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Branched carbon fibres and other carbon nanomaterials grown directly from 304 stainless steel using a chemical vapour deposition process

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ABSTRACT

The objective of this research is to examine and illustrate the effect of the preparation of temperatures for the direct synthesis of branched carbon fibres on 304 stainless steel sheeting without the addition of external metal catalysts and pretreatment by chemical vapour deposition. The effects of different temperatures (900, 1050 and 1200 °C) at a constant gas ratio of hydrogen, acetylene and nitrogen (1:1:2) on the direct growth of branched carbon fibres were investigated. The morphology obtained and the quality of branched carbon fibres as well as other carbon nanomaterials were examined with transmission electron microscopy, field emission scanning electron microscopy, thermogravimetry analysis and Raman spectroscopy. It was found that the temperatures are necessary for the growth of branched carbon fibres, tree branched carbon fibres and X-branched carbon fibres, as well as other carbon nanomaterials. In addition, the nanostructures of 304 stainless steel surfaces were investigated by atomic force microscopy at each temperature to describe the growth mechanism of branched carbon fibres and other carbon materials on the surfaces.

1. Introduction

Branched carbon fibres (BCFs) attracted researchers' attention many years ago [1]. Subsequently, the growth of branched carbon nanotubes was performed by arc discharge [2]. The various shapes of BCFs (e.g. Tree-, L-, Y-, T-, and X-shape) have garnered strong interest due to their excellent physical and electrical properties [3–5]. Recently, the methods of BCF synthesis have been studied by catalytic chemical vapour deposition [6–9], the template method [10,11] and electron beam welding in a transmission electron microscope method [12,13]. All of these methods required an external catalyst for success.

Several researches have reported a method to synthesise carbon nanomaterials (CNMs) directly on metallic catalytic substrate (e.g. Ni, Fe and stainless steel wafer) by chemical vapour deposition (CVD) [14–17]. This method is facile and robust. In addition, one of the most important advantages of this method is that the strong adhesion of CNMs on the substrate improves electron and thermal transport properties. This result supports the proposition that CNM-coated catalytic substrate can be useful for various applications such as electrocatalytic electrodes [18,19], fuel cells [20,21], sensors [22,23] and field emission probes [24].

The synthesis of CNMs on bimetallic catalysts has been a noteworthy topic in the past decade. Bimetallic catalysts have been observed on carbon nanotubes (CNTs) at higher growth rates and lower growth temperatures [25,26]. As a result, several scientists have attempted to synthesise CNMs directly on bimetallic catalytic substrate, particularly stainless steel. Stainless steel type 304 (304 SS) has been proposed as a bimetallic catalytic substrate for CNM direct synthesis because it is relatively inexpensive and readily available. In 2003, Vander Wal and Hall [27] were the first to successfully synthesise CNTs directly on 304 SS meshes with different pretreatments (e.g. oxidation, reduction, and combinations) by CVD using benzene/C_2H_2-CO mixtures as carbon precursor. The effectiveness of oxidation–reduction pretreatments on CNT growth has been explored by several other authors [28–30]. In addition, the direct growth of CNTs on 304 SS with strong acid pretreatment was another preparation method successfully conducted by CVD [31–33]. The surface of 304 SS was improved to stable catalyst sizes, which allowed the increased growth efficiency of CNTs. However, this process has a negative environmental impact due to acidic wastewater. Recently, researchers have attempted to grow CNTs directly without acid pretreatment. Another type of stainless steel, type 316, was used as catalytic substrate without any pretreatment by CVD because of stable catalyst size on its surface [17,34]. Most researches focusing on the study of direct growth of CNTs on stainless steel report no growth of other CNM shapes on stainless steel such as carbon nanofibres (CNFs), BCFs, bamboo-like carbon nanotubes (B-CNTs) and carbon nanospheres (CNSs), especially when using 304 SS without any pretreatment by CVD.

This research illustrated a simplified recipe for the direct synthesis of BCFs by CVD method using 304 SS as both catalyst and substrate. The 304 SS was used as catalytic substrate without the addition of external metal catalysts and without any pretreatments. In addition, the effects

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Table 1
Chemical composition of 304 SS from EDX analysis.

Element	Fe	Cr	Ni	Mn	C
Weight %	72.03	17.35	8.18	0.75	1.69

of various temperatures on the surface of 304 SS (size and shape of catalyst) and the growth of different shapes of BCFs were studied.

2. Experimental procedures

2.1. Materials and preparation

The 304 SS sheet with a size of 2 cm × 2 cm (4 cm^2) was degreased with ethanol in an ultra-sonic bath at room temperature for 5 min and then rinsed with distilled water. The surface morphology of 304 SS was characterised by scanning electron microscopy (SEM, Hitachi S-3400N) and atomic force microscopy (AFM, Park XE-120). Furthermore, the chemical composition of 304 SS was studied by electron dispersive X-ray (EDX, Hitachi S-3400N).

2.2. Growth of branched carbon fibres (BCFs)

The reactor was a horizontal ceramic tube (60 mm in diameter and 480 mm in length), which was enclosed in a temperature-controlled electrical furnace for temperature control. The cleaned 304 SS was used as the substrate and the catalyst for BCFs synthesis by being placed in a ceramic boat and inserted into the centre of the furnace at room temperature. The oxygen was purged from the furnace by nitrogen gas (N_2) at a flow rate of 500 ml/min for 15 min and then heated to 900 °C prior to the administration of hydrogen gas (H_2) at a flow rate of 500 ml/min for 30 min to reduce oxides on the surface of the 304 SS. Acetylene gas (C_2H_2) was used as the carbon source for BCF synthesis. The reaction began with the feed gas, which consisted of C_2H_2, H_2 and N_2 at a ratio of 1:1:2 with a total flow rate of 1200 ml/min for 30 min, followed by cooling down in a N_2 atmosphere at a flow rate of 300 ml/min. The effects of temperature on BCF growth were also examined at reaction temperatures of 900, 1050 and 1200 °C. In order to understand the effects of temperatures on the morphology and quality of the carbon materials (CMs) and BCFs, they were characterised by transmission electron microscopy (TEM, JEOL JEM-2010) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7800F). Raman spectrometry (Raman, Jobin Yvon Horiba T-64000) was used for structural analysis of the CMs. It operated with an incident laser beam at 1064 nm. Thermal gravimetric analysis (TGA, Shimadzu TGA-50) was used to study the thermal stability of the CMs and BCFs at a heating rate of 10 °C/min in air. In addition, the growth of BCFs and other CM mechanisms on the surface of 304 SS was also studied using atomic force microscopy (AFM, Park XE-120).

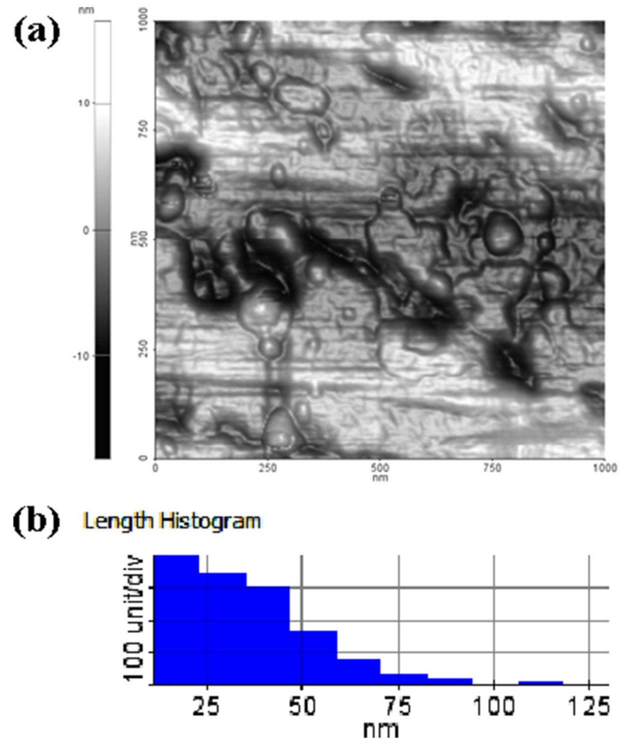

Fig. 2. AFM images of the 304 SS surface: (a) 1 μm × 1 μm scan and (b) nano-hill diameter distribution.

3. Results and discussion

3.1. Chemical composition and morphology of 304 SS substrate

Table 1 shows the chemical composition of the 304 SS surface by EDX analysis. It was observed and indicated that the 304 SS surface contained mostly Fe and Ni, which is a well-known catalyst for the synthesis of CMs (e.g. CNFs, BCFs, CNSs, CNTs and B-CNTs).

SEM images in Fig. 1 show the morphology of the bare 304 SS surface. It can be seen that the grain size of 304 SS was non-uniform (Fig. 1a) and had a rough surface (Fig. 1b). More thorough investigation of the surface roughness of 304 SS was analysed and calculated using AFM images and XEI software (v1.8.0), respectively. AFM imagery in Fig. 2a shows that the nano-hills appear on 304 SS with a root mean square roughness of 5 nm. In addition, nano-hills diameter distribution of the 304 SS surface (Fig. 2b) found that the nano-hills were very small, with an average lateral size of 35 nm. Subsequently, it was confirmed that the size of the catalyst was very small in nanoscale. The presence of nanoscale catalyst (Fe and Ni) on 304 SS surface is essential for CNMs synthesis using a CVD method [35,36]. These results were consistent with the observations made by Hashempour et al. [34], who

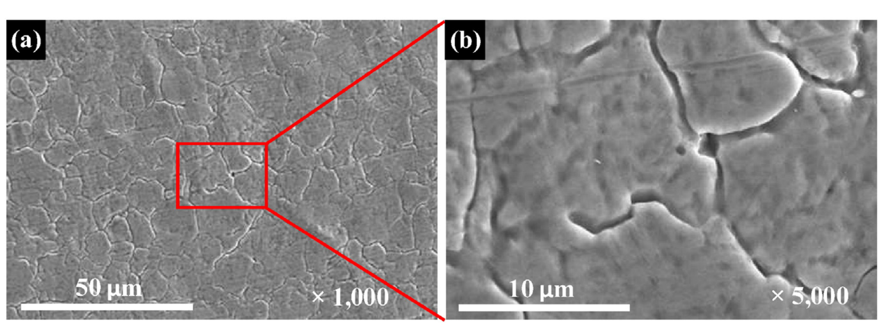

Fig. 1. Morphology of the bare 304 SS surface using SEM analysis: (a) non-uniform grain sizes of 304 SS and (b) heightened resolution of the red rectangular area indicates roughness in the grains of 304 SS.