

SPONTANEOUS MASS TRANSFER AND DEPOSITION OF CARBON AND SILICON ON TITANIUM IN LiCl-Li IONIC-ELECTRONIC MELTS

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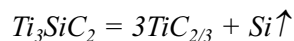
Abstract

Coatings and powders containing separate phases of silicides and carbides have been obtained during the joint saturation of titanium by carbon and silicon in ionic-electronic melt Li-LiCl.

Keywords: carbon, silicon titanium, ionic-electronic melt

Introduction

Ti_3SiC_2 is a rare example of so called “plastic ceramics”. It combines properties typical of ceramic compounds, such as high melting temperature, thermal and chemical stability, with mechanical properties of metallic systems. Physicochemical properties of this compound are defined by its electronic structure. The main difficulty while synthesizing Ti_3SiC_2 is the loss of silicon during reaction. It results in the formation of the second phase - titanium carbide [1]:



The reaction features depend on the Ti_3SiC_2 crystal structure that consists of titanium

carbide blocks divided by silicon layers. The inter-atomic dimension analysis shows that they are larger for silicon in Ti_3SiC_2 than for other compounds $Ti-Si-C$. At the same time, $Ti-C$ dimensions are close to those of titanium carbide. The weak bond of silicon in the Ti_3SiC_2 lattice can be the cause of its loss in thermal reactions.

The analysis of the electron energetic structure of Ti_3SiC_2 has been carried out before using photoelectron and X-ray emission [1]. Chemical bond features, zone structure, and charge distribution in Ti_3SiC_2 hexagonal high-temperature phase have been investigated by Novikov [2].

The interaction of titanium-carbon layers with silicon atomic monolayers has been found to be weak. It leads to the plasticity of carbon silicide.

The systematic investigation of arc-deposition physicochemical parameters effect on the chemical, phase composition and microstructure of $Ti-Si-N(C, O)$ films by using X-ray photoelectron spectroscopy, electron microscopy and electron microanalysis has been carried out in work [3]. The concentration and temperature regions favorable for mono-phase metastable $TiSi_xN(C)_yO_z$ solution formation have been found. The modeling of the electron energetic spectra of solid solutions in the system $Ti-Si-N(C, O)$ has been performed.

Earlier we have studied the possibility to synthesize zirconium, niobium, titanium and tantalum carbides and silicides in the form of powder using ionic-electronic melts $LiCl-Li$, $CaCl_2-Ca$, $MgCl_2-Mg$ as the transport media [4-7]. These melts were obtained by the dissolution of the given metal in its molten chloride. Such melts were called "ionic-electronic" because the dissolved metal undergoes dissociation: $Me \leftrightarrow Me^{n+} + ne^-$. The electric conductivity of these melts is partly electronic due to delocalized electrons and they are intermediate systems between ionic and metallic melts.

Surface coatings containing TiC phase have been obtained during titanium carbide synthesis. Ti_5Si_3 , $TiSi$ and $TiSi_2$ phases have been found when synthesizing titanium silicide. The spontaneous mass transfer of carbon and silicon onto titanium in $Li-LiCl$ melt has been investigated in order to develop new synthesis methods for plastic ceramics based on the $Ti-Si-S$ system [8].

2. Experimental

$Li-LiCl$ melt was chosen for our investigation because it has low vapor pressure at temperatures below 1000 °C. Experiments were carried out under *Ar* atmosphere in a container made of thermoresistant steel. There was a low-carbon steel crucible inside the container. Molten lithium chloride was put into the crucible, then metallic lithium was added in amount exceeding the solubility limit by 3-5 times. Titanium samples, silicon and amorphous carbon powder were introduced into the prepared melt in atomic ratios C:Si =1:3, 1:1 and 1:2, respectively. The fraction of carbon and silicon powder in the

melt was 5 and 10-wt.%. The container was then placed in vertical position in a furnace.

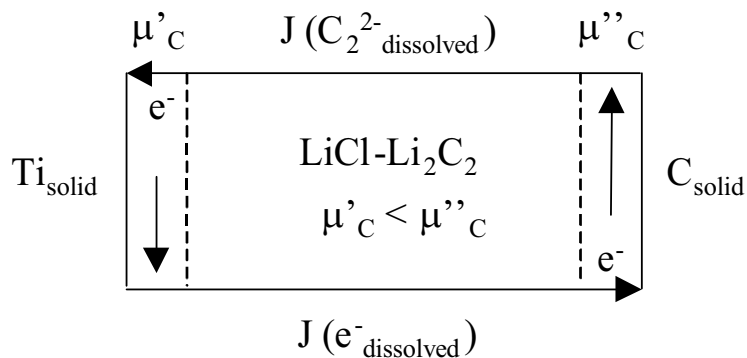
After heating under vacuum up to 200 °C the container was heated up to the working temperature and kept for the time needed. After that the container was removed from the furnace and cooled down. The samples were washed, weighed and taken to the X-ray phase analysis of coatings obtained. All experiments have been carried out in the melts saturated with lithium. Diffusants (carbon and silicon) had no direct contact with the base material (titanium). There was ionic-electronic melt between them: $C(Si)_{solid} / LiCl_{liq} + Li_{dissolved} + C(Si) / Ti_{solid}$.

The presence or absence of transfer was detected by the sample weight change as well as by micro-X-ray analysis of the sample surface layer and of the cross-section. Micro-X-ray spectroscopy of the surface layer has been carried out on a Comebax analyzer and electron microscope JSM-5900LV. An experimental set-up Dron-3 has been used for X-ray phase analysis.

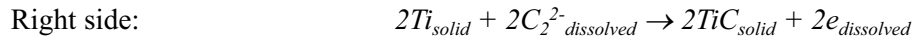
3. Results and discussion

Fine dispersed carbon used for the carbide synthesis was badly soaked with molten $LiCl$ and it floated on the surface of the melt in the beginning of the experiment, while titanium powder sank to the bottom of the crucible. Molten lithium has lower density than molten lithium chloride and it floats on the surface. Dvorkin et al. [9] have found the solubility of lithium in molten $LiCl$ at 900 °C to be 1.67 mol %. Carbon is not soluble in molten $LiCl$ but lithium forms with carbon a compound of ionic type - Li_2C_2 . Thus, the first stage of this process is lithium carbide formation that dissolves in the melt as it was shown by Morris [10]: $Li_2C_2 \leftrightarrow 2Li^+ + C_2^{2-} \leftrightarrow 2Li_{dissolved} + 2C_{solid}$.

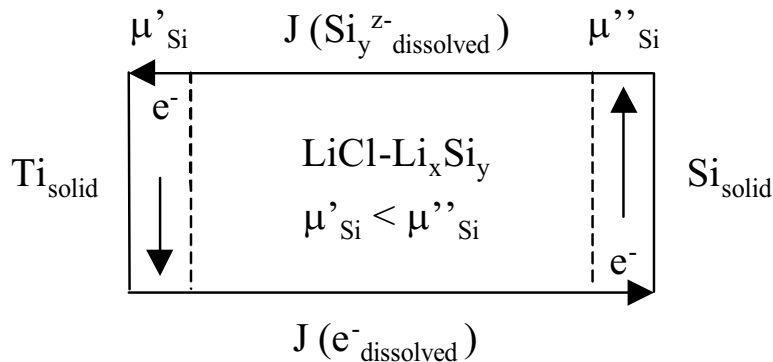
The second stage of the process is carbon transfer through the molten salt onto the titanium surface. The driving force of carbon transfer is the gradient of its chemical potential at the boundaries of solid phases with the melt.



Boundary reactions:



The slowest stage of the process is carbon diffusion into titanium with the formation of carbide layer. Carbon activity in lithium carbide must be higher than in titanium carbide. In other words, the bond energy *Li-C* is less than that of *Ti-C*. There are some compounds in the *Li-Si* system. Generalized data on the lithium-silicon system are presented in handbook [11]. According to them, there are 4 compounds in the temperature region 628-752 °C: *Li₂₂Si₅* (decomposition temperature - 628 °C), *Li₁₃Si₄* (melting point - 722 °C), *Li₇Si₃* (melting point - 752 °C), and *Li₁₂Si₇* (decomposition temperature - 648 °C). In our opinion, lithium silicides in ionic-electronic melts can partly dissociate to form lithium cations and silicon containing anions of hypothetical composition *Li_xSi_yⁿ⁻* [7]. These anions can be silicon carriers, transferring it from the powder to the metal with titanium silicide formation. Hypothetically, it can be presented as follows:



There are phases *Ti₅Si₃*, *Ti₅Si₄*, *TiSi₂* as well as *TiC*, *SiC* and, also, titanium oxides (*TiO* and *Ti₂O*) in the coatings on titanium at *C:Si* ratio 1:3. Maximum silicon content in the surface layer is 12.5-wt. % (according to micro-X-ray analysis). There are *TiC* and *SiC* phases in the coatings on titanium at *C:Si* ratio 1:1. Silicon concentration in the surface layer varies from 0.1 to 1.5-wt. %. There are *Ti₅Si₃*, *Ti₅Si₄* and *TiC* phases in the coatings on titanium at *C:Si* ratio 2:1; except for that, titanium oxides - *TiO*, *Ti₂O*, *Ti₂O₃* - have been found in some samples. In all cases the weight increase varies from 2.5 to 8 mg/cm². Powder alloy obtained from *Ti*, *Si* and *C* powders at a temperature of 900 °C

and 10 hours of exposition contains Ti_5Si_3 , TiC and SiC phases. X-ray patterns of the diffusion layer are presented in Figs. 1-4.

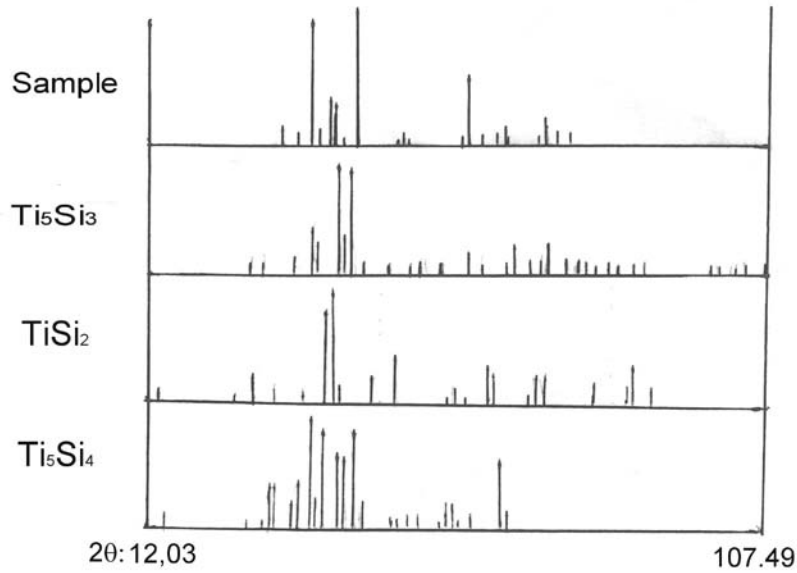


Figure 1. X-ray diffractogram of the diffusion layer obtained by the saturation of titanium with silicon and carbon at 950 °C for 5 hours (atomic ratio C:Si - 1:3, C+Si - 10-wt. %).

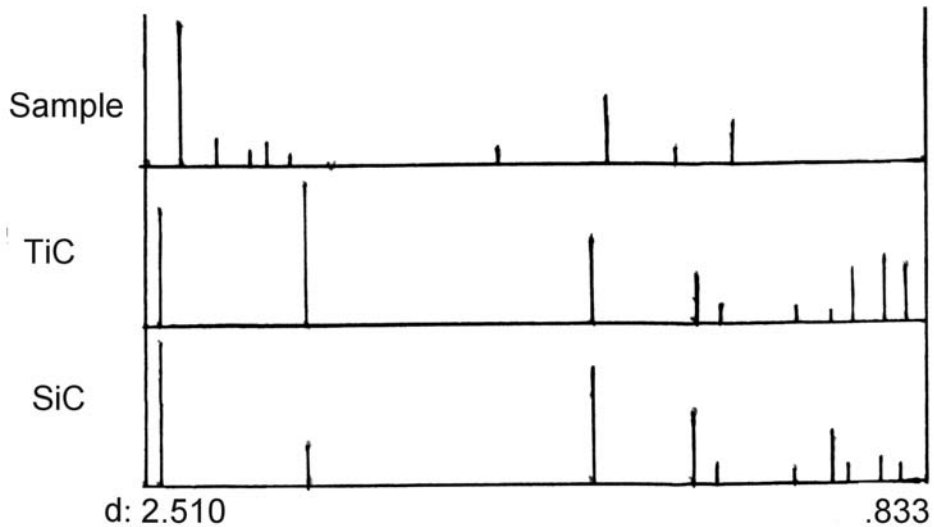


Figure 2. X-ray diffractogram of the diffusion layer obtained by the saturation of titanium with silicon and carbon at 950 °C for 5 hours (atomic ratio C:Si - 1:1, C+Si - 10-wt. %).

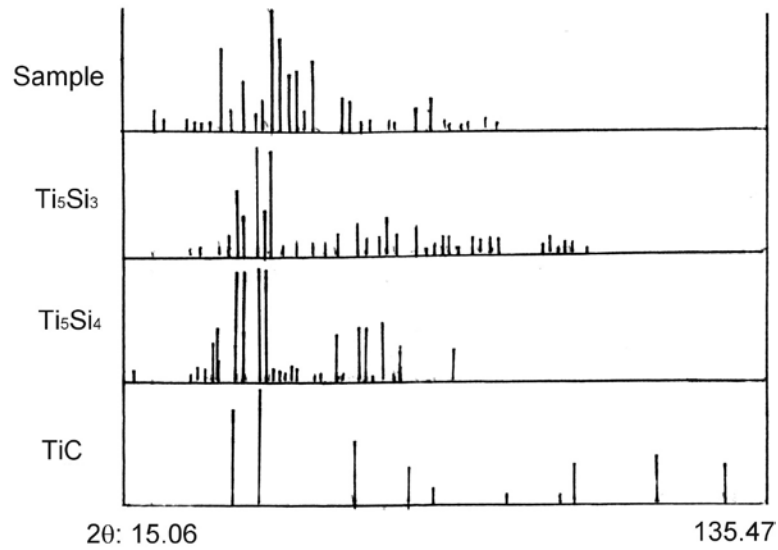


Figure 3. X-ray diffractogram of the diffusion layer obtained by the saturation of titanium with silicon and carbon at 950 °C for 10 hours (atomic ratio C:Si - 2:1, C+Si - 5-wt. %).

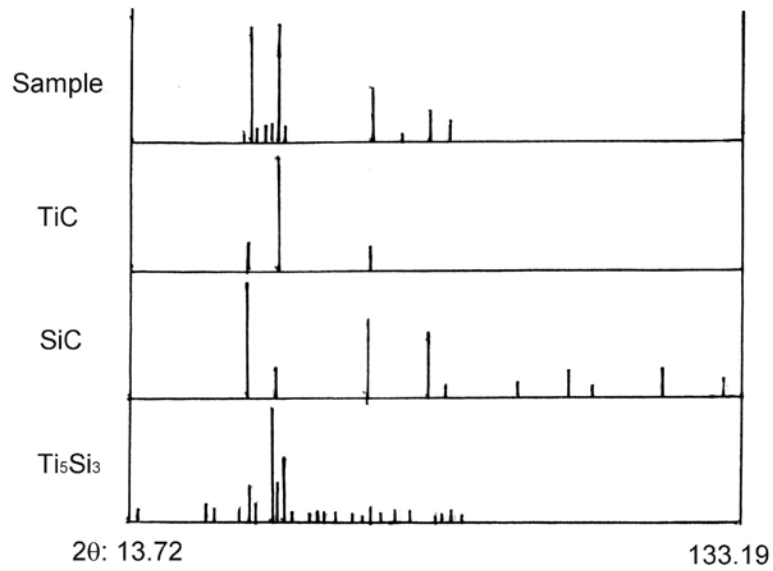


Figure 4. X-ray diffractogram of Ti+C+Si powder obtained at 950 °C (ex-position time: 10 hours).

4. Conclusions

Coatings and powders containing separate silicide and carbide phases have been obtained when saturating titanium jointly with carbon and silicon in *Li-LiCl* ionic-electronic melt. Ternary Ti_3SiC_2 compound has not been obtained. A possible reason for that is low temperature of the experiment.

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