Synthesis of single-walled carbon nanotubes using induction thermal plasma technology with different catalysts: thermodynamic and experimental studies

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Abstract. The effects of the type and quantity of three catalyst mixtures (i.e. Ni-Y2O3, Ni-Co-Y2O3, and Ni-Mo-Y2O3) on single-walled carbon nanotubes (SWCNT) synthesis by induction thermal plasma process have been examined in order to evaluate their individual influences on SWCNT production. Thermodynamic calculations, in gas and particularly in liquid solution phases, have also been performed to better understand the effects of the catalysts on the production of SWCNT. Characterization of the synthesized SWCNT by different techniques including Raman spectroscopy, high resolution scanning electron microscopy (HRSEM) imaging and thermogravimetric analysis (TGA) clearly indicated that the best quality of SWCNT was achieved using Ni-Co-Y2O3 catalyst mixture in the feedstock.

1. Introduction

Due to the very exceptional thermal, mechanical and electrical properties [1] of single-walled carbon nanotubes (SWCNT) discovered by Iijima in 1993 [2], much attention has been attracted to this novel nanostructured material. It has a broad range of applications in different fields such as sensors [3,4], polymers [5,6], microelectric devices [7], and biomedical engineering [8,9]. Different methods have been developed for the synthesis of SWCNT including arc discharge [2], laser ablation [10], chemical vapor deposition (CVD) [11], and induction thermal plasma [12]. These methods can be divided into two main categories depending on their catalytic or catalyst free synthesis. In catalytic synthesis methods, the presence of catalysts, mainly transition metals, in the feedstock or on the support plate is inevitable [13]. In laser ablation and arc discharge methods high temperature heating of the target, made from graphite-catalyst mixture plate, followed by a rapid cooling rate process of the generated vapor results in the formation of high quality SWCNT. However, in the induction thermal plasma method (ITP), the formation of SWCNT is based on the direct evaporation of feedstock materials containing carbon black (CB) and a mixture of catalysts in the high temperature plasma plume. For CVD methods, hydrocarbon decomposition takes place over the supported catalyst particles which indeed act as active sites for the nucleation of SWCNT [14]. Since different phenomena occur in various synthesis methods, it is somehow impossible to adopt a unique mechanism for the SWCNT formation. Among all suggested mechanisms so far, the nucleation and growth of SWCNT based on carbon-catalyst interaction [15] is more suited for the gas phase methods. Indeed, in the gas phase, SWCNT formation includes several steps (a) decomposition of catalysts and carbon source, (b) nucleation and growth of catalyst nanoparticles, (c) carbon diffusion or solubilization into the metal
particles and (d) precipitation and solidification in the form of SWCNT. In this mechanism, diffusion and solubilization of carbon atoms into the catalyst liquid droplets is a key factor. The rate of dissolution is mainly dependent on the type of catalyst, temperature, and the presence of other solutes. For example, it has been shown that small amount of sulfur can reduce the surface tension of liquid metal which favors the higher solubility of carbon [16]. It has been shown experimentally that the solubility of carbon in different catalysts varies notably. For example, the solubility of carbon is high in Mo and Fe, while it is very low in Cu [13]. Therefore, it is expected that changes in the type of catalyst can distinctly affect the formation of SWCNT. Although the efficiency of different catalysts in production of SWCNT with the other methods of synthesis has been intensively studied, no systematic experimental study has been conducted on the effect of the type and quantity of catalysts on the SWCNT synthesis by ITP.

In the present work, since the solubility of carbon and the gas phase composition of plasma are expected to affect the SWCNT synthesis, a complete thermodynamic study on a wide temperature range (500-5 000 K) was carried out in order to fully understand the effect of the type and quantity of catalyst on the gas phase during the synthesis of SWCNT by ITP process. The operating temperature window was limited to T< 5 000 K since at higher window temperature of plasma the system is noticeably far from the equilibrium state. It is expected that at lower temperatures considered in this work, thermodynamic studies will help to better understand the effect of different catalysts on the synthesis of SWCNT.

Following the thermodynamic study, the effect of three different catalyst mixtures on the SWCNT synthesis by ITP was experimentally studied. Along with Yttrium oxide (Y₂O₃), Ni, Co, and Mo have been selected due to their high efficiency in production of SWCNT using catalytic synthesis methods [13]. Moreover, since there is controversial data about the toxicity of metallic catalysts in the literature [17-19], it is important to find less harmful catalysts that are capable of producing high quality SWCNT.

2. Thermodynamic calculations

Theoretical thermodynamic study was carried out using FACTSAGE 6.2 software on the different carbon-catalyst mixture systems summarized in Table 1. To study the solution phase, particularly in liquid state the FSstel database was selected for the calculations. For the gas phase, the FACT53 database was considered without taking into account the inert gases (Ar, He). Moreover, the presence of sulfur in the CB was not neglected since it can alter the quality of SWCNT [20]. For these series of calculations, two group of mixtures were considered and their results were compared. In Group 1 (i.e. MIX 1, 2 and 3) three different mixtures of catalysts were considered and their results were compared. In Group 1 (i.e. MIX 1, 2 and 3) three different mixtures of catalysts were considered with a constant total amount of catalysts (i.e., 5.2 wt. %). In fact, the Co content present in MIX 1 was replaced by the same amount of Ni in MIX 2 and by the same amount of Mo in MIX 3 so that the total metallic catalyst content remained constant. Group 2 which includes MIX 4, MIX 5 and MIX 6, contains mixtures with different ratios of Ni-Y₂O₃ and Ni-Mo-Y₂O₃.

3. Experimental procedure and set-up

SWCNT were synthesized at large-scale using ITP system (feed stock injection rate of 2 g/min), as shown in Figure 1. Detailed information about the experimental set-up can be found in a previous paper [21]. The physical properties of the feedstock materials are summarized in Table 2. The same mixture compositions used for thermodynamic calculations (Table 1) were used in the experimental studies.

Table 1 Feedstock material content in weight percent (wt. %) used for the synthesis of SWCNT

| MIX No | Ni  | Co  | Mo  | Y₂O₃ | CB   | S*  |
|--------|-----|-----|-----|------|------|-----|
| 1¥     | 2.6 | 2.6 | 0   | 7.5  | 87.3 | 2   |
| 2¥     | 5.2 | 0   | 0   | 7.5  | 87.3 | 2   |
| 3¥     | 2.6 | 0   | 2.6 | 7.5  | 87.3 | 2   |
| 4¥     | 12  | 0   | 0   | 3    | 85   | 2   |
| 5¥     | 5.2 | 0   | 0.5 | 7.5  | 86.8 | 2   |
| 6¥     | 1.3 | 0   | 3.9 | 7.5  | 87.3 | 2   |

* wt. % of sulfur in CB, ¥ Group 1, £ Group 2
Schematic diagram of an ITP system designed for large-scale synthesis of high quality SWCNT

The synthesized SWCNT samples were characterized by means of Raman spectroscopy, X-ray diffraction (XRD, PANALYTICAL-X’Pret Pro MPD), thermogravimetric analysis (TGA, SETSYS 2400) and high resolution scanning electron microscopy (HRSEM, S4700, Hitachi). Raman spectroscopy was performed with Ar laser ($\lambda_{ex} = 514$ nm). TG was performed according to the protocol provided in [22].

| Size  | Purity (%) | $T_{\text{melting}}$ ($^\circ$C) | $T_{\text{vaporization}}$ ($^\circ$C) | Company                        |
|-------|------------|---------------------------------|-------------------------------------|--------------------------------|
| Ni    | 2$\mu$m    | 99.9                            | 1455                                | Cerac (CANADA)                 |
| Co    | 2$\mu$m    | 99.9                            | 1495                                | Sigma-Aldrich (CANADA)         |
| Mo    | 2$\mu$m    | 99.9                            | 2623                                | Sigma-Aldrich (CANADA)         |
| CB    | 45nm       | 98                              | N/A                                 | Grade: M280, Cabot Inc.(USA)    |
| Y$_2$O$_3$ | 5$\mu$m | 99.9                            | 2425                                | Hermann C.Starck               |

4. Results and discussion

4.1. Thermodynamic study

Thermodynamic calculations were performed on different SWCNT feedstock mixtures summarized in Table 1. The results of thermodynamic calculations in gas phase and liquid solution phase on Group 1 are depicted in Figure 2.
The comparison of the total gas phase of each mixture revealed that the total gas phase was poorly affected by the type of metallic catalysts since it ended at almost the same temperature with the same pattern for all the mixtures. Nonetheless, slight differences were observed at the temperature where the total gas phase was terminated for the three mixtures. For example, a more extended gas phase at lower temperature was observed for the MIX 3, MIX 1, and MIX 2 respectively. Details of gaseous species are illustrated under the gas phase (total) curve (Figure 2, red curve). The concentration and evolution pattern of the most important precursors of SWCNT (i.e., C$_i$, i= 1 to 5) seemed not to be affected by the change in the catalyst mixtures. The exothermic reaction of Y-C along with other reactions such as Y-S, Y-O and Ni-S can be considered as a key phenomenon to improve the yield of SWCNT synthesis process since the released heat increases the temperature locally and enhances the supersaturation of carbon in liquid solution phase [23]. The heat released due to Y-C and Y-S reactions will be higher as their concentration in gas phase are higher compared to other reactions, as seen in Figure 2 (a), (c) and (e). Figure 2 (b), (d) and (f) show the liquid solution phase formed during the high temperature plasma process of feedstock materials in Group 1. The graphs show that Y did not participate in liquid solution in contrast with the metallic catalysts (i.e., Ni, Co and Mo). The liquid solution was formed abruptly for all mixtures as seen in Figure 2. However, for MIX 3, (Figure 2, f), Ni content gradually increased up to a point (around T= 2 800 K) where it became the main solvent, while Mo started to diminish at 2500 K due to solidification. The whole liquid solution phase solidified at a temperature lower than 1500 K. The presence of liquid solution phase containing metals in such a wide range of temperature compared to the pure liquid metals is due to the solubility
of carbon which lowers the solidification temperature of metals [24,25]. The liquid solution phases depicted in Figure 2 showed also that along with the presence of liquid metals as solvent, and carbon as a solute, the other species including O, S and NiS exist in all liquid solutions. Compared to other species, a high degree of solubility for carbon in liquid metals favored the formation of SWCNT. Interestingly, Mo compared to other catalysts can markedly elongate the existence range of liquid solution phase about 1000 K.

The calculated liquid solution phase of MIX 1 and MIX 2 are depicted in Figure 3. The Mole-Temperature graphs of S and O for both mixtures were quite the same indicating that their solubility was the same in Ni and Co. However, three main differences between the liquid solution phase of MIX 1 and MIX 2 were observed (Figure 3). The first difference was the solubility pattern of C which started at a higher content for MIX 1 and ended at the same content as MIX 2. This observation firstly suggests that the solubility of C was enhanced by Co in the binary system of Ni-Co compared to unary Ni system. Moreover, taking into account the concentration gradient of C over temperature as a driving force for nucleation of SWCNT [26,27], the binary Ni-Co system, having a bigger $\Delta C/\Delta T$ in the same range of temperature than unary Ni system, eases the nucleation of SWCNT. The second difference was the range of temperature in which the liquid solution phase exists. As shown in Figure 3, this temperature range seemed to be slightly wider for MIX 1 than MIX 2. According to the very high temperature gradient and cooling rate along the induction thermal plasma reactor [23], the wider temperature range in which the liquid solution phase exists can increase the time of SWCNT growth leading to a higher quality final product. The third difference is that unlike Ni, Co did not react with S in liquid solution phase which consequently allowed the active catalysts sites to uptake more carbon atoms.

Figure 4 and Figure 5 show thermodynamic calculations for another mixture of Ni (MIX 4) and two other mixtures of Mo (MIX 5 and MIX 6). Figure 4 shows the gas phase and liquid solution phase of MIX 4 in which the amount of Ni and Y$_2$O$_3$ was changed. By reducing the amount of Y$_2$O$_3$ in the feedstock mixture, the oxygen content was also reduced. The gas phase composition of the feedstock mixture was consequently affected by this change in the oxygen content as observed in the thermodynamic calculation results (Figure 4, a). On the other hand, the liquid solution phase was more affected by the change in the Ni content. High content of Ni in the gas phase makes the formation of NiS thermodynamically more favorable which in turn may partially compensate the diminution in the heat released by the exothermic reaction of Y-C $\rightarrow$ YC$_2$. The shortage of O in the reaction system results in an increase in sulfur cluster (S$_2$) followed by the formation of another cluster (S$_3$) in the lower temperature regions (T < 3000 K) (Figure 4, a). The formation of the clusters of sulfur at temperatures where liquid solution phase exists can reduce the effectiveness of the process since these clusters can compete with carbon precursors in being solubilized into the liquid solution and occupy it and form the soluble NiS. This can be a reason why the amount of S and NiS in the liquid solution phase has been remarkably increased in Figure 4 (b).

Figure 3 Superimposed liquid solution phase of MIX 1 (dashed-line) and MIX 2 (solid-line)
The total gas phase and also carbon precursors (C₁-C₅) seemed to be independent from the amount of metal catalysts and follow the same pattern, as shown in Figure 5. The total heat of dominant exothermic reactions, mentioned above, was poorly affected since the gas phase composition did not significantly change between MIX 5, MIX 6, and MIX 3 as shown in Figure 2 (c). The main changes were detectable from the liquid solution phases (Figure 5, b and d). By adding small amount of Mo (i.e., 0.5 wt. %) the liquid solution phase temperature window and the solubility of solute species were changed compared to MIX 2. By increasing the amount of Mo, the solubility of C was changed compared to MIX 2 which is in total agreement with the experimental observations where the solubility of carbon is very high in Mo [13].

Figure 5 Thermodynamic equilibrium composition in gas phase (left side) and liquid solution phase (right side) of (a) MIX 5 and (b) MIX 6
4.2. Experimental results

HRSEM images of SWCNT samples synthesized with different feedstock mixtures are depicted in Figure 6. All samples represent the existence of SWCNT bundles entwined with impurities including graphitic particles, catalysts and amorphous carbon. HRSEM images demonstrated also the different morphology of SWCNT produced using different types and amounts of catalysts.

To compare the structural quality of SWCNT samples synthesized with different catalyst mixtures, Raman spectroscopy was performed and the results are summarized in Table 3. The intensity of tangential vibration mode of graphite at 1582 cm\(^{-1}\) (G-band), over the intensity of disordered sp\(^3\) carbon at 1350 cm\(^{-1}\) (D-band), is an informative value for the structural quality assessment of SWCNT [28]. A higher G/D ratio is an indicator for a better quality of SWCNT. The Raman analysis showed that the highest quality of the SWCNT was achieved using MIX 1 in which Co was present. In contrast, the lowest quality of SWCNT was obtained using MIX 6 in which Mo had the highest content. Sample obtained with MIX 2, possessed SWCNT with a lower quality than those produced by MIX 1. Therefore, Ni-Co binary mixture would be a better choice than Ni alone for production of high structural quality SWCNT. Furthermore, Co can be considered as a promoter for the synthesis of SWCNT. The results of Raman analysis for MIX 1 and MIX 2 are in good agreement with the thermodynamic calculations that predicted a superior potential of Ni-Co mixture in the synthesis of higher quality SWCNT. For MIX 4, SWCNT quality seemed similar to that obtained using MIX 2. This observation is in good agreement with the thermodynamic results. Although the increase and decrease in the Ni and Y\(_2\)O\(_3\) contents respectively, could affect the reaction system individually, their overall impact on the SWCNT synthesis seemed to be neutral.

![Figure 6](https://example.com/figure6.png)

**Figure 6** HRSEM images of SWCNT samples synthesized with (a) MIX 1, (b) MIX 2, (c) MIX 3, (d) MIX 4, (e) MIX 5 and (f) MIX 6.

| Raman G/D | MIX 1 | MIX 2 | MIX 3 | MIX 4 | MIX 5 | MIX 6 |
|-----------|-------|-------|-------|-------|-------|-------|
| G/D       | 15.2  | 13.6  | 4     | 14    | 4.5   | 3.8   |

Table 3 Quality assessments of SWCNT synthesized with different catalysts mixtures
To closely examine the crystalline structure of SWCNT synthesized with different catalyst mixtures in Group 1, XRD analysis was performed and the results are shown in Figure 7.

The XRD analysis revealed that unlike pure Ni and Co, pure Mo did not exist in the final SWCNT product. However, the carbide form of Mo (MoC) was found. This observation suggested the higher tendency of Mo to form carbide than Ni and Co catalysts in the present ITP operating conditions. It should be mentioned that the carbide formation can reduce the yield of the SWCNT synthesis by putting away the active catalysts from the SWCNT nucleation sites. Therefore, the formation of MoC in high quantity during the ITP process is unfavorable and has to be minimized.

To further investigate discrepancies observed between experimental results and thermodynamic calculation for Mo, the temperature profile of the reactor along the central axis was plotted regarding to the numerical simulation of the ITP synthesis system (Figure 8) [29]. The eutectic temperature of Mo-C system ($T_{\text{eutectic}} = 2500$ K) [30] and Ni-C/Co-C ($T_{\text{eutectic}} = 1600$ K) [29] are located at 0.6 and 0.75 m respectively from the torch exit (Figure 8). Two temperature zones are depicted in this graph: 3000-2000 K and 2000-1000 K. Since it has been experimentally proven that the optimal synthesis temperature lies 100-200 K below the $T_{\text{eutectic}}$ [25,31], the Zone 1 is expected to be a region in the ITP reactor which is more appropriate for the synthesis of SWCNT with Mo catalyst while the Zone 2 is suitable for using Ni and Co catalysts. As shown in Figure 8, the length of Zone 1 is only 13 cm in the reactor while the length of the Zone 2 is 30 cm. Therefore the nanotubes synthesized with Ni and Co have at least 2.3 times greater residence time in their suitable temperature zone than those synthesized with Mo.
Given that Co and Ni eutectic temperature is almost the same, this observation enables to explain why both Ni and Co produced SWCNT with similar quality but higher than that synthesized using Mo. Therefore, to overcome the problem observed with Mo it is necessary to optimize the ITP operating conditions to obtain similar temperature zone for Mo with the same effective length as Ni and Co.

To characterize the thermogravimetric behavior of each SWCNT sample produced with the feedstock mixtures in Group 1, TG analysis was performed (Figure 9). All SWCNT samples demonstrated a multistep weight loss in the temperature range of 200-800 °C indicating the presence of different carbonaceous structures including SWCNT. The mass loss became zero at temperatures above 800° C where the residual mass, attributed to the residual catalyst content, was calculated to be 15, 12 and 11 wt. % for the SWCNT samples synthesized with MIX 1, MIX 2, and MIX 3, respectively. The mass gain at temperature around 200 °C was due to the oxidation of metal catalysts in the samples which was then followed by a rapid mass loss at a temperature around 350 °C due to the fast reaction of amorphous carbon with oxygen [32]. The temperature at which SWCNT samples start to lose weight (T_{onset}) seemed to be identical. However, the multistep weight loss event (TG graph) was more identical for the samples synthesized with MIX 1 and MIX 3 than MIX 2. This observation suggested that the ternary mixture of catalysts with the identical catalyst oxide produced SWCNT samples with the same TG behavior while this behavior was slightly changed when the binary mixture was used.

![Figure 9 TG graphs of SWCNT samples synthesized using MIX 1 (dashed-dotted line), MIX 2 (dashed line) and MIX 3 (solid line)](image)

5. Conclusion

The effect of metallic catalysts and their quantity in the feedstock material on the synthesis of SWCNT were thermodynamically and experimentally studied. High quality SWCNT can be produced with a ternary catalyst mixture containing Ni, Co and Y_2O_3 or with a binary mixture of Ni and Y_2O_3. Thermodynamic calculations indicated that type and quantity of metal catalysts would affect more the liquid solution phase formed in the ITP reaction system during SWCNT production and less the gas phase, while the content of Y_2O_3 changed the gas phase with less impact on the liquid solution phase. Considering the eutectic temperature of the metallic catalyst-carbon system, the effective residence time for Ni/Co was found to be 2.3 times more than Mo in the ITP resulting in a higher quality Ni/Co-grown SWCNT. Thus, Mo potential for the synthesis of SWCNT can be improved through ITP process optimization by increasing the length of higher temperature zone (T > 2000 K).

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