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学位論文題目	STUDY ON PREPARATION AND ELECTRICAL PROPERTIES OF CARBON COMPOSITE MULTIDIMENSIONAL MATERIALS （多次元炭素複合材料の作製および電気特性に関する研究）
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論文内容の要旨

In order to fabricate carbon filled functional material with high dispersibility, electrical conductivity, and superior mechanical property, the multi-dimensional carbon composites were fabricated in this research. The fabricated carbon composites were formed as carbon nanoparticles/polymer 2D membranes, carbon nanoparticles/silica 3D ceramic bulk materials, as well as carbon nanotubes/silica 3D ceramic bulk materials. The variety of carbon composites were then studied their properties such as electrical conductivity and mechanical property. After that, the results were compared in order to investigate the effect of carbon material structures as well as carbon composites forms on their properties.

In Chapter 2, a micro-phase separation technique was chosen to fabricate carbon nanoparticles/polymer 2D membranes because it is one of the most common methods for preparation and production of a polymeric membrane. The micro-phase separation process studied here was in polymer system of cellulose acetate/acetone/water ternary solution. The carbon nanoparticles were added into the solution then the micro-phase separation occurred. After that, the carbon nanoparticles/polymer networks were heated so as to remove polymer from them. The carbon nanoparticles/polymer 2D membranes

were further studied their electro-conductivity. The results revealed that the additional carbon nanoparticles in the ternary solution were provided network by the driving force of non-solvent, which is related to thermodynamic and compatible properties between particles and ternary solution. Meanwhile, the surface properties of nanoparticle had an effect on the binding force between neighboring particles as a result in the continued formation of a nanoparticle network structure. However, the membranes of carbon nanoparticle membrane attached to glass substrate are quite lack of the possibility of independent existence. Which may possibly reduce their electrical property. To overcome such the problem, carbon materials in the next chapter were prepared without any glass substrate. Moreover, the other material used as a base matrix for carbon nanoparticles may provide higher mechanical properties than the glass substrate used.

Therefore, the silica ceramic was chosen to be a base matrix for carbon nanoparticles in the Chapter 3. In Chapter 3, the carbon nanoparticle/silica 3D ceramic composite matrixes were fabricated via non-firing process. The different volume percentages of carbon nanoparticles were added into silica ceramic in order to investigate the relationship between amount of carbon additive and the physical properties of the carbon nanoparticle/silica 3D ceramic composite matrixes including electro-resistivity and mechano-property. The results revealed that the highest amount of carbon in the carbon nanoparticles/silica to achieve solidified body percolates was 40 vol.%. According to the three-point bending tests, the carbon nanoparticle/silica 3D ceramic composite matrixes containing 20 vol.% carbon exhibited the highest strength as compared to other samples in this study. It can be inferred that the highest strength was possibly provided by the shrinkage prevention due to the aggregation of carbon nanoparticles leading to improve their mechanical property. However, the increased amount of carbon nanoparticles may break the bond between silica therefore the strength of those decreased. Moreover, the usage of a large amount of carbon used to form a network in ceramic matrixes is necessary for achieving a good electrical conductivity in the produced carbon nanoparticles/silica 3D ceramic composite matrixes of this chapter. Thus, carbon nanotubes (CNTs) have much attention to solve that problem because they have a better dispersibility than the carbon nanoparticles leading to decrease the amount of carbon in ceramic matrixes. They also have a lower conductive percolation threshold to add into a ceramic matrix with the basis of ensuring mechanical strength for various applications.

In Chapter 4, CNTs/silica ceramic composite with electro-conductivity was fabricated and its application on electromagnetic filed also discussed. Carbon composite ceramics have attracted much attention in the industry because of their excellent properties such as strong toughness, high electrical conductivity as well as low percolation threshold. Therefore, carbon nanotubes (CNTs) were used to incorporate silica ceramics in order to improve their electromagnetic properties. The number of CNTs in CNTs/silica composite ceramics was varied in order to investigate its effect on morphologies and electromagnetic properties of those. The composites were successfully fabricated by a non-firing process. The results revealed that the obtained CNTs/silica composite ceramic performed both electrical resistivity and bending strength. Meanwhile, the electromagnetic wave absorption ability achieved over a wide frequency. This indicates that the CNTs in CNTs/silica composite ceramics can be potentially applied as electromagnetic wave reflective material. This chapter not only proposed and realized the probability of a functional CNTs/silica ceramic material using a more facile and environmental method but the CNTs/ceramic composites also have perfect properties such as the mechanical strength and the dispersibility of CNTs fillers.

Chapter 5 introduced that CNTs/ceramic composites have attracted much attention for the industry because of their excellent properties. The additional interfacial bonding of silane functionalized multi-walled carbon nanotubes adding silica ceramic composites prepared by a non-firing process was therefore investigated in this work. MW-CNTs were previously oxidation treated by mixed acid for the further surface modify with the participation of a silane 3-aminopropyl triethoxysilane (APTES), which improves the chemical bonding and dispersibility of CNTs in ceramic bodies. The existence of APTES chemical functionalization and mechanical property of CNTs/silica ceramic composites were investigated. Results showed the composites were facilely prepared without calcining or sintering to form ceramic materials. They also showed that oxidization treatment introduced functional groups to CNTs surface for stable interfacial reacting with the amino groups on APTES. Obtained APTES-CNTs was sequentially combined with surface activated silica. This finding confirmed the improvements in dispersibility and enhanced mechanical property of composite material successfully.

Based on the above-mentioned studies, they can be concluded that our studies focused on investigating the ability of carbon materials filled multidimensionality (2D and 3D) functional nanocomposites. The ceramic materials prepared by the phase-separation process and an environmental friendly method known as the non-firing process can be potentially applied as electrical and EMI shielding materials. The different kinds of carbon materials having excellent conductive properties are added to the membrane polymer material and the bulk ceramic material so that the insulating material has electrical conductivity. The dispersibility and percolation threshold of carbon materials in the matrix materials were studied and finally applied to conductive composite materials and electromagnetic shielding materials. In recent years, most researchers believe that carbon nanotube-reinforced ceramic materials mainly depend on the dispersion of carbon nanotubes in the matrix, sufficient densification, and proper interfacial bonding between the carbon nanotubes and the matrix. In addition, it is also related to the number of carbon nanotubes added and the structural integrity.

論文審査結果の要旨

本研究は、種々のカーボン充填構造を有する複合機材料の機能発現についての研究を行っている。研究対象とした多次元カーボン複合材料は、カーボンナノ粒子/ポリマー二次元膜、カーボンナノ粒子/シリカ三次元セラミック材料、ならびにカーボンナノチューブ/シリカ三次元セラミック材料が用いられた。これら試料を比較検討しマトリックス内の炭素材料の構造と炭素複合体の機能化について結論を得ている。第 1 章では、研究背景、本研究の位置付けが述べられていた。第 2 章では、炭素ネットワーク構造が任意に制御できるミクロ相分離法でカーボンナノ粒子/ポリマー二次元膜を作製している。ナノ粒子ネットワーク構造の連続性が制御できることを見出している。また、電気抵抗率の評価かからカーボン粒子の二次元パーコレーションモデルとの整合性を明らかにしている。第 3 章では、カーボンナノ粒子/シリカ三次元複合材料をカーボンにダメージを与えない無焼成プロセスによって作製していた。第二章で得た電気抵抗率とカーボン構造の評価を三次元に拡張して議論している。40vol.%で電気低効率が著しく変化することを見出している。一方で、20vol.%で三点曲げ強度が最も高くなることを見出している。40vol.%はパーコレーション理論から推定すると炭素量が多いことから、カーボン粒子の凝集の存在を推測し、分散を向上させれば、電気伝導率と強度のトレードオフの関係に折り合いがつく領域があることを推定していた。よって、本章以下ではカーボンナノチューブ（CNT）を用いることとでパーコレーション閾値を低減し、さらにシリカ界面の反応量を向上することで導電性と強度向上について検討していた。第 4 章では、CNT /シリカセラミック三次元複合体を作製し議論していた。その結果、予想通り、電気抵抗率と曲げ強度の両方を示した。高い靭性、また、高い導電率、低いパーコレーション閾値などの優れた特性を有することが示されていた。 また、電磁波吸収性材としての可能性にも言及していた。第 5 章では、第 4 章で優れた特性を示した CNT /セラミック三次元複合材の更なる機能性向上を目指し、シランカップリング剤を用いてシラン官能化カーボンナノチューブを作製し、CNT の分散性向上と界面反応による材料強度向上を試みていた。カップリング材で導入されたアミノ基とシラノール基の界面相互作用により、分散性および機械的性質の向上に成功していた。

上記のように、本論文では、炭素材料複合材料を対象とし、炭素材料のマトリックス内での充填状態と電気伝導性、機械的強度、電磁波吸収などの諸特性の関係を調査し炭素分散系複合材料の新たな設計に関する方針が示されていた。よって、本研究はこの分野への応用展開可能であり、材料科学における工学的意義は大きい。以上より、本論文は、博士（工学）の学位授与に相当する内容であると認められる。