

# Electron-energy loss spectroscopy and Raman studies of nanosized chromium carbide synthesized during carbothermal reduction process from precursor $\text{Cr}(\text{CO})_6$

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## Abstract

Nanosized chromium carbide has been prepared by metal–organic chemical vapour deposition (MOCVD) method in a fluidized bed and carburized in the mixture of  $\text{CH}_4/\text{H}_2$  atmosphere in temperature range 700–850 °C. The carburization process involves carbon deposition on the outer surface of the  $\text{Cr}_2\text{O}_3$  powder, followed by carbon diffusion into the powder, leading to formation of metastable  $\text{Cr}_3\text{C}_{2-x}$  phase and stable  $\text{Cr}_3\text{C}_2$ . The phase transformation from  $\text{Cr}_2\text{O}_3$  to  $\text{Cr}_3\text{C}_2$  via an intermediate state  $\text{Cr}_3\text{C}_{2-x}$  has been identified using electron-energy loss spectroscopy (EELS) and micro-Raman spectroscopy. We could hypothesize that the formation of carbon nanofilms surrounding the carbide crystallites provides the stress and assist the phase transformation from metastable  $\text{Cr}_3\text{C}_{2-x}$  to stable  $\text{Cr}_3\text{C}_2$ .

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## 1. Introduction

Over the past several decades, there have been efforts on improving the strength and the toughness of alumina, by the use of nanocomposites.<sup>1–4</sup> The incorporation of hard particulate reinforcement has been shown to be an easy, safe and economically toughening technique for alumina ceramics. The carbides are good reinforced materials for oxide ceramics due to their high melting point, high hardness, high Young modulus and wear resistance. Among the carbides, the  $\text{Cr}_3\text{C}_2$  used for the second phase has been proved to exhibit improved mechanical properties and enhanced temperature oxidation resistance of  $\text{Cr}_3\text{C}_2$ /alumina composites.<sup>3–5</sup> In addition,  $\text{Cr}_3\text{C}_2$  is a material with high electrical conductivity and the  $\text{Cr}_3\text{C}_2$ /ceramic composite has potential applications for electrical discharge machining (EDM).<sup>6</sup>

The mostly reported  $\text{Cr}_3\text{C}_2$  were prepared from the reduction of chromium oxide by methane gas.<sup>7</sup> However, besides the three stable chromium carbides such as  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$ , and

$\text{Cr}_{23}\text{C}_6$ , several metastable carbides were reported including  $\text{Cr}_3\text{C}$ ,  $\text{CrC}_{1-y}$ ,  $\text{Cr}_5\text{C}_2$ , and  $\text{Cr}_3\text{C}_{2-x}$  which were exist during different preparation methods and for various Cr/C contents.<sup>8–10</sup> Lerch and Rousset<sup>11</sup> indicated that the  $\text{CrO}_{1.9}$  with high surface area (200–350  $\text{m}^2/\text{g}$ ) reduces at 700 °C in the mixture of methane and hydrogen atmosphere and produces  $\text{Cr}_3\text{C}_2$  and metastable  $\text{Cr}_3\text{C}_{2-x}$ . The metastable  $\text{Cr}_3\text{C}_{2-x}$  powder was also prepared by Loubière et al.<sup>12,13</sup> using  $\text{CH}_4\text{–H}_2$  atmosphere to carburize metastable chromium oxide. Summarizing above literatures, it is observed that the metastable  $\text{Cr}_3\text{C}_{2-x}$  is a  $\text{Re}_3\text{B}$ -type structure which can be found by carburization of high specific surface chromium oxide and usually present together with  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_3\text{C}_2$  and free carbon.

Electron energy loss spectroscopy gives information about the electronic structure of chromium and carbon in  $\text{Cr}_3\text{C}_2$ . Lozzi et al.<sup>14</sup> have studied the electronic structure of Cr clusters on graphite by measuring  $L_{2,3}$  ionization edges using EELS technique. They observed that there is a variation in the intensity ratio of  $L_3\text{–}L_2$  ionization core edges. The EELS core edge energy is that required to excite an electron from a core level to the first unoccupied state above Fermi level  $E_f$ . Therefore, these variations in  $L_3/L_2$  ratio are due to the empty d states above  $E_f$ . Fan et al.<sup>15</sup> have studied the electronic structure of Cr as well

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as carbon of chromium-doped diamond like-carbon films from Carbon K edge and Cr L edge using EELS analysis.

Raman spectroscopy is a best tool for characterization of carbon based materials. Different Raman modes for diamond, graphite and amorphous carbon have been studied by different groups.<sup>16–18</sup> Barshilia et al.<sup>19</sup> have studied the Raman spectra of  $\text{Cr}_x\text{O}_y/\text{Cr}/\text{Cr}_2\text{O}_3$  multilayer coatings on Cu substrates. They have observed the  $A_{1g}$  and  $E_g$  Raman modes, which are the characteristic of  $\text{Cr}_2\text{O}_3$ .

In our previous study,<sup>20,21</sup>  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  composite powders were prepared by the decomposition of chromium hexacarbonyl in a fluidized bed. The composite powder then hot-press sintered in a graphite mode and transformed as  $\text{Cr}_3\text{C}_2/\text{Al}_2\text{O}_3$  nanocomposite. But some residual  $\text{Cr}_2\text{O}_3$  reacted with  $\text{Al}_2\text{O}_3$  in high temperature became solid solution thereby decreasing  $\text{Cr}_3\text{C}_2$  contents. In order to carburize the chromium oxide completely, the present paper reports the nanosized chromium carbide from precursor carburization in a  $\text{CH}_4/\text{H}_2$  mixture gas. The phase evolution and formation mechanisms were characterized by the EELS and micro-Raman spectroscopy.

## 2. Experimental procedure

The decomposed powder was fabricated by metal–organic chemical vapor deposition (MOCVD) method in a fluidized bed. The schematic diagram of the homemade apparatus is given in our earlier paper.<sup>22</sup> The precursor comprising of metal–organic chromium hexacarbonyl ( $\text{Cr}(\text{CO})_6$ , 99% Strem Chemicals Co., USA) was initially heated for evaporation at 75 °C. He gas was used as the carrier gas for transporting these precursor vapors into the reaction chamber for coating on the fluidized alumina powder ( $\alpha\text{-Al}_2\text{O}_3$ , 99.9%, A16SG, Alcoa, USA), which was used as the matrix powder. The pressure of reaction chamber was controlled at 10 torr and the reaction temperature was kept at 300 °C. The as-received powder then carburized in an alumina tube furnace in the presence of methane–hydrogen mixture (1:9) gas at 700–850 °C for 5 h.

The electron-energy loss spectroscopy (EELS) of prepared samples was characterized by field emission gun scanning transmission electron microscopy (FEG-STEM) equipped with energy dispersive X-ray detector (EDS) and energy filter (Gatan). The presence of the chromium oxide, carbide and carbon phases was analyzed by micro-Raman spectroscopy using a solid laser (514.5 nm) with an output power of 50 mW for 30 seconds (LabRAM HR). The Raman spectra are taken in the range of 1100–1800  $\text{cm}^{-1}$  and 200–800  $\text{cm}^{-1}$  for the detection of C–C and Cr binding energy, respectively. The microstructures have been studied by (FE-SEM, PHILIPS / FEI XL 40) and (FEG-TEM, TEI Tecnal F20, USA).

## 3. Results and discussion

The pyrolysis of Cr based precursor  $\text{Cr}(\text{CO})_6$  at 300 °C results the formation of  $\text{Cr}_2\text{O}_3$ , C–Cr and C–C bonds observed from XPS spectra.<sup>22</sup> The decomposed precursor deposits uniformly over  $\text{Al}_2\text{O}_3$  and the deposited nanoparticles (~30 nm) are shown

in the TEM micrograph (Fig. 1(a)). The insert shows the TEM pattern of the deposited nanoparticles, which is amorphous in nature. From the EDS spectrum shown in Fig. 1(b), it is confirmed that the nanoparticles consist of mostly Cr and O along with small amount of C. The presence of Cu is the contribution from Cu grid.

Fig. 2 shows the EELS spectra of Cr L edge for the sample of the decomposed precursor and the samples carbonized at 800 °C and 850 °C. The chromium L edges have features comprising two sharp  $L_2$  and  $L_3$ , known as “white lines”<sup>14</sup> and a continuum background following the edge. The sharp double peaks are due to transitions from the  $2p^{1/2}$  and  $2p^{3/2}$  core levels towards 3d states above  $E_f$ . The sharp peaks of  $L_2$  and  $L_3$  at threshold are due to the transitions from the  $2p^{1/2}$  core levels to  $3d^{3/2}$  states and the  $2p^{3/2}$  core levels to  $3d^{3/2}$   $3d^{5/2}$ , respectively. The  $L_3/L_2$  white line ratio is correlated to the electron occupancy and spin pairing in 3d band. The variations of the ratio are due to the interaction between chromium and surrounding atoms. A change of the  $L_2$ ,  $L_3$  edge intensities in the samples indicates a variation of the d holes because the edge intensity is proportional to the number of the empty final states available. The ratio of  $L_3/L_2$  of sample shown in Fig. 2(a) is higher than that of carbonized samples. According to the results of Arévalo-López et al.<sup>23</sup> the ratio of  $L_3/L_2$  for the  $\text{Cr}_2\text{O}_3$  is about 1.6 and from the report of Fan et al.<sup>15</sup> the ratio of  $L_3/L_2$  for the Chromium carbide is about 1. A comparison between Fig. 2(b) and (c) shows  $L_3$  edge of the sample carbonized at 850 °C is 577.72 eV, while that of sample carbonized at 800 °C is 575.42 eV. The shift in energy (2.3 eV) is called the chemical shift. This result is due to the transformation from the metastable carbide to stable carbide, because the EELS represent the difference in energy between a core-level initial state and the lowest energy final state of an excited electron. But the energy loss close to 577.72 eV for the decomposed precursor,<sup>24</sup> which consists of  $\text{Cr}_2\text{O}_3$  is same as the sample carbonized at 850 °C. It is observed that there is no chemical shift between this two species because  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_3\text{C}_2$  are both chemically stable compounds.

The  $\pi$  electron formed  $sp^2$  bonding observed from the EELS spectra of C K edges as shown in Fig. 3. The peak of  $sp^2$  bonding is sharper when the carbonized temperature increases from 800 °C to 850 °C. The sharpening of  $sp^2$  peak is attributed to the formation of graphite like carbon according to Fan et al.<sup>15</sup> In  $\text{Cr}_3\text{C}_2$ , C is graphite like rather than diamond like, which comprising of  $sp^3$  bonded carbon atoms. For the as decomposed precursor, the content of carbon was little and formed amorphous phase. More carbon produced from the pyrolysis of methane coated on the  $\text{Cr}_2\text{O}_3$  surface and then formed graphite phase and metastable carbide of  $\text{Cr}_3\text{C}_{2-x}$ , when the sample was treated at 800 °C for 5 h. The increase of treated temperature to 850 °C, enhanced the process of carbonizing reaction leading to more graphite formation followed by transformation of metastable  $\text{Cr}_3\text{C}_{2-x}$  to stable carbide of  $\text{Cr}_3\text{C}_2$ .

The SEM micrographs of the decomposed precursor at different carburized temperature are shown in Fig. 4. The as decomposed precursor exhibits particle size of 20–30 nm shown in Fig. 4 (a) and the particle size increases with the increase of carburized temperature observed from Fig. 4(b)–(e). The maxi-

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