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学位論文題目	多層カーボンナノチューブ分散強化型アルミニウム複合材料の作製と界面制御に関する研究
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論文内容要約

Fabrication and interfacial control of multi-walled carbon nanotube reinforced aluminum matrix composites

Recently, carbon nanotubes (CNTs) have been investigated as reinforcements in metal matrix composites (MMCs) for the extraordinary mechanical, thermal, and electrical properties of CNTs. Many researchers have attempted to fabricate CNT-Al matrix composites, which could be used in advanced applications such as aerospace and automotive materials, as well as thin electric wires in which lower weights would save energy. Unfortunately, the strengthening enhancement of Al matrix by incorporating MWCNTs is still unsatisfied and far from our expectation. It should be attributed to two faced challenges: one is the poor dispersion of CNTs within the matrix, attributed to strong CNT entanglement caused by Van der Waals forces; the other is the imperfect CNT/Al interfacial bonding, which is caused by the poor wettability between the CNTs and the Al matrix. In recent decades, high-energy ball milling (HEBM), friction stir-processing, flake metallurgy, and nano-scale dispersion have been used in fabricating CNT-Al composites. However, most studies focused on the problem of CNT dispersion, which sometimes caused damage in the CNTs or left work hardening and contaminations in the matrix. Despite the strengthening reported in many of these studies, it is still not clear whether it was directly attributed to the load transfer from Al matrix to CNTs (through high interfacial resistance, which is caused either by a clean interface or an interfacial compounds like aluminum carbide (Al_4C_3), and/or the work hardening of the Al matrix induced from fabrication, and/or dislocation formation at the CNT/Al interface because of different Young's modulus and coefficients of thermal expansion between the CNTs and the Al matrix. Furthermore, less attention has been devoted to the study of the CNT/Al interface compared with the dispersion problem of CNTs. It was thought that the interaction of CNT/Al interface could be partially enhanced by the internal compressive stress during fabrication. Whereas, such physical bonding at the CNT-Al interface is generally weak, thereby leading to the local interfacial slipping of

MWCNTs during external loading. Therefore, formation of chemical bonds at the CNT/Al interface should be an effective approach. Unfortunately, the interfacial reactions at the CNT/Al interface have not been fully understood so far. It severely hinders the exploitation of the intrinsic behavior of CNTs in CNT-Al matrix composites. In order to ensure the interfacial phenomena in CNT-Al matrix composites to satisfactorily happen, it is quite important to induce and control nanodefects located on the surface of MWCNTs, where dangling bonds of carbon atoms are expected to preferentially reactable with Al matrix.

In order to form sufficient functional groups and control surface nanodefects without serious degradation, the acid treatment was employed to modify the pristine multiwalled carbon nanotubes (MWCNTs). The concentrated HNO_3 was initially employed for purifying the pristine MWCNTs at 323 K for 2-12 h. It was confirmed that MWCNTs purified for 12 h had the reduced amount of carbonaceous impurities and metal catalyst within MWCNTs, but no structural degradation of MWCNTs was induced. Then the defect-type evolution and gradual increase in nanodefects in the outer walls of MWCNTs in a chemically oxidizing environment were thoroughly investigated using a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). A fairly low temperature of 323 K was employed for the acid treatment, and this limited the reaction rate to provide a mild acidic environment for gradual chemical oxidation compared to commonly used treatment conditions (higher than 873 K). High-resolution transmission electron microscopy (HRTEM) observations clearly demonstrated the formation of groove-type defects in the outer walls of MWCNTs in the early period around 0.5-3 h, followed by a morphological change into circumference-type defects and further into unzipped graphene nanoribbons. The variation of the intensity ratio of D and G bands (I_D/I_G) of MWCNTs during the early stage of acid treatment started from the ratio being 0.1, and then clearly increased in a parabolic manner in the early stage between 0.017 h and 1.5 h, followed by a gradual increase up to 6 h. This unique parabolic variation in the I_D/I_G ratio was for the first time observed. This observation supports the gradual oxidation of graphitic walls with increasing acid treatment time and corresponds well with the formation and evolution of nanodefects. We obtained that the tendency of zeta potential to change with the increase of treatment time was approximately inversed of the variation in the I_D/I_G ratio. The zeta potential was decreased rapidly from 0.017 h to 6 h, while it slightly fluctuated at about -50 mV beyond 6 h. This result suggested that the concentration of functional groups in outer walls was increased during the early oxidization stage, and then reached a saturate because of the limited intrinsic defect sites of MWCNTs, which were expected for providing unpaired electrons. Furthermore, the results of FTIR confirmed that a sufficient amount of oxygen-containing functional groups were induced in the outer walls of acid treated MWCNTs over 4 h. Herein, MWCNTs acid-treated for 4 h to 6 h would result in an effective number of nanodefects via

suitable carboxyl functionalization, providing preferential nanocarbide sites for interfacial improvement as well as uniform dispersibility of MWCNTs without any serious structural degradation.

By using the MWCNTs acid-treated for 4 h, a novel MWCNT-Al composite was successfully fabricated by a combination of colloidal mixing process, spark plasma sintering (SPS) and hot extrusion. This composite is fully dense MWCNT-Al matrix composite, which has a microstructure free of most strain and dislocations, in which individually dispersed MWCNTs are unidirectionally aligned to the hot extrusion direction and form a clean MWCNT/Al interface, in an effective absence of interfacial impurities. Furthermore, the sword-in-sheath CNT failures were observed during hot extrusion. This fracture indicates that the radial compressive stress is applied to MWCNTs in hot extrusion, and implies that the hot extrusion process can enhance the inter-wall interactions and enable load distribution. This composite can allow us to demonstrate the contribution of load transfer to MWCNTs on the tensile response of Al matrix, and to evaluate the MWCNT/Al interface for understanding the interfacial reactions based on the thermodynamics and kinetics, thereby providing the ability to control carbide formation.

For the first time, an experimental technical named the in-situ pullout test has been developed to directly determine the interfacial strength in this novel composite. Twelve individual MWCNTs were pulled out from the tensile fracture surface of MWCNT-Al composites using a nanomanipulator system installed in a SEM chamber. As confirmed by HRTEM, no MWCNT failures were observed during the pullout test. The six MWCNTs having a straight embedded part, nearly perpendicular to the fracture surface and without serious degradation could be used for calculating the interfacial strength. It is obtained that the interfacial strength of directly contacted MWCNT/Al interface without any chemical compound was determined as 6-29 MPa (average: 16.7 MPa), which was lower than the theoretical value (half of the tensile yield strength of Al matrix, 44.2 MPa), indicating the MWCNT/Al interface has limited load-bearing ability.

The tensile test showed that the ultimate tensile strength (UTS) of MWCNT-Al composites increased linearly with the volume fraction of MWCNTs up to 1.5 vol. %, and then tended to saturate to 178.1 MPa beyond 1.5 vol. %, while the ductility of composites remained nearly undegraded. That is because the applied tensile load to Al matrix is not transferred to the point of the tensile fracture strength of MWCNTs; Al-MWCNT composite is finally fractured because of the ductile failure of Al matrix while MWCNTs bear a certain level of the applied tensile load when the average length of MWCNTs is smaller than the critical length. The experimental UTS values of composites were consistent with the values estimated by shear lag model using the interfacial strength of 29 MPa, supporting the validity of the pullout test and the presence of interfacial load transfer. Furthermore, after tensile test, the nano-cavity was commonly observed at the

MWCNT/Al interface near the fracture surface along the loading direction, indicating the local interfacial slippage occurred at some clean interfaces. In this case, the strong mechanical interlocking of the surface nanodefects in acid treated MWCNTs with Al matrix would be disappeared. That resulted in a weaker shear resistance of the MWCNT/Al interface, thereby a relatively lower measured average interfacial strength during in-situ pullout test. Thus, It was thought the interfacial strength was 29 MPa in this MWCNT-Al composite. In addition, the slight deviation between the experimental UTS and theoretically expected values was attributed to the local interfacial slippage of MWCNT during tensile test. However, it is noted the load transfer efficiency of 70 % has been realized by the directly contacted MWCNT/Al interface, indicating the promising load-bearing capability of MWCNTs was effectively exploited. It suggests that there is the possibility of increasing further the tensile property of Al-MWCNT composites by the formation of Al_4C_3 at the Al/MWCNT interface.

To improve the interfacial bonding, the formation of chemical bonds at the CNT/Al interface by favorable and controlled interfacial reactions is promising. It is important to understand the formation mechanism of aluminum carbide in the MWCNT-Al composites. The interfacial reactions between the MWCNT and Al matrix were investigated in a fully dense MWCNT-Al composite by precisely controlled heat treatments at temperatures below the Al melting point. It was shown that MWCNT (002) formed a coherent interface with low-index Al planes of Al (111), Al (220), and Al (002), all of which created relatively stable interfaces. HRTEM examination and a novel technical observation by FE-SEM clearly revealed that Al_4C_3 was preferentially formed at the active prism plane edges located at the open ends and acid treatment-induced sidewall nanodefects of the MWCNTs. It was confirmed that Al_4C_3 was single-crystalline and frequently contained unusual twinning features because of the internal compressive stress and different growth paths of Al_4C_3 on the MWCNTs. The Al_4C_3 maintained the shape of the pristine MWCNT and showed a typical orientation relationship with Al matrix, that is, Al (111)// Al_4C_3 (001). Furthermore, the activation energy of Al_4C_3 formation, calculated as approximately 195.8 kJ/mol, as well as the parabolic relation between the quantity of Al_4C_3 and heat-treatment time, supported the generation of Al_4C_3 at the prism plane edges and the growth of Al_4C_3 by the diffusion of Al atoms through the Al_4C_3 crystal. These results suggested that the open tip-originated Al_4C_3 may quickly grow in the $\langle 100 \rangle$ direction of the MWCNT, while nanodefekt-originated Al_4C_3 may simultaneously grow in the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions of the MWCNT.

The UTS of MWCNT-Al composites was really slightly increased after formation of small amount of Al_4C_3 nanostructures (11%) at 873 K for 0.1 h, while it dramatically reduces beyond 11 % of Al_4C_3 formation. This result indicates that the effect of Al_4C_3 formation on the strengthening of MWCNT-Al composite was

not clear, which still needs further clarification. As we know, the thermal expansion behavior of composites was very sensitive for the interfacial properties between the matrix and reinforcements, the thermal expansion behaviors of the MWCNT-Al composites were evaluated. It was obtained that the coefficient of thermal expansion (CTE) of composites decreased with increasing MWCNT concentrations, because of the constraining effect of MWCNTs for the thermal expansion of Al matrix during heating process. Furthermore, the CTE becomes close to the Schneider's micromechanical model after forming appropriate amount of Al_4C_3 . The cyclic thermal expansion behavior of the MWCNT-Al composite showed a clear hysteresis phenomenon during loading. However, after heat treatment, the hysteresis phenomenon nearly disappears; because of the reduction of interface sliding by Al_4C_3 caused by anchor effect even at 673 K. This is the evidence that could Al_4C_3 effectively improve the interfacial load transfer.

In this study, we confirmed that MWCNT-Al composites could be highly expected for the electric wires due to the high electrical conductivity, the improved UTS and the undegraded ductility, compared with the traditional Al alloys.