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High temperature thermal stability of pure copper and copper–carbon nanotube composites consolidated by High Pressure Torsion

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ABSTRACT

The thermal stability of ultrafine-grained (UFG) microstructures in pure copper samples and copper–carbon nanotube (CNT) composites processed by High Pressure Torsion (HPT) was compared. The UFG microstructure in the sample consolidated from pure Cu powder exhibited better stability than that developed in a casted Cu specimen. The addition of CNTs to the Cu powder further increased the stability of the UFG microstructure in the consolidated Cu matrix by hindering recrystallization, however it also yielded a growing porosity and cracking during annealing. It was shown that the former effect was stronger than the latter one, therefore the addition of CNTs to Cu has an overall benefit to the hardness in the temperature range between 300 and 1000 K. A good agreement between the released heat measured during annealing and the calculated stored energy was found for all samples.

1. Introduction

A promising application of carbon nanotubes (CNTs) is their incorporation as reinforcing fillers into composites [1–3] due to (i) the extremely high elastic modulus (~1 TPa), (ii) the large strength (~40 GPa), (iii) the high aspect ratio (~100–1000), (iv) the very low density (1.5–2 g/cm^3), (v) the excellent chemical and thermal stabilities (up to 750 and 2800 °C in air and vacuum, respectively) and (vi) the high thermal and electrical conductivities (for plastic and ceramic matrix composites). In the last decades many processing techniques have been developed to produce metal matrix – CNT composites such as: powder metallurgy [4–9], melting and solidification [10–12], thermal spraying [13,14] and electrochemical deposition [15] methods. The aim of the different processing techniques is to reach a homogeneous distribution of CNTs in the metal matrices and improve the interfacial bonding between the matrix and CNTs.

In the case of metal matrix – CNT composites the Young's modulus increases linearly with increasing the volume fraction of CNTs and their pinning effect on the lattice defects (dislocations and grain-boundaries) causes an increment in yield strength [4–9]. It is noted that CNT clusters often prevent sufficient bonding between the metal matrix particles, leading to fine pores and cracks in the nanocomposite. Subsequently, these fine cracks and pores act as nucleation sites for plastic instability, which account for the significant degradation of strain to failure of metal matrix – CNT composites [13]. It is confirmed that the key issue to enhance the toughness of CNT/metal nanocomposites is the homogeneous distribution of CNTs in the matrix [4]. Powder metallurgy methods usually apply milling to reach a uniform distribution of CNTs [6–9]. The dispersion of the nanotubes can be improved by increasing the energy of milling during the mixing step of processing [9]. However, it should be noted that high energy milling can damage the structure of the CNTs [6]. Another strategy for increasing the dispersion of CNTs in the matrix material is the treatment of CNTs by surfactants [16]. The mechanical properties of metal matrix – CNT composites can be further improved by a strong interfacial bonding between the matrix and CNTs [17–19]. Chu et al. [18] reached a good interfacial bonding through the formation of a thin transition layer of Cr_3C_2 at the interface between CNTs and Cu–Cr matrix. The improved interfacial bonding leads to an enhancement in both yield strength and hardness. Cha et al. [19] achieved an effective bonding between CNT and pure copper matrix using molecular-level mixing method. The better interfacial bonding in Cu–CNT composites resulted in an increment of yield strength and Young-modulus by about 300% and 170%, respectively, compared with the pure Cu matrix.

Most of the metal matrix – CNT composites are produced by powder metallurgy techniques [3–9,16–20]. After the mixing step the blend of CNTs and the powder of the matrix is consolidated to high density. A wide range of compaction processes is applied to reach a sufficient densification, such as cold isostatic pressing, hot isostatic pressing, spark plasma sintering, rolling or High Pressure

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Torsion (HPT). Although, the method of HPT is usually applied for the grain refinement in bulk coarse-grained metals [21–27], it is also capable to consolidate pure metallic powders [28,29] or their blends with CNTs [30–33]. Due to the very high applied pressure and imposed strain, ultrafine-grained (UFG) or nanocrystalline microstructures can be achieved in the consolidated samples, even if the initial powder consisted of coarse grains.

In a recently published paper [33], we compared the defect structure and the hardness of pure Cu and Cu–CNT composites consolidated by HPT. In this work, the high temperature thermal stability of these samples is investigated. To the knowledge of the authors, the study of the influence of CNTs on the thermal stability of UFG Cu is missing from the literature, although it is very important from the point of view of the practical application of Cu–CNT composites.

2. Experimental procedures

Copper powder having 99.5% purity and average particle sizes less than 44 μm (325 mesh, manufacturer: Chang Sung Co., Korea) and 3 vol.% multi-walled CNTs (MWCNTs) were mixed by high-energy milling (manufacturer: Applied Carbon Nano Co., Korea). The diameter and the length of the CNTs produced by Catalytic Chemical Vapor Deposition (CCVD) were 5–20 nm and 1–10 μm, respectively. The powder blend was pre-compacted by cold isostatic pressing. The pre-compacted disks having a diameter of 19 mm and a height of 3 mm were consolidated by HPT at RT and 373 K. The applied pressure and the number of revolutions were 2.5 GPa and 10, respectively. The HPT-processed disks were 20 mm in diameter and 0.7 mm in thickness. In order to study the effect of CNTs on the thermal stability of the HPT-processed microstructure, an additional sample was consolidated solely from the Cu powder at RT by the same way as in the case of the composite specimen. The stability of the UFG microstructure in the consolidated Cu sample was compared with a bulk, casted coarse-grained oxygen-free copper sample with 99.98% purity which was processed by HPT under 4 GPa for 10 revolution at RT in order to achieve fine-grained structure. In the following, the UFG samples processed from bulk, casted Cu, pure Cu powder, blend of Cu and CNTs at RT and 373 K are referred to as bulk-Cu, consolidated-Cu, Cu–CNT-RT and Cu–CNT-373, respectively. The difference between bulk-Cu and consolidated-Cu samples is emphasized again: in the first case only grain refinement occurred during HPT while in the second case both consolidation and grain refinement were performed in HPT-processing.

The thermal stability of the HPT-processed samples was investigated by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC2 calorimeter at a heating rate of 40 K/min. At the characteristic temperatures of the thermograms, the annealing was stopped and the specimens were quenched to RT. The microstructure of these disks was investigated at the half-radius by X-ray line profile analysis (XLPA). The X-ray line profiles were measured by a high-resolution rotating anode diffractometer (Nonius, FR 591) using CuK_1 radiation ($\lambda = 0.15406$ nm). Two-dimensional imaging plates detected the Debye–Scherrer diffraction rings. The line profiles were determined as the intensity distribution perpendicular to the rings obtained by integrating the two-dimensional intensity distribution along the rings. The line profiles were evaluated by the convolutional multiple whole profile (CMWP) analysis [34,35]. In this method, the experimental pattern is fitted by the convolution of the instrumental pattern and the theoretical size and strain line profiles. The theoretical profile functions used in this fitting procedure are calculated on the basis of a model of the microstructure, where the crystallites have spherical shape and log-normal size distribution, and the lattice strains are assumed to be caused by dislocations and twins. As an example, Fig. 1 illustrates a CMWP fitting of the X-ray diffraction pattern measured on Cu–CNT-RT sample after heating up to 620 K. The open circles and the solid line represent the measured and the fitted patterns, respectively. The area-weighted mean crystallite size ($\langle x \rangle_{area}$), the dislocation density (ρ) and the twin boundary frequency (β) were obtained from the fitting. The latter quantity is defined as the relative fraction of twin boundaries among {1 1 1} lattice planes. The area-weighted mean crystallite size ($\langle x \rangle_{area}$) was calculated from the median and the variance of the assumed log-normal crystallite size distribution as: $\langle x \rangle_{area} = m \cdot \exp(2.5\sigma^2)$.

The grain structure was examined using a Philips CM-20 transmission electron microscope (TEM) operating at 200 kV. The morphology of CNTs after HPT was studied by high resolution TEM (HRTEM) carried out by JEOL-3010 transmission electron microscope operating at 300 kV. The TEM foils were prepared at the half-radius of the HPT-processed disks and thinned by mechanical grinding and then by Ar–ion milling (10 kV, 2 mA) till perforation and were post-cleaned with 3 kV Ar–ions.

The porosities in the as-received and the annealed samples were characterized by the volume fraction of pores which was determined from the area fraction of the pores in scanning electron microscopy (SEM) images. The pictures were taken on the polished cross-section of the HPT-processed disks at their half-radius using an FEI Quanta 3D scanning electron microscope. The porosity values were evaluated from about ten SEM micrographs which corresponds to an inspected area of about 1000 μm^2. Additionally, the change of the microhardness during annealing was measured using a Zwick Roell ZHμ Vickers indenter with an applied load of 500 g and a dwell time of 10 s.

3. Results and discussion

3.1. The as-processed microstructures

The morphology and distribution of CNTs as well as the microstructural parameters of the Cu matrix in the four as-processed UFG samples obtained by XLPA and TEM have already been presented in our recently published paper [33]. However, since the changes of these parameters during annealing are investigated in the present study, their values at the half-radius of the HPT-processed disks are listed again in Table 1. No difference between the microstructures of the bulk-Cu and consolidated-Cu samples

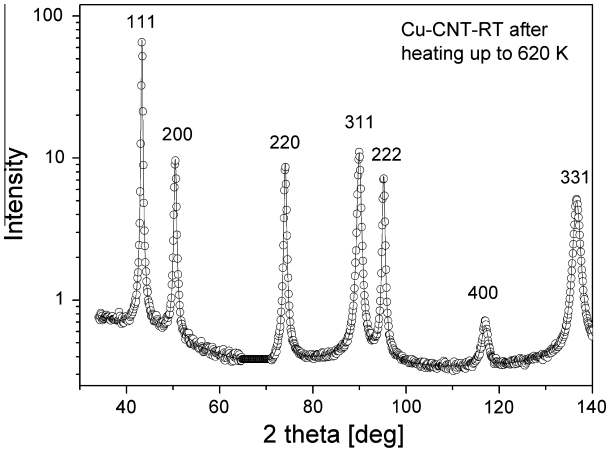

Fig. 1. CMWP fitting of the X-ray diffraction pattern taken on sample Cu–CNT-RT after heating up to 620 K in a DSC at a rate of 40 K/min, and then quenched to RT. The open circles and the solid line represent the measured and the fitted X-ray diffraction patterns, respectively. The intensity is in logarithmic scale.