Note

Carburization of Titanium Oxide by Means of Plasma Jet

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The metal carbides such as VC¹⁾, ZrC^{2),3)} and NbC⁴⁾ were formed by carburization of respective oxides with carbon by heating with plasma jets. However, the formation of stoichiometric TiC by carburization of TiO₂ is difficult, because TiO and TiC form solid solution (δ -phase) of fcc crystal structure. Therefore, TiC has been formed so far in the solid state in vacuum or in an inert atmosphere^{5),6)}. In the present experiment, the carburization of TiO₂ with graphite by heating with argon plasma jet was attempted and some properties of the product were investigated.

TiO₂(rutile type powder supplied by Toho Titanium Mfg. Co. and having a purity of 99.5% up) and graphite powder (spectroscopic grade, Tokai Electrode Co.) were mixed in a desired ratio. About 1 g of mixture was pressed into a tablet of 15 mm in diameter and 3 mm thick. The method of carburization of TiO₂ with graphite was the same as mentioned previously^{2),3)}. The surface temperature of TiO₂-graphite mixture tablet under the argon plasma jet was higher than the melting point of TiO₂ at the current of 60 A and increased with increasing current. The temperature reached the melting point of TiC (3130°C) at the current of 140 A.

After the plasma jet bombardment, a metallic cakes of varying color from gold to blackish, were obtained on the graphite hearth anode. The products were found to be the mixture of TiC, TiC_xO_y (δ -phase), TiO and graphite by X-ray diffraction. Chemical analyses showed that the carbon content in the cake varied considerably with the experimental condition. CO was the only detectable gaseous product by gas chromatography.

The chemical analyses and X-ray diffraction data of products formed in various molar mixing ratio of graphite to TiO₂ (C/TiO₂) are listed in Table 1. The combined carbon content increased with increasing C/TiO₂ up to C/TiO₂=3. The combined carbon content at C/TiO₂=3 corresponded to that of stoichiometric TiC. The lattice parameter of the product ob-

Table 1 Chemical analyses and X-ray diffraction data of the products under various C/TiO₂

C/TiO ₂	Ti content (wt. %)	Free C content (wt. %)	Combined C content (wt. %)	Identified species by X-ray diffraction	a_0 of fcc phase (Å)
1.0	70.7	0.27	0.33	TiO	—
2.0	78.7	0.43	6.90	TiC _x O _y	4.280
2.5	78.8	0.38	12.40	TiC _x O _y	4.316
3.0	79.7	1.53	19.91	TiC	4.325
3.5	72.7	8.43	19.06	TiC, C	4.325
4.0	68.2	14.54	17.18	TiC, C	4.325

Reaction conditions: 150 A, flow rate of Ar 4liters/min, 3 min

tained at C/TiO₂=3 was 4.325 Å. It was confirmed to be stoichiometric TiC.

The influence of the current on the reaction was investigated by heating the tablet of C/TiO₂=3 for 3 min under various current. When the current exceeded 130 A (about 3000°C), the combined carbon content increased remarkably and the product was stoichiometric TiC. Therefore, it is considered that the reaction in the liquid state proceeds more rapidly than that in the solid state.

The influence of the reaction time on the carburization at C/TiO₂=3 and at 150 A was investigated. The combined carbon content increased with increasing reaction time up to 2 min and then it remained constant. When the reaction time exceeded 2 min, the stoichiometric TiC was formed and the deoxidation was almost complete.

From the results obtained above, the optimum mixing molar ratio of graphite to TiO₂ was 3 and the overall reaction may be as TiO₂+3C=TiC+2CO. In this case, the reaction proceeded quickly in the liquid state.

The relation between the lattice parameter of fcc phase in the product and the combined carbon content is shown in Fig. 1. The products except stoichiometric TiC were solid solutions of TiO and TiC (δ -phase). The lattice parameter increased with increasing com-

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Fig. 1 Lattice parameter vs. combined carbon content

—○— : This work, ● : TiC, ○ : TiC_xO_y,
 : Nishimura et al.
 —. — : Kubo et al.

bined carbon content up to 40 at. %. Although small amounts of oxygen was included in the lattice, the lattice parameter was nearly equal to that of stoichiometric TiC. The measured density of stoichiometric TiC by the water displacement method was 4.90 g/cm³. The X-ray density of stoichiometric TiC was 4.91 g/cm³.

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<図 書 案 内>

合本「電気化学測定法」

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本誌掲載の講義シリーズ“電気化学測定法”は完結しました。

電気化学測定法は、化学反応機構の解明、生体機能の計測など基礎的研究の面から、各種のプロセス計測にみられる応用面にいたるまで、幅広い分野でますます発展し、情報化社会において重要な役割りを果しております。

このシリーズでは、「どのようにして必要な電気化学的情報をとり出すか」、「とり出した情報の質は、どのようなものであるか」または「複雑系からの情報のとり出し方ならびにその処理」についてまとめられました。

このたび、本講義シリーズを抜粋、集録して、合本「電気化学測定法」を刊行しました。皆さまの重ねてのご愛読をお待ちします。

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