The transport behaviour of the Ti- and Mo-silicides was studied with halogens (Cl₂, I₂, HCl) as transport agent. The experimental behaviour agrees well with the calculated results. Monocrystals of Ti-silicides were obtained.

Introduction

The chemical transport of some transition metal silicides is possible with halogens as transport agent according to the literature [1 - 5]. In the case of the transport with I₂ as transport agent the transport direction is dependence on pressure [1]. Moreover the silicides can be formed during isothermal transport reactions, in which either the metal (M) is transported to Si (M = Ti, V, Cr, U) or the Si to the metal (Ta, W, Mo) [2].

In the binary system Ti-Si the following compounds exist: Ti₅Si, Ti₅Si and Ti₅Si₂. The phase Ti₅Si₃ has a homogeneity range: 37.5 - 40 at% Si. Two further phases have been discussed in the literature: the phase Ti₅Si₂, forming by peritectic reaction at 1170 °C after 2Ti + Ti₅Si₃ = Ti₅Si₂ [6, 7] and the phase Ti₅Si₄ [6]. In the phase diagram Mo-Si three binary compounds exist: Mo₅Si, Mo₅Si₃ and Mo₅Si₂. It was to investigate the conditions of the crystal growth of Mo- and Ti-silicides by chemical transport with halogens as transport agent.

Thermodynamic analysis

The chemical transport in the system Ti-Si-X can be described by an improved Schäfer model [8, 9]. It could be assumed, that both in the source and in the crystallization zone the gas and the solid phase are in equilibrium. From the knowledge of the gas phase composition in one zone it is possible to establish the gas phase composition in the other one via a connecting flow relation. Consequently the transport direction, transport rate and the composition of transported phases can be predicted even in the
case of a subsequential transport which is typical in systems with several coexisting phases. For numerical calculations the data were taken from the tables \([10, 11]\), corrected for consistence between the Ti-silicides and Si.

### Results of Ti-silicides

**Ti-Si-Cl system**

The calculated gas phase composition above the deposited solid \(\text{TiSi}_x\) at 1173 K shows, that the gaseous species \(\text{TiCl}_4\), \(\text{TiCl}_3\), \(\text{TiCl}_2\), \(\text{Ti}_2\text{Cl}_3\), \(\text{SiCl}_4\), \(\text{SiCl}_3\) and \(\text{SiCl}_2\) are transport-effective species (\(p_i > 1\) Pa). With increasing the gross composition value \(X = \text{Si/Ti}\) the Si-containing species become dominating. On the other hand over \(\text{Ti}_5\text{Si}_3\) in equilibrium with Ti the gas phase does not contain any species with silicon with a remarkable concentration. It may be concluded that in this case a transport of the silicides is not expected. The partial pressure of the \(p_{\text{TiCl}_4}\) and \(p_{\text{Ti}_2\text{Cl}_6}\) decrease with increasing temperature, at the same time the partial pressure of the other species increases.

In conformity with the calculated transport direction the transport of the Ti-silicides takes place from hot to cold. The transport rates are between 0.4 and 4 mg/h, and agree well with the calculated ones.

Table I shows the transport sequence of the Ti-silicides when starting with a two-phase solid.

#### Table I

Transport sequence in the Ti-Si-Cl system

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Transported phase</th>
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<tbody>
<tr>
<td>Ti + (\text{Ti}_5\text{Si}_3)</td>
<td>(\text{Ti}_5\text{Si}_3) Si-richer phase</td>
</tr>
<tr>
<td>(\text{Ti}_5\text{Si}_3) + TiSi</td>
<td>TiSi Si-richer phase</td>
</tr>
<tr>
<td>(\text{TiSi}_2) + Si</td>
<td>(\text{TiSi}_2) Si-poorer phase</td>
</tr>
</tbody>
</table>

Monocrystals of \(\text{Ti}_5\text{Si}_3\), TiSi and \(\text{TiSi}_2\) were obtained at temperatures \(T_{\text{hot}} = 1273\) K and \(T_{\text{cold}} = 1173\) K. Under the applied transport conditions, preferential isometric and needle-like crystals grow in the case of \(\text{Ti}_5\text{Si}_3\) and TiSi, respectively. The TiSi-needles are up to 20 mm long and the faces show striations along the longitudinal direction. TiSi\(_2\)-crystals are isometric, needle-like and flat-like, respectively, having mirror-smooth surfaces (Fig. 1).