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論 文 の 内 容 の 要 旨

Titanium Silicon Carbide (Ti_3SiC_2) is one of the $M_{n+1}AX_n$ (MAX) phases – layered ternary carbides and nitrides with a hexagonal crystal structure. MAX phases exhibit unique combination of metallic and ceramic properties. They are typically good thermal and electrical conductors apart from being thermal shock-, wear-, and oxidation resistant, and damage tolerant. These properties of the MAX phases make them possible candidates for industrial applications in high temperature and/or corrosive environments, as electrical contacts, contacts for 2D electronic circuits, as wear protective and lubricant coatings. Owing to their anisotropic crystal structure and chemical bonding MAX phases offer myriad of anisotropic material properties which remain unexplored due to the lack of large enough single crystals. Despite tremendous work on MAX phase materials in the past decade, capability of the present state of art for MAX phase ceramics is low as regards real industrial application. Ti_3SiC_2 was chosen for this research from the point of view of its viability for industrialization. There remains a necessity to synthesize Ti_3SiC_2 powders suitable for colloidal processing and pressureless sintering in order to realize the various potential applications.

The objective of this thesis was to highlight the applicability of colloidal processing techniques for fabrication of Ti_3SiC_2 and to explore ways to develop methods to obtain high density textured bulks and films of Ti_3SiC_2 by application of external fields, electric and magnetic, during the colloidal processes followed by pressureless sintering. Further, it was also aimed to study the effect of texture on some of the properties of Ti_3SiC_2. The following are the accomplishments of this thesis –

Synthesis of TiC free Ti_3SiC_2 powder by heating (pressureless) in Ar atmosphere at relatively low temperature: Ti_3SiC_2 powders with good pressureless sinterability could be synthesized from 1Ti/1.2Si/0.3Al/2TiC at 1200 °C in argon atmosphere. This powder is free from binary TiC impurity. The effects of particle size of Ti, amounts of Si and Al on synthesis of TiC-free Ti_3SiC_2 were confirmed. Although TiC-free Ti_3SiC_2 could be synthesized, this powder

contained trace amounts of Al_2O_3, Al, and Si. The trace amounts of Al and Si was actually effective in the densification during pressure-less sintering of the powder compacts. This powder has plate-like particle morphology with D_{50} = 2.8 μm and could be easily de-aggregated using an alumina mortar and pestle. The synthesized powder was suitable for colloidal processing and texture development in a strong magnetic field.

Dispersion behavior of Ti_3SiC_2: Cationic dispersant polyethelenimine (PEI) was found to be suitable for dispersing Ti_3SiC_2 in aqueous, ethanol and mixed solvent. PEI rendered a positive charge on the incipiently negatively charged Ti_3SiC_2 over a broad range of pH. It was found that the minimum amount of PEI needed to maintain a stable Ti_3SiC_2 suspension, with good fluidity, is 0.3wt % (3mg/g). Higher amounts of PEI were necessary for preparing stable, well dispersed, suspensions with high solid loading.

Feasibility of gel casting Ti_3SiC_2 and texture development: The feasibility of gelation of ternary MAX phase carbide – Ti_3SiC_2 – by using the new monomer, glycerol monoacrylate was shown. It was confirmed that Ti_3SiC_2 grains get aligned with their a-axis parallel to the direction of the magnetic field.

Mechanism of deposit formation during electrophoretic deposition – pH localization: pH localization – the change in local pH – increase at the cathode and decrease the anode during electrophoretic deposition was verified as the mechanism for deposit formation. The initial bulk pH of the suspension was found to be important for the phenomenon of pH localization and consequently important for the formation of deposits. The initial bulk pH of the suspension should neither be too far from the isoelectric point (IEP) nor too near it. The change in local pH was characterized by fluctuations at the initial period of time, after which the pH changed significantly towards IEP of the particles in suspension and facilitated formation of deposits. The pH localization phenomenon during EPD was also verified for the Ti_3SiC_2 in aqueous and mixed (water:ethanol = 1:1) suspension. A delay in the attainment of IEP near the vicinity of the deposition electrode was observed in case of the mixed suspension along with a slower deposition rate.

Fabrication of textured Ti_3SiC_2 films by EPD: Textured free standing deposits of Ti_3SiC_2 could be fabricated by EPD in a strong magnetic field of 12 T. The process for preparing Ti_3SiC_2 films on alumina ceramic substrates by EPD followed by pressureless sintering was optimized. The films fabricated could not be densified to full density. Nonetheless, the results reveal possibility of further densification and in spite of the low density, electrical resistivity of the films, with elongated microstructure, was 390 μΩcm and the films with roughly symmetrical microstructure, was 180 μΩcm.

Fabrication of dense textured Ti_3SiC_2 by slip casting in a strong magnetic field:: Highly textured, dense, Ti_3SiC_2 ceramics were fabricated by slip casting in a 12 T strong magnetic field followed by pressureless sintering. The relative density, bending strength, fracture toughness, and electrical resistivity of the textured Ti_3SiC_2 ceramics was 99.4%, 623 MPa, 5.9 $MPam^{1/2}$, and 30 μΩcm. Development of texture led to improvement of mechanical response - bending strength and fracture toughness – by factors of 1.6 and 1.4, respectively. The anisotropy in electrical conductivity for Ti_3SiC_2 was found to be limited. The conductivity along c-plane is higher than the conductivity along the c-axis by a factor of 1.2. The measurement of conductivity was affected by the trace impurities existing at the grain boundaries. In our work we were able to eliminate the TiC impurity; however some oxide phases were included due to addition of Al. Nonetheless, the addition of Al was found to be important for the pressureless sinterability of Ti_3SiC_2 and the electrical conductivity of the fabricated textured Ti_3SiC_2 bulk is still at par with metals like Ti.

審 査 の 結 果 の 要 旨

MAX 相と呼ばれる層状３元系炭化物セラミックスは、金属的な特性とセラミックス的な特性を合わせ持

つ新素材として注目されている。Ti_3SiC_2 は最も研究されてきたMAX相セラミックスであるが、従来、緻密なバルク体を得るため、ホットプレス、パルス通電加圧焼結、などの加圧焼結が行われてきた。本論文では、出発原料粉末としてTi、Si、TiC粉末を用い、Siを過剰に加え、Alを添加することにより、常圧焼結で緻密焼結体が作製可能な粉末の合成に成功した。ついで、Ti_3SiC_2 粉末の成形技術の高度化に取り組み、高密度で複雑形状成形が可能なゲルキャスト、膜や積層体成形に適した電気泳動堆積（EPD)、およびスリップキャストを強磁場中で行い、配向成形体の作製に成功した。特に、Ti_3SiC_2 粉末に対して、粉砕および分散手法の確立、無毒な水系新規硬化剤を用いたゲルキャストの適用、EPDの堆積過程を電極付近のpH変化と表面電位の関係からの説明、a 軸が磁化容易軸であることの実証、回転磁場成形による一方向配向体の作製、は特筆すべき成果である。回転強磁場中でスリップキャストした成形を常圧焼結することで緻密な c 面配向焼結体を作製し、無配向体に比べて、曲げ強度、破壊靱性に優れていること、緻密焼結体は高い電気伝導を示すことを実証した。

これらの成果は、多くのMAX相セラミックスに適用可能であり、配向制御と粒径制御を行うことでさらなる特性向上が期待される。また、ゲルキャスト、スリップキャスト、EPDなどの成形技術は、常圧焼結による微構造制御のみならず、複雑形状の成形体作製にも優れた手法であり、MAX相セラミックスの各種部材への適用に大きく貢献することが期待され、高く評価できる。

平成25年2月14日、数理物質科学研究科学位論文審査委員会において審査委員の全員出席のもと、著者に論文について説明を求め、関連事項につき質疑応答を行った。その結果、審査委員全員によって、合格と判定された。

上記の論文審査ならびに最終試験の結果に基づき、著者は博士（工学）の学位を受けるに十分な資格を有するものと認める。