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THERMODYNAMIC CALCULATION OF THE TWO PHASED DEPOSITION DOMAINS WITH SiC IN THE Si-Ti-C-Cl-H CHEMICAL SYSTEM

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Résumé - Dans le système Si-Ti-C, les nouveaux matériaux dispersoïdes à base de carbure de silicium suscitent un vif intérêt dans la recherche de l'amélioration de la ténacité. L'étude thermodynamique du système chimique complexe Si-Ti-C-Cl-H a permis de représenter les domaines de dépôt des équilibres biphasés SiC-TiC et SiC-Ti₃SiC₂ dans le repère des paramètres de variance. Pour une composition donnée de la phase gazeuse à l'équilibre, la composition de la phase condensée peut varier dans des proportions importantes en fonction du mélange gazeux initial. A partir de cette unique représentation, les domaines de dépôt sont déduits pour un mélange gazeux initial quelconque.

Abstract - New ceramic materials with dispersed phases within a silicium carbide matrix in the Ti-Si-C chemical system seem very attractive to improve toughness properties. Deposition domains of SiC-TiC and SiC-Ti₃SiC₂ are determined by thermodynamic calculation in the Si-Ti-C-Cl-H chemical complex system, and presented in the coordinate system of the variance parameters. The representation of these domains in the coordinate system of the initial gas mixture is then easily deduced whatever the bearing molecule considered. For a given composition of the gas mixture at equilibrium the ratio between the deposited phases can present very large variations according to the initial gas-mixture.

1- INTRODUCTIVE COMMENTS

In the field of advanced materials either in bulk form or as coatings, CVD is an attractive way to avoid the difficulties encountered with sintering and to overcome the limitations of the PVD process. Due to its versatility the composition (1) and structure of the deposits can be controlled to a large extent. It has recently been shown that complex ceramic materials with dispersed or multilayered phases can also be grown by CVD (2) (3). This new range of structures has mainly been developed to improve the toughness of ceramics as mentioned in recent papers dealing with dispersed composites (4)(5).

In relation with the Ti-Si-C system, dispersed two-phased materials presenting improved toughness have already been obtained, such as TiC-SiC by Wei (6) or TiSi₂-SiC by Stinton (7). More recently, Hirai (8) obtained by CVD the various multiphased domains and the pure ternary phase T1 in agreement with Nickl's previous study of this system (9).

In order to improve the understanding of the CVD process or the knowledge of its behavior with respect to the variation of T, P or the concentrations of the various precursors, the thermodynamic equilibrium of the chemical complex system has been studied. Our purpose is to obtain information on the two-phased deposition fields starting from a large variety of gaseous species and conditions.

2 - GENERAL PROCEDURE

The minimization calculations of the total Gibbs free energy in the system Si-Ti-C-Cl-H are computed with the SOLGASMIX program(11) using a coherent set of thermodynamic data (12). These are obtained from compilations or are estimated in accordance with the solid phase diagram as discussed in a previous paper (12):

- The Si, Ti, C, SiC β as well as the gaseous species values come from the SGTE data bank (13).
- The titanium silicide data from Barin & Knacke (14) are modified and completed as previously mentioned(12) in order to agree with the binary Ti-Si phase diagram.
- In the same way the Ti₃SiC₂ (T1 phase), Ti₅Si₃C_x (T2 phase) Gibbs free energy of formation are estimated

and adjusted (see ref(12)), taking into account the variation of the Gibbs free energy of TiC_x with respect to the composition determined in a previous work (15).

The isothermal section presented in figure 1 (12) is calculated with these data.

Considering the Ti-Si-C-Cl-H system the vectors of titanium, silicium and carbon can be chosen among the following species: $TiCl_4$ for Ti, SiH_4 - SiH_3Cl - SiH_2Cl_2 - $SiHCl_3$ or $SiCl_4$ for Si, TMS for Si and C, all the hydrocarbons for C. The initial gas mixture also includes H_2 , which is generally the main component used as carrier gas and reducing agent. Due to the numerous possible initial mixtures for the gas phase, the two-phased deposition fields are determined and presented independently of the input molecular species. Two independant intensive and invariant appropriate variables then need to be specified to describe those equilibria when T and P are fixed. This kind of representation is an intrinsic feature of the chemical system. Assuming that all condensed phases are stoichiometric compounds, these two ratios of elemental abundances (or combinations of elemental abundances) correspond to the number of degrees of freedom of the system and are used as coordinate to plot the two-phased deposition domains. In our case, the large departure from stoichiometry presented by TiC_x would not allow the use of such a description. Nevertheless the experimental ternary phase diagram(10) as well as the calculated ternary phase diagram (figure 1) show that a narrow range of composition ($TiC-TiC_{0.89}$) is in equilibrium with SiC. Therefore the calculation of the deposition diagram is obtained considering only the stoichiometric composition of TiC.

The two-phased deposition diagrams are afterwards deduced for each combination of the input species without any new minimization calculation.

3 - RESULTS

The following results are relative to the deposition of SiC + TiC and SiC + T1 but all the possible two-phased mixtures involving stoichiometric compounds may be discussed in the same way.

3-1 Deposition fields and trends with precursors

In the case of TiC+SiC the variance parameters are Cl/H and (Si+Ti-C)/H. The calculated codeposition domain is presented in figure 2 at T=1500 K and P=1 atm. The boundaries of the TiC-SiC domain with the three-phased fields TiC-SiC-T1 and TiC-SiC-C are fitted by second order polynomial expressions. These equations are combined with the elemental formula of the initial bearing molecules of Si, Ti, C. One additional relation is given by the imposed total flow rate which is constant. Starting from these equations, a curve representing a boundary becomes a surface in the three dimensional coordinate system of the initial gaseous mixture. The influence of the nature of the initial gaseous species on the shape and width of the TiC-SiC domain is presented in figure 3. For a selected C bearing molecule the width of the two-phased domain varies with the number of Cl in the silicon bearing molecule: the domain increases significantly from SiH_4 to $SiCl_4$. This modification is mainly due to the shifting of the boundary with the TiC-SiC-T1 domain whereas the boundary with the TiC-SiC-C one remains almost unchanged. This behavior can be explained in the following way:

As hydrogen is the major component of the initial gas mixtures, the substitution of SiH_4 by $SiCl_4$ will have a strong influence on the chlorine content when the amount of hydrogen is modified to a lesser extent. As a consequence the boundary with SiC-TiC-C which corresponds to the condensation of carbon is slightly shifted. This condensation mainly depends on the initial concentration of methane into hydrogen because carbon is only present as hydrocarbon in the equilibrium gas phase. On the other hand the formation of Ti_3SiC_2 is strongly dependent on the chlorine content as titanium and silicium gaseous species are chlorides. When substituting CH_4 by C_4H_{10} the trends are identical but less dependent on the input silicon molecular species. The two-phased domain extends, to a first approximation, in a range inversely proportional to the number of carbon atoms in the initial species.

The same calculation is applied to the two-phased domain SiC-T1. The deposition domain is presented as a function of the appropriate parameters (Ti+3Si-3C)/H and Cl/H on figure 4. The general shape of the domain is very similar to that of TiC-SiC. Nevertheless, the evolution of the SiC-T1 domains with respect to the initial gas-mixture are quite different (figure 5). With respect to the Si bearing molecule the width of the domain is almost unchanged and only the position of the domain in the coordinate system is modified. In this case the neighboring three-phased domains correspond to the formation of either $TiSi_2$ or TiC which both involve elements present in

the equilibrium gas phase as chlorides. We can then suppose to a first approximation that the chlorine content of the initial gas mixture has the same influence on both boundaries.

3.2 Composition variation inside the TiC-SiC domain.

As the thermomechanical properties of dispersed phases are highly dependent on the volume molar fraction of the solid phases, the theoretically allowed SiC/TiC ratios inside the deposition domain are deduced from the previous results in the following way:

A point in the variance coordinates (**figure 2**) gives a line in the initial gas mixture coordinates (**figure 3**). In other words the same gas phase equilibrium can be reached from an infinity of initial gas phase composition modifying at the same time the amount of condensed species. Such lines for various Cl/H values and a fixed (Si+Ti-C)/H ratio form a plane displayed as an example in **figure 6** for (Si + Ti-C)/H = 0,012.

Each line becomes independent of the C bearing species in the particular case when SiCl_4 is the silicon vector. One mole of SiCl_4 can then be replaced by the same amount of TiCl_4 without modification of the variance parameters.

The variations of the SiC/TiC along these lines are presented on **figure 7** against the initial molar fraction of SiH_2Cl_2 for a fixed (Si + Ti - C)/H ratio. Each curve is relative to one Cl/H ratio within the boundary values of the TiC + SiC domain which are respectively 0,11 and 0,19 when (Si + Ti - C)/H = 0,012. The variation range of the calculated SiC/TiC for the lowest value of Cl/H is obtained with the smallest change of the molar fraction of SiH_2Cl_2 and a given composition of the condensed phase is deposited for an initial molar fraction of SiH_2Cl_2 increasing with Cl/H. The same curves are presented in **figure 8** when SiCl_4 is used as Si bearing molecule. In this case the previous trends are enhanced and the corresponding variation range of the molar fraction of SiCl_4 is shifted towards lower values for the same composition of the solid phase. Moreover, when substituting SiCl_4 to SiH_2Cl_2 the range of the molar fraction of CH_4 involved by a given set of variance parameters is reduced. As previously mentioned in **figure 3**, using rich chlorine content silicon vector tends to extend the two-phased deposition domain towards the lowest values of CH_4 whereas SiH_4 gives the narrowest one.

If various TiC/SiC ratios can be deposited for a fixed composition of the gas phase, extremum values of this ratios strongly depend on the variance parameters. **Figure 9** shows the influence of Cl/H on SiC and TiC. The major phase can be either TiC or SiC depending on the SiH_2Cl_2 molar fraction when Cl/H = 0.11, but only rich SiC deposits can be obtained when Cl/H = 0.15.

In conclusion, the composition of the two-phased deposits may range from a rich SiC mixture to a rich TiC one depending on the input mixture.

4 - CONCLUSION

The evolution of the two-phased fields SiC + TiC and SiC + T1 with respect to the various bearing molecules has been calculated in the Ti-Si-C-Cl-H system. The TiC + SiC deposition domain increases with the amount of chlorine into the initial silicon vector whereas the SiC + T1 remains unchanged. The composition of the solid phase can be controlled to a large extent by the initial gas mixture composition. Deposits ranging from a silicon carbide matrix to a titanium carbide one may be theoretically obtained for appropriate but fixed compositions of the gas phase.

Notice

The deposition diagram presented in ref(12) was calculated taking into account the departure from stoichiometry of TiC_x . As a solid solution is not compatible with this kind of representation, this calculation has been made another time with the assumption previously mentioned leading to a slight difference in the deposition diagram.

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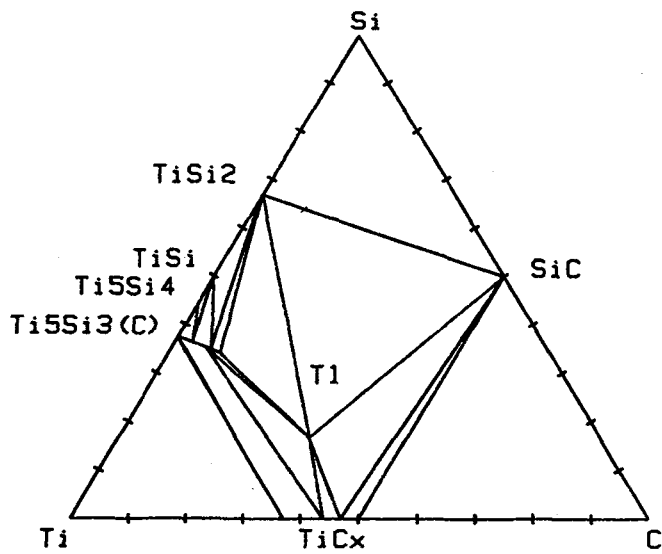


Fig 1. Calculated Si-Ti-C phase diagram.

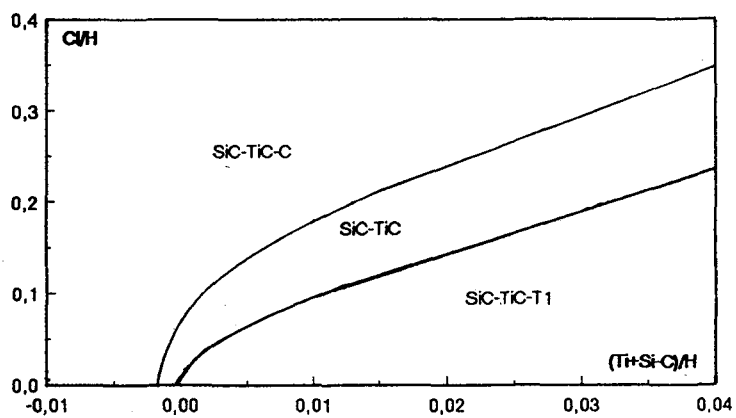


Fig 2. SiC-TiC deposition domain as a function of $(\text{Si}+\text{Ti}-\text{C})/\text{H}$ and C/H .

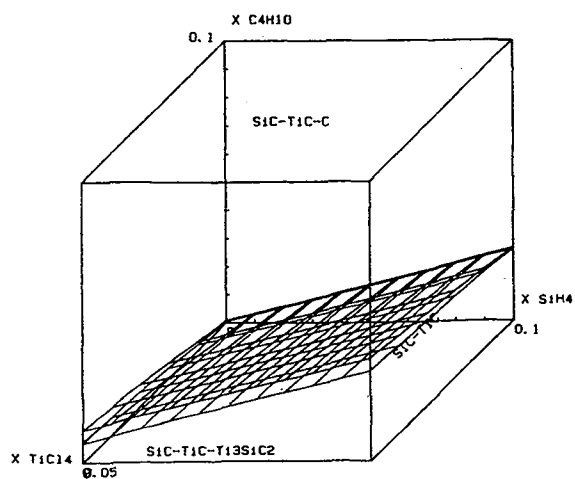
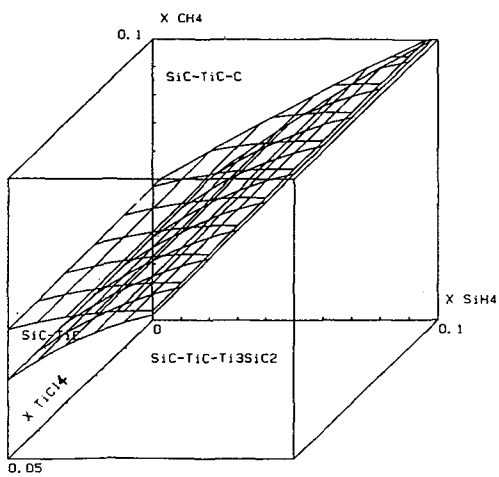
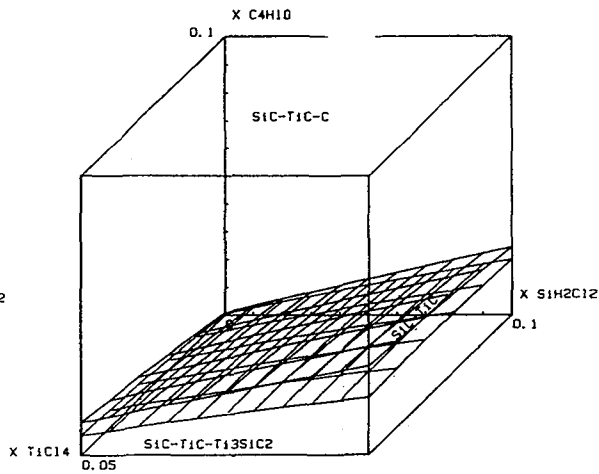
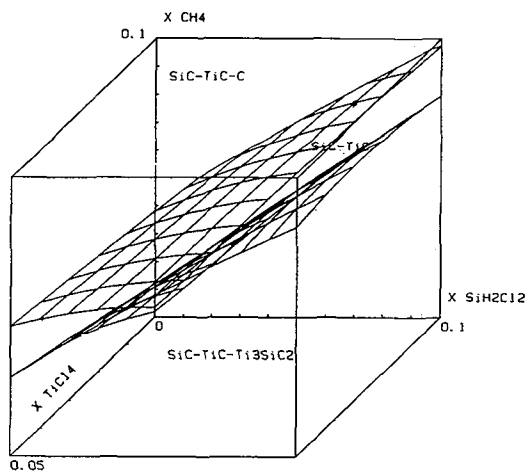
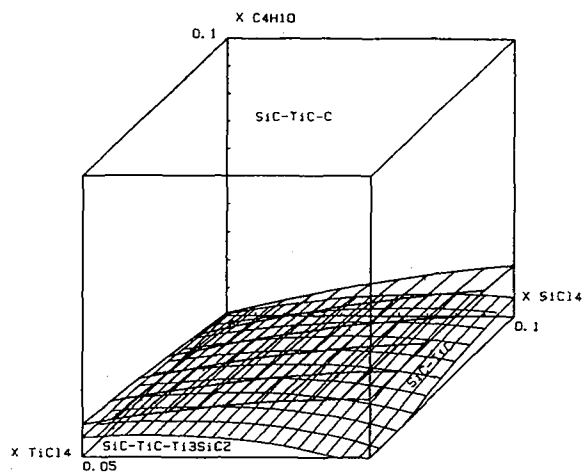
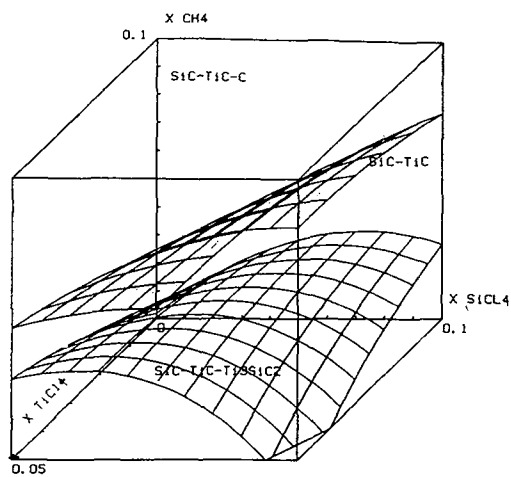


Fig 3. SIC-TiC domain plotted as a function of initial gaseous species.

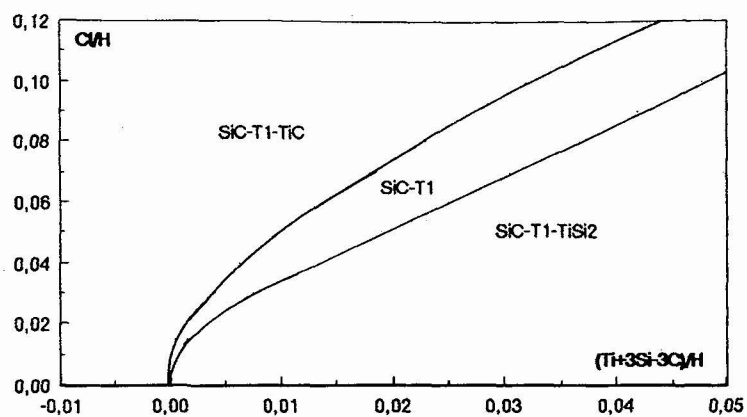


Fig 4. SiC-Ti₃SiC₂ deposition domain as a function of (Ti+3Si-C)/H and Cl/H.

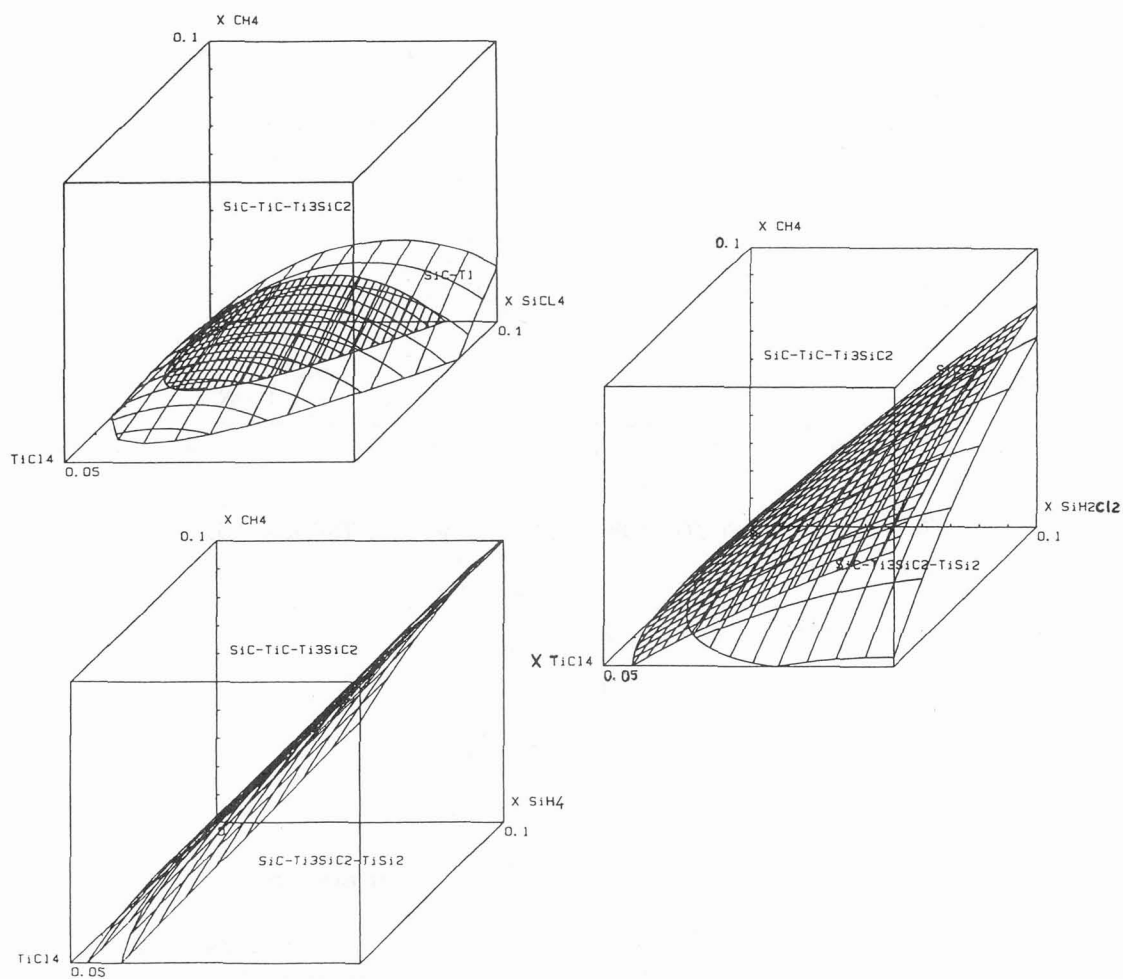


Fig 5. Influence of silicium precursor on the shape of SiC-T1 deposition domain.

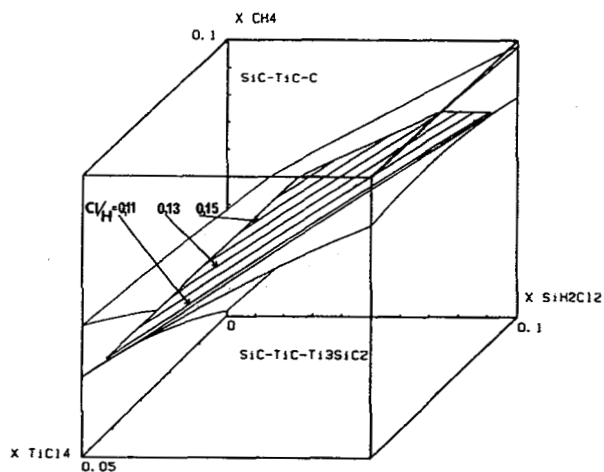


Fig 6. Plane corresponding to $(Si+Ti-C)/H=0,012$.

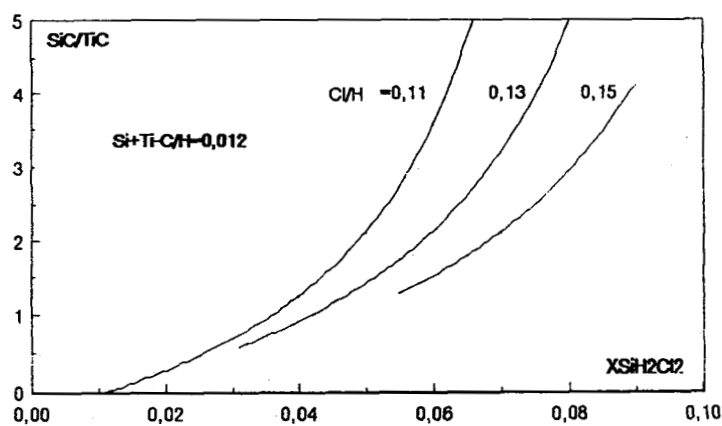


Fig 7. Evolution of SiC/TiC ratio with $X_{SiH_2Cl_2}$ at $(Si+Ti-C)/H=0,012$.

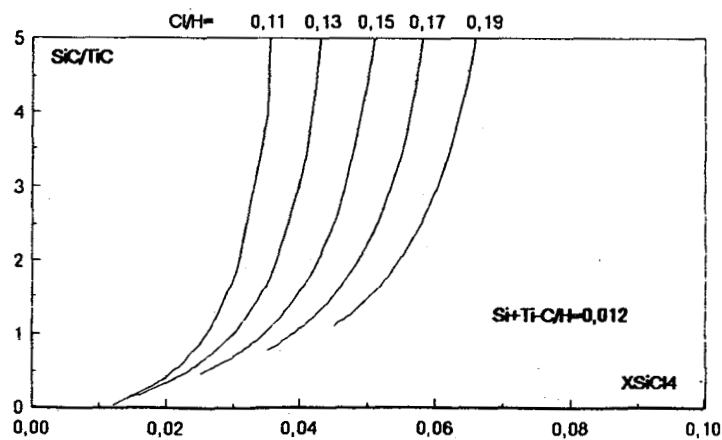


Fig 8. Evolution of SiC/TiC ratio with X_{SiCl_4} at $(Si+Ti-C)/H=0,012$.

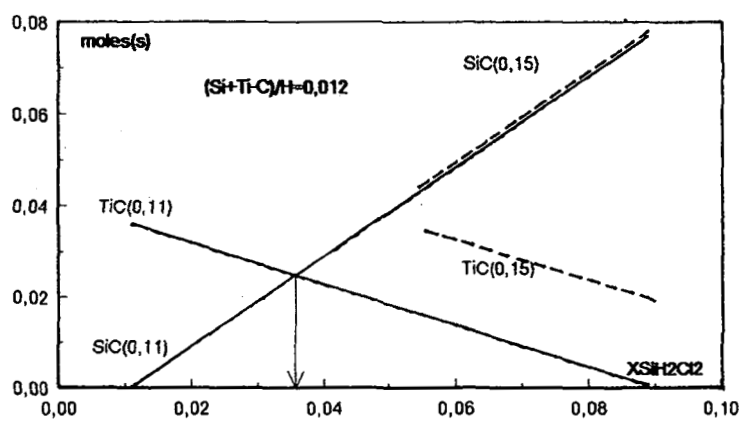


Fig 9. Variation of solid phases amount with respect to XSiH_2Cl_2 at
 — $\text{Cl}/\text{H}=0.11$ and - - - $\text{Cl}/\text{H}=0.15$