

# マテリアル先端リサーチインフラ利用報告書

## ARIM User's Report

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### 課題データ / Project Data

課題番号 Project Issue Number	24TU0085
利用課題名 Title	金属溶湯脱成分法による多孔質金属炭化物の研究
利用した実施機関 Support Institute	東北大学 / Tohoku Univ.
機関外・機関内の利用 External or Internal Use	内部利用 (ARIM事業参画者以外) / Internal Use (by non ARIM members)
ARIM半導体基盤PF 関連課題 Related to ARIM-SETI	指定なし / No Designation
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	マルチマテリアル化技術・次世代高分子マテリアル/Multi-material technologies / Next-generation high-molecular materials 革新的なエネルギー変換を可能とするマテリアル/Materials enabling innovative energy conversion
キーワード Keywords	脱成分 (デアロイング), ポーラス金属, 多孔質金属炭化物, 電子顕微鏡/ Electronic microscope, 集束イオンビーム/ Focused ion beam

### 利用者と利用形態 / User and Support Type

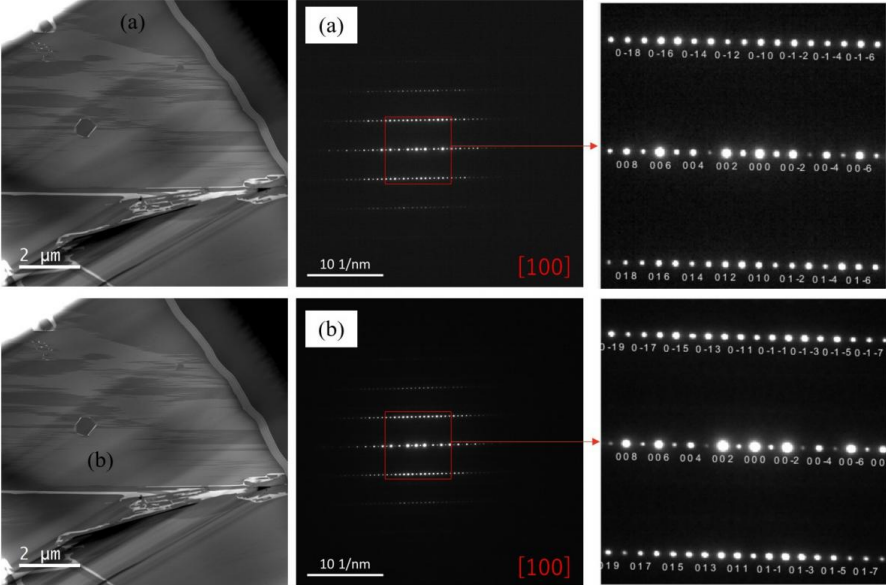
利用者名 (課題申請者) User Name (Project Applicant)	劉 方舟
所属名 Affiliation	東北大学金属材料研究所
共同利用者氏名 Names of Collaborators Excluding Supporters in the Hub and Spoke Institutes	
ARIM実施機関支援担当者 Names of Supporters in the Hub and Spoke Institutes	長迫実, 竹中佳生
利用形態 Support Type	技術代行/Technology Substitution

### 利用した主な設備 / Equipment Used in This Project

<b>利用した主な設備</b> <b>Equipment ID &amp; Name</b>	TU-504 : 超高分解能透過電子顕微鏡 TU-508 : 集束イオンビーム加工装置 TU-507 : 集束イオンビーム加工装置
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## 報告書データ / Report

<b>概要 (目的・用途・実施内容)</b> <b>Abstract (Aim, Use Applications and Contents)</b>	<p>MAX phases, known for their unique layered structure combining metallic and ceramic properties, face synthesis challenges with already developed direct synthesis and indirect synthesis methods like SPS, CVD, and molten salt methods. Many thermodynamically stable and unstable MAX phases remain unexplored due to the difficulty in controlling reaction conditions and the formation of unwanted phases. The Liquid Metal Layer Replacement (LMLR) method offers a promising alternative by selectively replacing A-layer atoms with molten metal baths, thereby enabling the synthesis of novel MAX phases. This method not only addresses the limitations of conventional synthesis techniques but also provides greater control over composition and structure, facilitating the discovery of new MAX phases.</p>
<b>実験</b> <b>Experimental</b>	<p>Currently, most non-equilibrium methods for synthesizing MAX phases are focused on thin films and powders. Since LMLR takes advantage of diffusion between metals, we chose bulk <math>Ti_3SiC_2</math> precursor to emphasize the potential of this method. The bulk <math>Ti_3SiC_2</math> was synthesized using powder metallurgy. Initially, titanium powder (Ti, purity 99.5%), carbon powder (C, purity 99.9%), and silicon powder (Si, purity 99.9%) were weighed in a molar ratio of 3Ti:2C:1Si. To ensure uniform mixing of the raw materials, ball milling was performed at 300 rpm for 20 hours. During the ball milling process, the ductile cast iron tank was evacuated and filled with argon at 0.5 atm to prevent oxidation of the powders. The milled powder mixture was then placed in a graphite mold and sintered using induction heating and spark plasma sintering (SPS). The sintering was conducted at 1400 °C in an argon atmosphere at one atmosphere of pressure, with an axial pressure of 60 MPa maintained throughout. The heating time for sintering was 30 minutes, with a dwell time of 60 minutes.</p> <p>The synthesized <math>Ti_3SiC_2</math> sample was then cut into 30 × 15 × 1 mm blocks and polished. The samples were suspended above a crucible using a molybdenum wire (<math>\phi</math> 1.5 mm), and the crucible was placed in an induction furnace. The furnace was heated to 1100 °C to melt the copper in the crucible. Once the temperature stabilized, the <math>Ti_3SiC_2</math> precursor was gradually immersed in the molten Cu for 5–30 minutes for the LMLR reaction. After the reaction, the sample was cooled and extracted for further structural and compositional analyses.</p> <p>The phases present in the sample were identified using an X-ray diffractometer (XRD, Rigaku Ultima IV) equipped with a Cu tube. The microstructure and composition were investigated using a scanning electron microscope (SEM, Carl Zeiss Ultra 55) equipped with an energy-dispersive X-ray spectrometer (EDX, Bruker X-flash). High-resolution atomic-level structural analysis was also performed using a high-angle annular dark-field (HAADF) imaging and energy-dispersive spectroscopy (EDS) equipped scanning transmission electron microscope. The TEM lamellas were prepared by Focused ion-beam (FIB).</p>

<p style="text-align: center;"><b>結果と考察</b> <b>Results and Discussion</b></p>	<p>In this study, we introduced a novel Liquid Metal Layer Replacement (LMLR) method for synthesizing the MAX phase <math>Ti_3(Si_{1-x}Cu_x)C_2</math> and its derivative material, layered <math>Cu-TiC_x</math> composites. By immersing bulk <math>Ti_3SiC_2</math> precursor into molten copper at 1100 °C, we demonstrated that copper atoms could effectively replace silicon atoms in the A-layer through a diffusion process driven by mixing enthalpy. Our results show that the <math>Ti_3(Si_{1-x}Cu_x)C_2</math> MAX phase initially forms at the reaction front, characterized by a directional, jagged substitution region, as shown in Fig.1. As the Si concentration further decreases, this MAX phase becomes thermodynamically unstable in the 1100 °C Cu bath and decomposes into a nanolaminate <math>TiC_x-Cu</math> composite. Similarly, immersing <math>Ti_3AlC_2</math> in molten Ag at 1000 °C causes Al atoms to dissolve and be replaced by Ag, forming <math>Ti_3(Al_{1-x}Ag_x)C_2</math>. When Al continues to dissolve, the new <math>Ti_3(Al_{1-x}Ag_x)C_2</math> MAX phase decomposes into a nanolaminated <math>TiC_x-Ag</math> composite material.</p>
<p style="text-align: center;">図・表・数式 1 Figures, Tables and Equations 1</p>	 <p>Fig.1:(a) The diffraction pattern of the unreacted <math>Ti_3SiC_2</math> precursor (b) The diffraction pattern of <math>Ti_3(Si_{1-x}Cu_x)C_2</math> after the replacement</p>
<p>その他・特記事項 (参考文献・謝辞等) Remarks(References and Acknowledgements)</p>	

**成果発表・成果利用 / Publication and Patents**

<p>DOI (論文・プロシーディング) DOI (Publication and Proceedings)</p>	
<p>口頭発表、ポスター発表 および、その他の論文 Oral Presentations etc.</p>	
<p>特許出願件数 Number of Patent Applications</p>	1件
<p>特許登録件数 Number of Registered Patents</p>	0件