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Mohit Kumar
Rochester Institute of Technology

Naveen Rawat
Rochester Institute of Technology

KSV Santhanam
Rochester Institute of Technology

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Effect of Nanostructure on the Thermal Oxidation of Atomized Iron

M. Kumar [1], N. Rawat [1] and K.S.V. Santhanam [1,2]

[1]Center For Materials Science and Engineering, [2]Department of Chemistry
Rochester Institute of Technology, Rochester, NY 14623

Abstract

The effect of nanostructure on the thermal oxidation of atomized iron has been investigated. Above 500°C atomized iron is oxidized in the presence of air. However, when iron is compacted with multiwalled carbon nanotubes (MWCNT) this oxidation is shifted by more than 100°C. Iron is protected by the nanostructure environment A large number of compositions of atomic ratios of iron and MWCNT have been examined in this study to understand the effect in detail. The effect of nanostructure in the thermal oxidation of iron is interpreted as due to iron atom experiencing extensive overlap and confinement effect causing spin transfer. Based on the theoretical calculations reported in the literature this confinement effect of iron is suggested to produce a transformation from $3d^6 4s^2$ to an effective configuration of $3d^8 4s^0$ producing spintronics effect.

Key words: Multiwalled carbon nanotubes, atomized iron, thermogravimetric analysis, thermal oxidation

INTRODUCTION

The interaction of transition metals with carbon has been of interest in recent times and has been theoretically studied using density function calculations (1-6). An understanding of the interaction is of importance in synthesizing new materials having nanostructures. With carbon nanotubes this interaction can be considered in two ways; in one way iron atom as interacting with the outside surface of the tube that is dependent on configurational geometry. In this case an effective configuration of $3d^7 4s^1$ can be picturized for the iron atom. In the second case the iron atom is considered to be inside the nanotube resulting in higher hybridization with effective configuration of $3d^8 4s^0$ (1). This interaction inside the carbon nanotube results in anti ferromagnetic ordering (2). Doping of transition metal atoms inside the carbon nanotube has also been considered theoretically for understanding spintronics (3). These   calculations suggest that iron atom adsorbing on hexagonal center of the nanotube as having the most stable configuration.(4). When a carbon nanotube interaction is with magnetic materials it results in magnetization of the nanotubes. (7-9). For example, with ferromagnetic metal a spin polarized charge transfer occurs at the interface between carbon nanotube and the ferromagnetic metal with the result a spin transfer of about 0.1 μ_B per contact carbon atom (7) has been determined by magnetic force microscopy. Insertion of a magnetic atom into carbon nanotube will have applications in recording devices and magnetic inks (10). Several investigations have also been carried out on the properties of transition metals on carbon (11-16). Films formed by the interaction of transition metal with carbon have been studied for UV reflectivity in the range of 6-36 nm (14) and magnetic properties (9).

In this paper we report the first observation of the effect of nanostructure on the thermal oxidation of atomized iron. The thermogravimetric studies of the compacted iron-multiwalled carbon nanotubes shows higher thermal stability for atomized iron.

EXPERIMENTAL

Chemicals: Atomized iron (Hoeganaes-D300gbt #0025600019) has been used in this work. Multiwalled carbon nanotubes (MWCNT) (Helix Material Solutions, Texas or Deal international, Rochester) (diameter ranging from 60-100 nm and length 0.5-40 µm) of high purity was used.

Compositions: The following samples were prepared where the weights of iron and MWCNTs are listed in Table 1. The samples were compacted before use.

Table 1: Compositions of samples with MWCNT

Sample	Atomized Fe, mg	MWCNT, mg	Sample	Atomized Fe, mg	MWCNT, mg
A	5.6210	5.6210	E	6.5128	1.6282
B	5.3120	5.3120	F	1.0722	4.2888
C	1.6884	6.7536	G	11.5648	2.8912
D	4.7312	1.1828	H	1.5196	6.0784
			I	4.9500	4.9500

RESULTS AND DISCUSSION

TGA curve of atomized iron in Figure 1 shows a **weight gain** at a temperature of $520^{\circ}C$ that continues up to about $1000^{\circ}C$. This characteristic behavior of iron results in the formation of Fe_2O_3 (17). When the experiments were carried out in inert atmosphere, the weight change remained negligible up to $1000^{\circ}C$. This result is in conformity with the thermodynamic stability of Fe (18) under inert or reducing conditions In contrast the TGA of MWCNT in Figure 2 shows a **weight loss** from $600^{\circ}C$ reaching a net 100% loss at about $810^{\circ}C$. Here we observed small differences in TGA of Helix MWCNT and Deal MWCNT. The former samples showed weight loss occurring at about the same temperature as Deal (Figure 2) but complete weight loss reaches at about $700^{\circ}C$. Nevertheless the other behavioral patterns observed here were identical between the two samples of MWCNT. The weight loss observed in both samples is due to oxidative conversion of MWCNT to oxides of carbon that escape out of the TGA pan (19-23). Hence two distinct diametrically opposite features are observed with atomized iron and MWCNT. When they are alone; it is the thermal oxidation that is observed in the TGA experiments. In the case of iron it results in the formation of metal oxide on the surface that results in weight gain. When the atomized iron is present in the environment of MWCNT as in iron-MWCNT compacted mixtures, the behavioral pattern completely changes. A typical TGA of iron under this condition is shown in Figure 3. Up to about $600^{\circ}C$ there is no weight change observed for iron in this environment; instead a weight loss is observed till about $800^{\circ}C$ that is followed by a weight gain. In all the samples A-I (see Table 2), the expected thermal oxidation of Fe that results in the

weight gain is not observed at 520°C. Instead in all cases a weight loss starts at temperatures beyond 605°C. and reaches a maximum weight loss at the expected temperature of complete
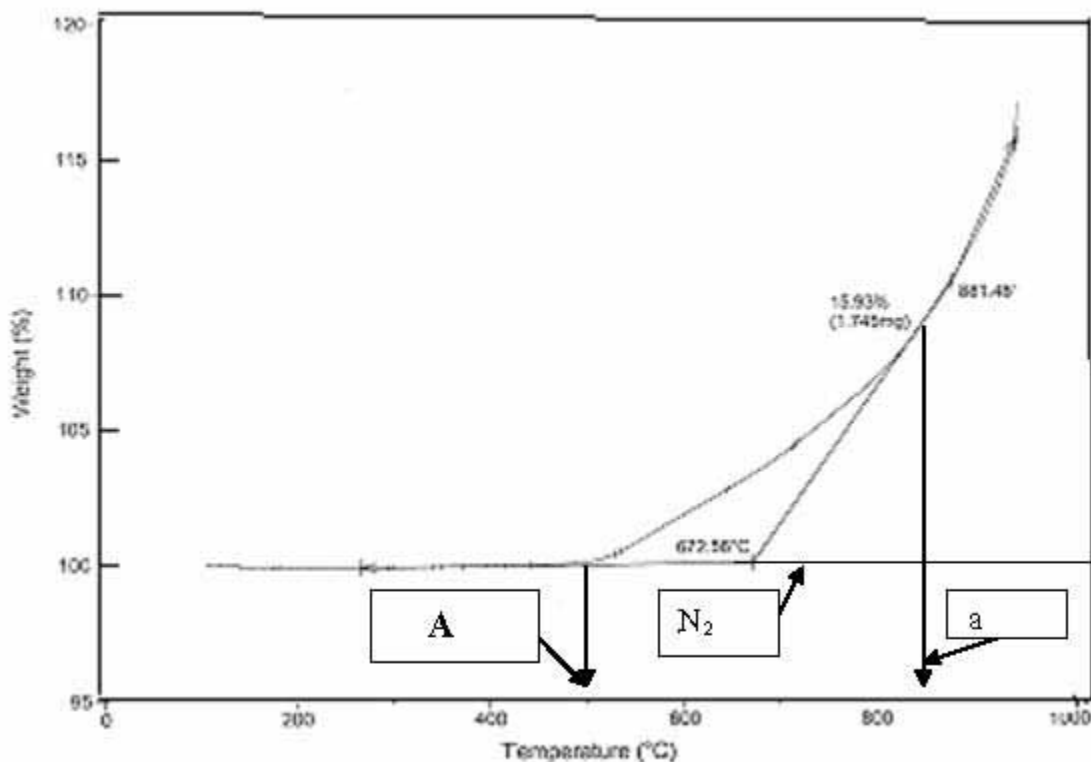

Figure 1. Thermogravimetric curve of atomized iron in air

Table 2: Weight Distribution Analysis with Carbon nanotubes

Sample	Weight of sample, mg	Weight at transition, mg	Weight Gain/loss of material, mg	Sample	Weight of sample, mg	Weight at transition, mg	Weight Gain/loss of material, mg
Fe^a	10.9540	12.6990^b	+1.7450	F	5.3610	3.4846^c	-1.8763^d
Fe^a	10.7930	12.4940^b	+1.7010	G	14.4560	12.1430^c	-2.3129^d
A	11.2420	5.3961^c	-5.8458	H	7.5980	4.7107^c	-2.8872^d
B	10.6240	4.7808^c	-5.8432	I	9.9000	6.0390^c	-3.8610^d
C	8.4420	0.9286	-7.5133	MWCNT	8.8640	0.000^c	-8.8640^d
D	5.9140	3.0161^c	-2.9570				
E	8.1410	4.7217^c	-3.4192				

a: Atomized iron; b: Point a in Figure 1; c: Point b in Figure 3; d. unopened tubes

conversion of MWCNT (compare Figure 3 with Figures 2 and 1). The slopes of the falling

regions of the curves are about 1.1°/C for Figure 2 and 0.4°C for figure 3. These results suggest that iron is interacting with MWCNT that is in agreement with the theoretical prediction (1). Table 2 gives the details of the weight changes at different temperatures that establishes iron is protected from the thermal.oxidation up to about $600°C$ The weight loss observed with
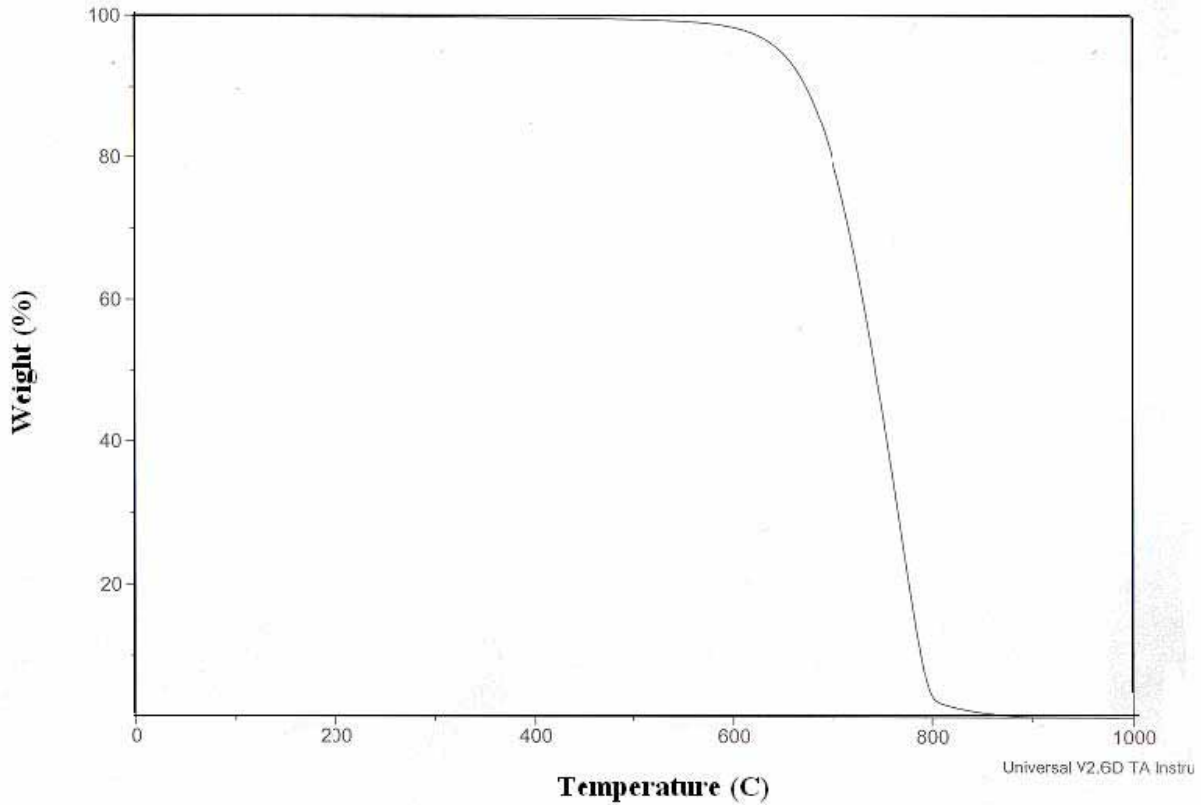

Figure 2 Thermogravimetric curve of MWCNT in air

iron-MWCNT system beyond $605°C$ may be attributed to the behavioral pattern observed with MWCNT alone where it is oxidized to carbon dioxide. All the measurements with samples A-I in Table 1 showed consistent weight loss. An interesting feature that has been observed here is that the samples made with opened carbon nanotubes always showed at the transition temperature b (Figure 3) a weight value that is less than that of atomized iron in the original composition (A-E); it appears that part of iron is lost by reaction with the break down product of MWCNT as gaseous species. The other unopened carbon nanotube samples yielded higher weights than iron present in the compacted powder at the transition temperature presumably due to formation of iron oxide. These results suggest that when an iron atom is at the side walls or on outer surface its susceptibility to oxidation is higher than when the iron atom is completely inside the tube. With the iron atom entering inside the nanotube, the weight gain is less as it is not shielded. Earlier it has been recognized that the bonding of the atoms on SWCNT has been shown to be dependent on the contact conditions (15,16). Thus these results are interesting in the context of several reports (24,25) in the literature on self assembled
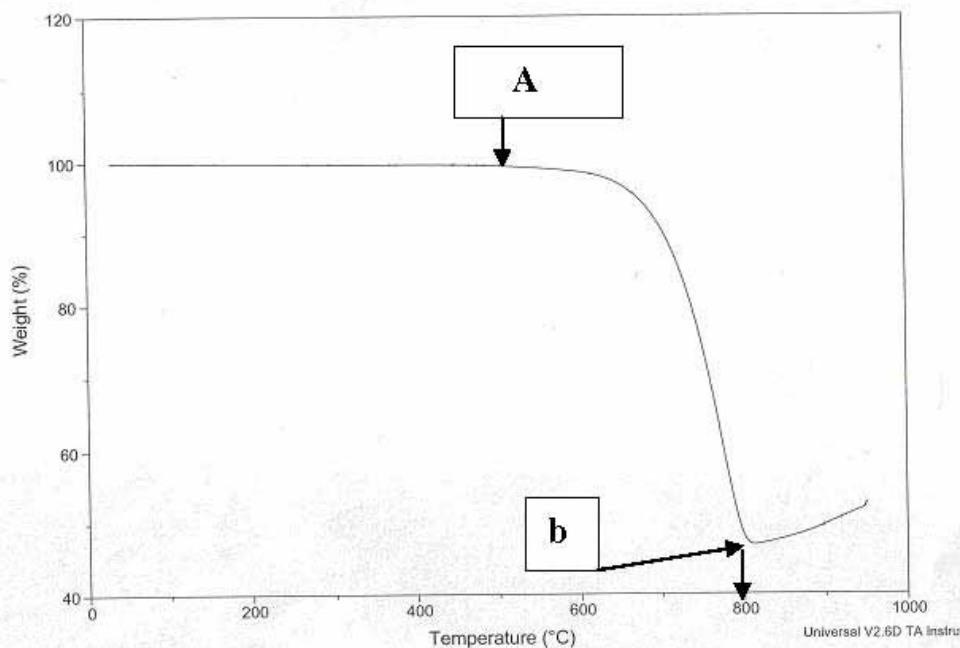
**Figure 3 Thermogravimetric analysis of sample B in air. Arrow A indicates the expected temperature for weight gain for Fe
Arrow b gives the transition temperature point.**

monolayer coatings on amorphous iron and iron oxide nanoparticles and zero valent iron nanoparticles in the remediation of aqueous metal contaminants. Iron encapsulating carbon nanotubes and nanoparticles has been synthesized (25) from iron carbonyl that results in a cup-like and centipede like nanostructures.

The above results demonstrate stabilization of iron against oxidation in the presence of MWCNT and it is believed that stabilization occurs by nanotubular interaction with iron.

CONCLUSIONS

Atomized iron thermal oxidation is prevented by having a nanostructured environment of MWCNT. TGA analysis showed the absence of weight gain due to oxidation of iron at the expected temperature of 500°C. It showed a weight loss at 620°C reaching a minimum at 820 C. This is followed by a weight gain beyond this temperature. The results suggest that iron undergoes morphological changes beyond 820 C. The thermal oxidation of iron is protected by multiwalled carbon nanotubes.

ACKNOWLEDGEMENT

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