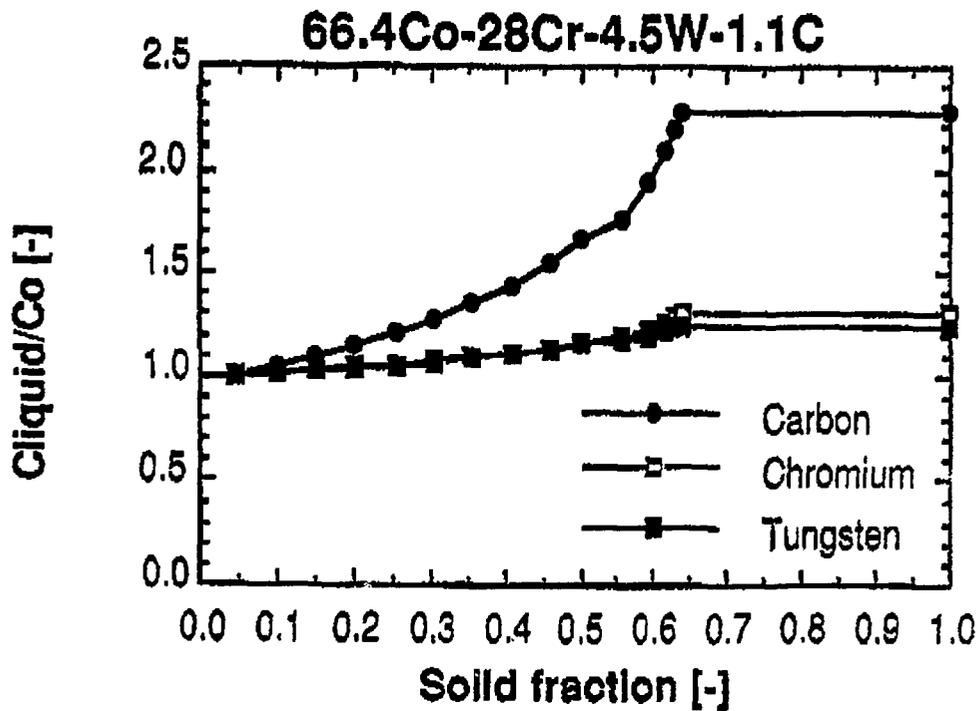the eutectic valley.

66.4Co-28Cr-4.5W-1.1C

Legend:
- Carbon
- Chromium
- Tungsten

X-axis: Solid fraction [-]
Y-axis: Cliquid/Co [-]

FIGURE 3 : METAL GAS VECTOR INFLUENCE IN CVD OF W-SILICIDES.
T=1000K, P(AR)=0.9 ATM, P(WF$_6$ + SIH$_4$ + H$_2$)=0.1 ATM.

$\bar{P}_{WF_6}$ (atm)

10^{-2}

10^{-3}

10^{-4}

10^{-5}

W

W . W$_5$Si$_3$ ⟶ ⟵ WSi$_2$

WSi$_2$ + Si

W$_5$Si$_3$ + WSi$_2$

10^{-5} 10^{-4} 10^{-3} 10^{-2}

$\bar{P}_{SiH}$ (atm)

$\bar{P}_{WCl_6}$ (atm)

10^{-2}

10^{-3}

10^{-4}

10^{-5}

W

W$_5$Si$_3$+W

W$_5$Si$_3$ ⟶

⟵ WSi$_2$

Si + WSi$_2$

⟵ W Si$_2$ + W$_5$Si$_3$

10^{-5} 10^{-4} 10^{-3} 10^{-2}

$\bar{P}_{SiH}$ (atm)

10

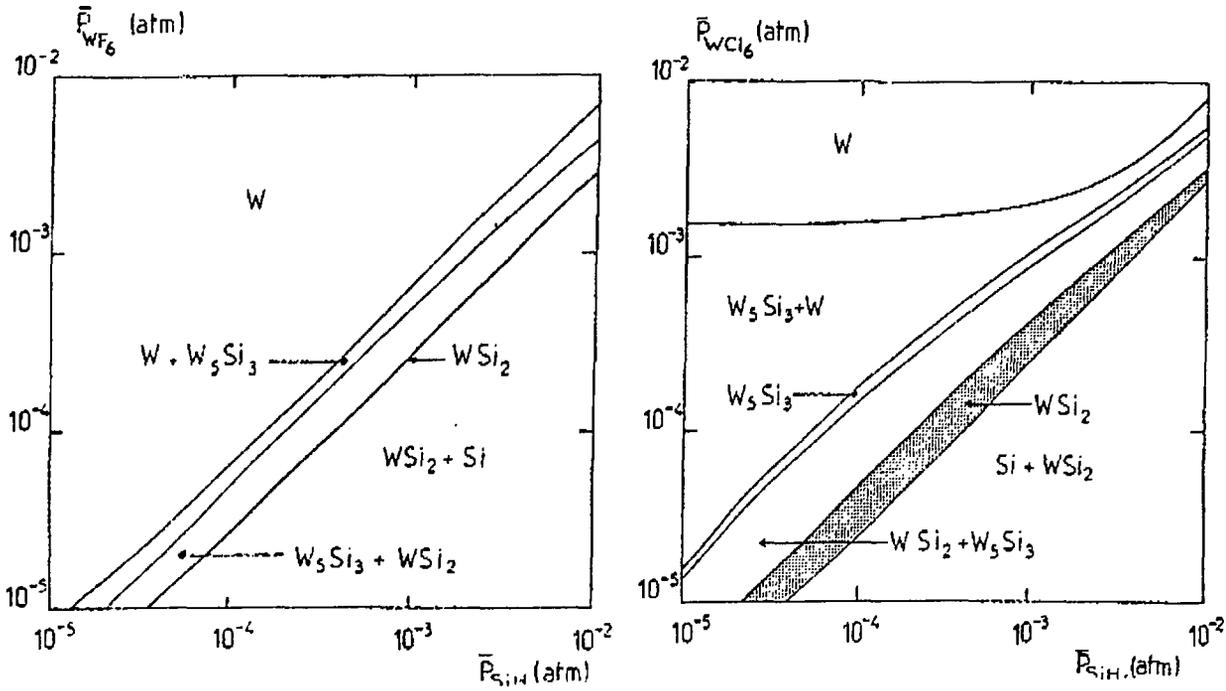**FIGURE 4 : SILICON GAS VECTOR INFLUENCE IN CVD OF TA-SILICIDES.**
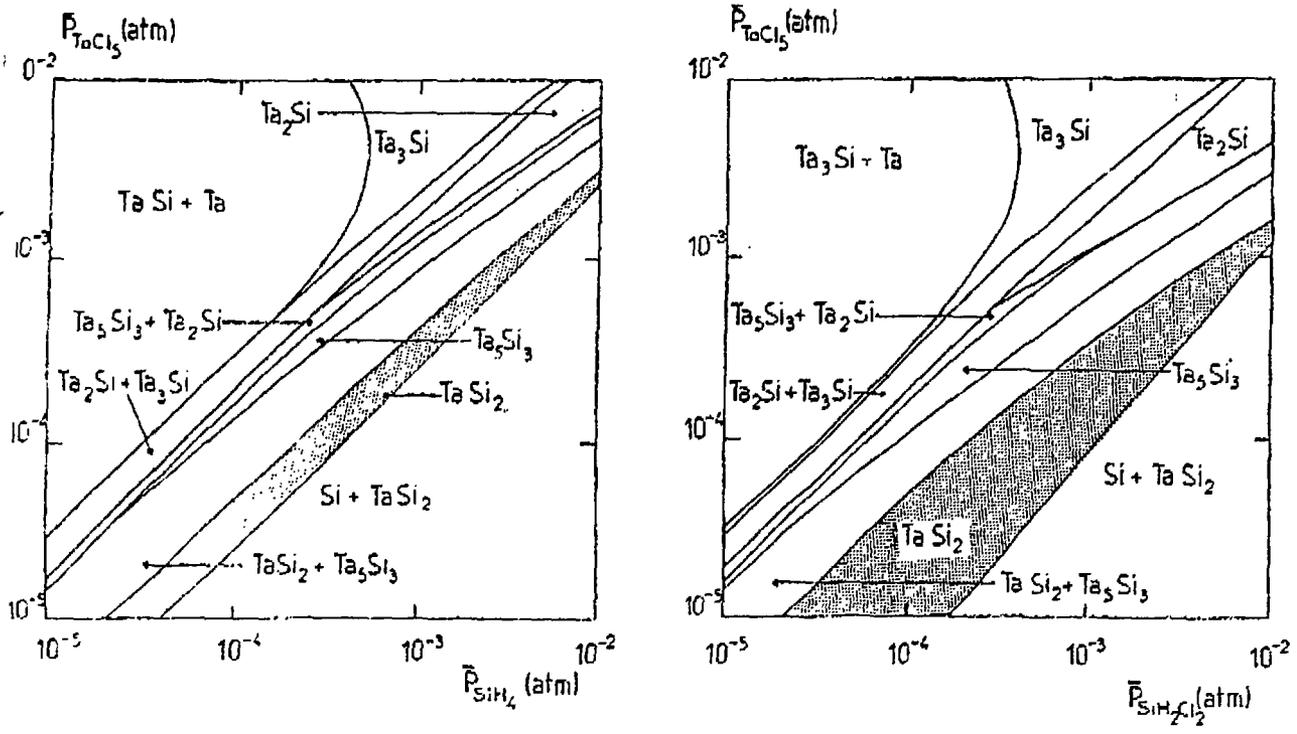**T=1000K, P(AR)=0.9 ATM, P(TACL$_5$ + SIH$_4$ + H$_2$)=0.1 ATM.**

$\bar{P}_{TaCl_5}$(atm)

Ta$_2$Si   Ta$_3$Si

Ta Si + Ta

Ta$_5$Si$_3$ + Ta$_2$Si

Ta$_2$Si + Ta$_3$Si

Ta$_5$Si$_3$

Ta Si$_2$

Si + TaSi$_2$

TaSi$_2$ + Ta$_5$Si$_3$

$\bar{P}_{SiH_4}$ (atm)

$\bar{P}_{TaCl_5}$(atm)

Ta$_3$Si + Ta   Ta$_3$Si   Ta$_2$Si

Ta$_5$Si$_3$ + Ta$_2$Si

Ta$_2$Si + Ta$_3$Si

Ta$_5$Si$_3$

Si + Ta Si$_2$

Ta Si$_2$

Ta Si$_2$ + Ta$_5$Si$_3$

$\bar{P}_{SiH_2Cl_2}$(atm)

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FIGURE 5 : SELECTED METAL (TI) INFLUENCE IN CVD OF SILICIDES.
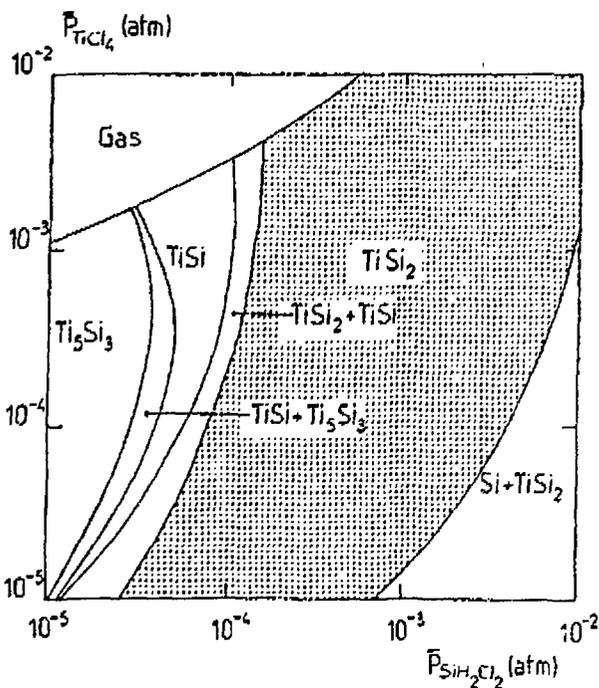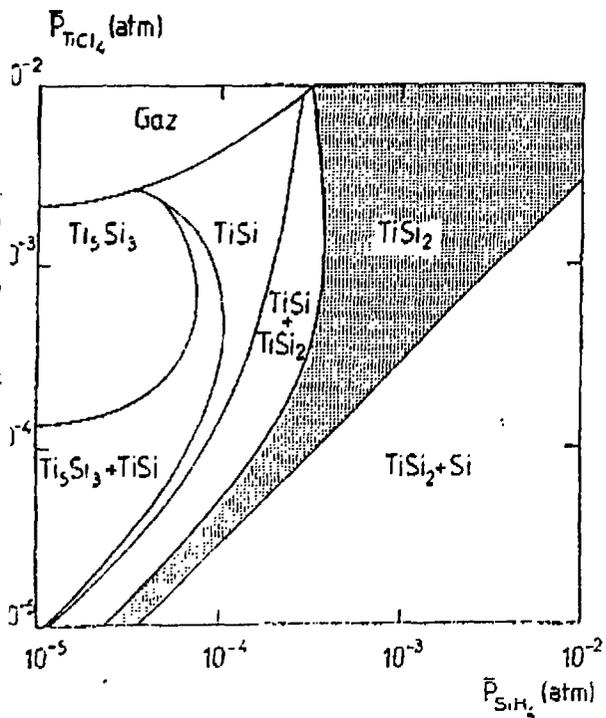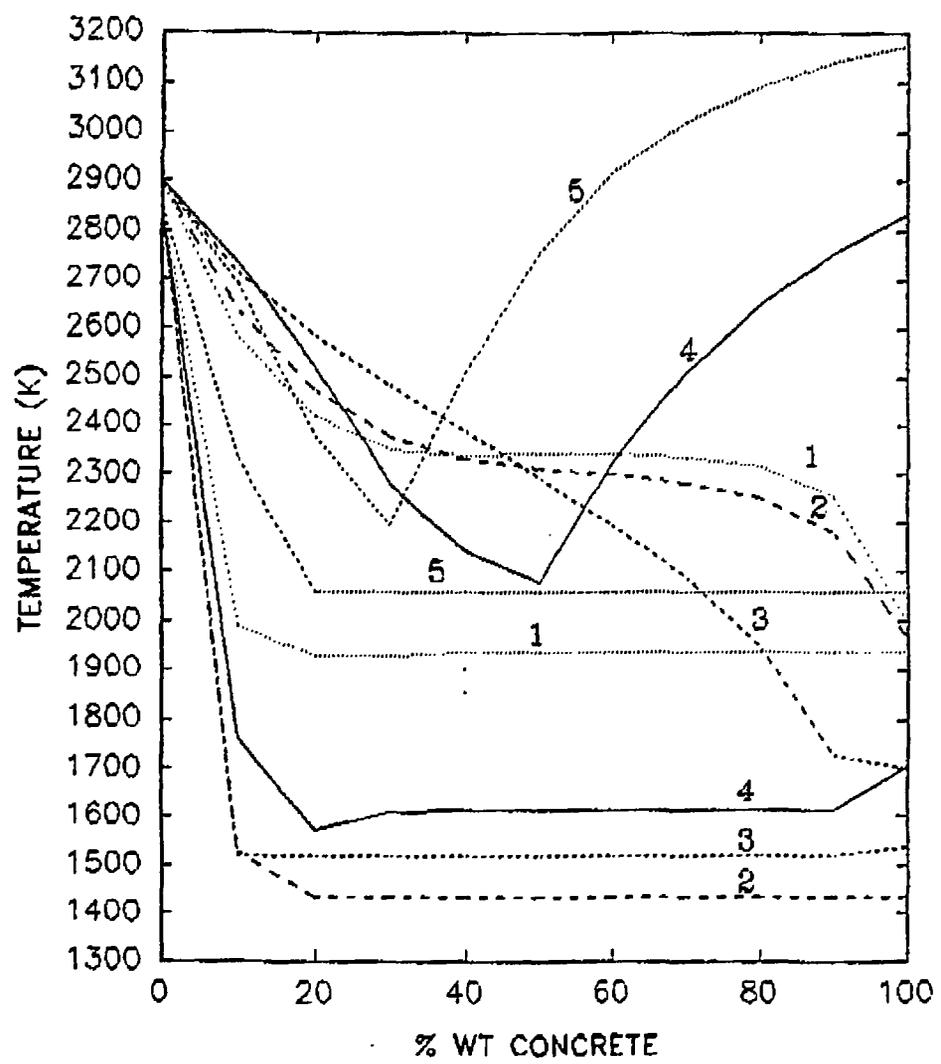T=1000K, P(AR)=0.9 ATM, P(TICL$_4$ + SIH$_4$ + H$_2$)=0.1 ATM.

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CALCULATED LATTICE OF LIQUIDUS AND SOLIOUS CURVES FOR DIFFERENT CORE (UO2-ZRO2) - CONCRETE (AL2O3-CAO-SIO2) MIXTURES.

LEGEND: 1 = silica ; 2 = siliceous ; 3 = limestone sand ; 4 = limestone ; 5 = lime

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