Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2016, Article ID 2565137, 7 pages
http://dx.doi.org/10.1155/2016/2565137

Research Article

Fabrication of SiC Composites with Synergistic Toughening of Carbon Whisker and *In Situ* 3C-SiC Nanowire

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Received 1 June 2016; Revised 1 August 2016; Accepted 25 August 2016

Academic Editor: Mikhael Bechelany

The SiC composites with synergistic toughening of carbon whisker and *in situ* 3C-SiC nanowire have been fabricated by hot press sinter technology and annealed treatment technology. Effect of annealed time on the morphology of SiC nanowires and mechanical properties of the C_w/SiC composites was surveyed in detail. The appropriate annealed time improved mechanical properties of the C_w/SiC composites. The synergistic effect of carbon whisker and SiC nanowire can improve the fracture toughness for C_w/SiC composites. The vapor-liquid-solid growth (VLS) mechanism was proposed. TEM photo showed that 3C-SiC nanowire can be obtained with preferential growth plane ({111}), which corresponded to interplanar spacing about 0.25 nm.

1. Introduction

Silicon carbide (SiC) was widely applied in high-temperature industries as refractory lining for blast furnace and as a smelting refractory owing to its excellent slag resistance, corrosion resistance, high hardness, better thermal stability, and so forth [1–4]. However, covalent nature of Si-C bonding and low self-diffusion coefficient had hindered densification and mechanical properties of SiC ceramics. So liquid phase sinter method was applied to improve densification behavior.

As an effective reinforced material, one-dimensional nanowire was widely applied due to its excellent mechanical properties. Recently, some novel manufactured techniques of SiC nanostructure were developed. Some reports were brought forward for synthesis of SiC nanowires (SiC_{nw}) [5–10], including arc discharge, laser ablation, and carbon thermal reduction. However, expensive manufacturing cost and inferior dispersion uniformity of reinforcement were obvious. In order to solve above problems, conception of *in situ* growth was put forward and some efforts have been developed in the past score years [11]. However, it was scarcely reported that rare-earth oxide La_2O_3-Al_2O_3 was utilized to fabricate *in situ* SiC nanowires in the C_w/SiC composites [12]. In the present investigation, an attempt was made to analyse the growth behavior of SiC nanowire in the SiC substrate under different annealed time. The main purpose was to investigate influence of different annealed time on the microstructure and mechanical properties of C_w/SiC composites compared with the hot press sinter C_w/SiC composites. The toughening mechanisms of C_w/SiC composites were analyzed in detail.

2. Fabrication and Characterization

Industrial α-SiC powder (PHI = 0.5 μm) and carbon whisker (D = 7 μm, L = 120~140 μm) were used to fabricate C_w/SiC composites. Volume proportion of SiC and carbon whisker was 7 : 3. The molar proportion of Al_2O_3 and La_2O_3 was designed as 1 : 1. The total weight percentage of Al_2O_3 and La_2O_3 was 10 wt%. The total weight percentage of SiC and carbon whisker was 90 wt%. The mixing process was performed by attrition milling with SiC balls in an alcoholic medium for 8 h at 200 RPM and the ratio of SiC ball to material was 10 : 1. The mixture was dried in a rotary evaporator, crushed, and screened through a 60-mesh sieve and put into a graphite crucible. Sintering was performed in a graphite hot press furnace (High-Multi 5000 type hot pressing sintering

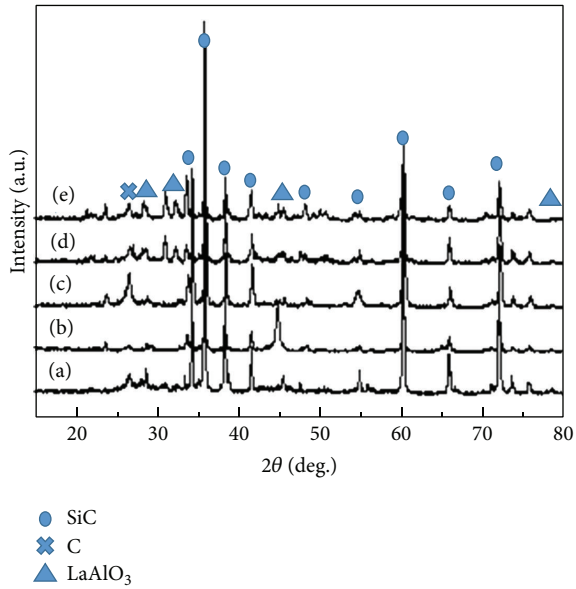
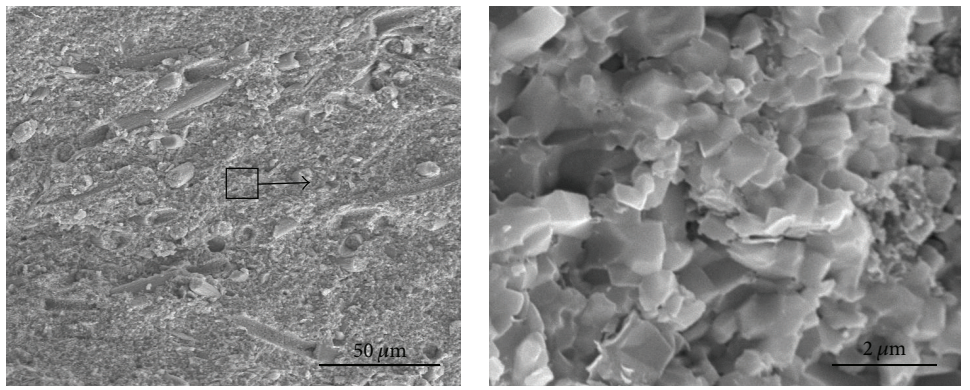


FIGURE 1: X-ray patterns of specimens with different annealed time. (a) represented hot pressed specimens and (b), (c), (d), and (e) represented annealed specimens AM10, AM30, AM60, and AM90.



(a) (b)

FIGURE 2: Hot pressed specimen of the C_w/SiC composites.

furnace, made in Japan) with heated rates of 25°C/min from room temperature to 1920°C. During the annealed process, the flowing argon atmosphere gas flow ratio: 500 sccm) was introduced and the gas pressure was kept at 0.05~0.06 MPa. Hot press process was kept at 1920°C for 1 h under 30 MPa pressure and then graphite hot press furnace was cooled into room temperature. Above specimens were annealed at 1750°C for 10 min, 30 min, 60 min, and 90 min, which were defined as AM10, AM30, AM60, and AM90, respectively. All specimens were cut into 2 mm × 4 mm × 22 mm bars to measure fracture toughness (K_{IC}) by single edge notched beam specimen techniques (SENB). Density was measured by water immersion method and phase constitution was determined by X-ray diffraction (XRD: Bruker D8 Advance type, German). The interface was tested by using a 200 kV TEM microscope (Model JEM 2010, Japan).

3. Results and Discussions

X-ray patterns of hot pressed and annealed specimens were shown in Figure 1. The phase constitution of C_w/SiC composites after annealed treatment was similar to that for hot press materials (Figure 1). For all specimens, α-SiC was present as a major crystal phase. Amorphous phase was detected (26°) for all specimens, which was amorphous carbon fiber. $LaAlO_3$ phase was found as minor phase. A certain amount of reaction-formed $LaAlO_3$ by reaction between La_2O_3 and Al_2O_3 was found in all specimens. There was not obvious variation for phase constitution of C_w/SiC composites after annealed treatment compared with that of C_w/SiC composites after hot pressed sintering.

Figures 2(a) and 2(b) represented fracture morphology of hot pressed specimen. The typical characterization of the

C_w/SiC composites was found in the fracture zone; that is, pull-out of carbon whisker was a main method of toughened mechanics. According to the observation of fracture morphology of hot pressed specimen, intergranular fracture was the main fracture mode of silicon carbide substrate.

Figures 3(a), 3(b), 3(c), 3(d), 3(e), 3(f), 3(g), and 3(h) represented fracture morphology of annealed specimens of AM10, AM30, AM60, and AM90. For all materials, carbon whisker pull-out and debonding were obvious, which were main toughened mechanics. When annealed time was about 10 min (Figures 3(a) and 3(b)), SiC_{nw} began to grow and nucleation site of SiC_{nw} was mainly distributed at the grain boundary area. As annealed time was extended to 30 minutes, short-rod structure could be detected (Figures 3(c) and 3(d)). As annealed time was extended to about 60 minutes, SiC_{nw} with continuous mesh structure was evenly distributed in the grain boundary area of SiC composites (Figures 3(e) and 3(f)). However, as annealed time was about 90 min, diameter of SiC_{nw} became bulky and surface morphology became coarse (Figures 3(g) and 3(h)). Under this condition, the negative air pressure led to the volatilization of liquid sintering aids in some degree and then more pore structure was retained in the subsurface of SiC bulk materials. During the annealed process, the evaporation process of gas phase material resulted in the weightlessness behavior. This phenomenon was found in the SiC material with different aids system. Samanta et al. [13] found that, for the SiC ceramics, the gas pressure procedure affected decomposition reactions in the SiC-Al-Y-O system and it led to weight loss due to volatilization of reaction product. In our research, we found that annealed time could control volatilization degree of sintering additives, it could change distribution of pore channels in the SiC matrix, and it could affect flexural strength and fracture toughness of AM90. Other relative investigation about effect of annealed atmosphere pressure, oxygen partial pressure, and so forth on the C_w/SiC composites was ongoing in the subsequent work.

Mechanical properties of all specimens were illustrated in Table 1. The relative density of each sample was higher than 98%. La_2O_3/Al_2O_3 aid was effective for densification of the C_w/SiC composites. For hot pressed specimens, flexural strength was 235 MPa and K_{IC} was 5.21 MPa·$m^{1/2}$. Compared with other specimens, AM60 had more excellent mechanical properties. Flexural strength and K_{IC} of AM60 reached 294 MPa and 6.43 MPa·$m^{1/2}$, respectively. Compared with hot press specimen, mechanical properties of AM60 were improved after annealed treatment, which was relevant to growth of SiC nanowire. Candelario et al. [14] fabricated SiC ceramics with $Y_3Al_5O_{12}$ liquid phase aids by means of the aqueous colloidal processing technology. $Y_3Al_5O_{12}$ aids could promote densification degree of SiC ceramics even if content of $Y_3Al_5O_{12}$ additives was limited below 10 wt%. SiC discs were sintered within powder bed at 1950°C for 1 h in a flowing Ar-gas atmosphere. But it was worth noting that fracture toughness was 2.9 ± 0.3 MPa·$m^{1/2}$, which was nearly equal to previous experimental result for the conventional PLPS SiC ceramics prepared with the same content of Y_2O_3/Al_2O_3 additives [15]. Compared with aforementioned reports, fracture toughness in the present work was improved by 220%. Other factors (such as annealed atmosphere pressure, oxygen partial pressure, and briquetting pressure) were not considered.

Table 1: Mechanical properties of hot-press sinter and annealed specimen of C_w/SiC composites.

Material	Relative density	Flexure strength (MPa)	Fracture toughness (MPa·$m^{1/2}$)
HPM	99.1%	235 ± 6.1	5.21 ± 0.34
AM10	98.9%	241 ± 4.7	5.24 ± 0.32
AM30	98.5%	246 ± 5.5	5.35 ± 0.19
AM60	98.4%	294 ± 4.2	6.43 ± 0.36
AM90	98.1%	278 ± 2.9	5.59 ± 0.27

SEM photos of fracture surface for annealed materials were illustrated in Figure 4. *In situ* SiC nanowire grew out at the grain surface region (Figure 4(a)) and uniformly dispersed in the SiC grain boundaries (Figure 4(b)). No catalytic balls at the tips of SiC nanowire were present in other areas (Figure 4(b)), which implied VS mechanism [16]. Some catalytic balls were observed at the tips of SiC_{nw} (Figure 4(c)), which implied that SiC nanowire grow by VLS mechanism [17]. Diameter of SiC nanowire ranged from 20 nm to 100 nm and the length of SiC nanowire was several micrometers. VLS mechanism and VS mechanism were responsible for formation mechanism of SiC nanowires. The twine and branch structure of SiC nanowire can be detected (Figures 4(d) and 4(e)), which would improve mechanical properties even if above structure was considered as the defects, whereas the debonding and pull-out of nanowire were rarely observed due to a strong bonding between SiC nanowire and SiC matrix. The strength of SiC nanowire was more higher than that of SiC matrix and grain boundary phase, even if SiC nanowire possessed the defects structure such as twine and branch structure. The spot energy spectrum (arrow in the local area in Figure 4(e)) proved that the nanowires consisted of silicon and carbon element (Figure 4(f)). It is noteworthy that the combination of toughened mechanisms of pull-out of carbon whisker and SiC nanowire bridging can improve fracture toughness of the C_w/SiC composites.

TEM photo and high resolution image of AM60 specimen were shown in Figure 5. As shown in Figure 5(a), it can be seen that *in situ* growth SiC nanowire was distributed in the grain boundary region. High resolution image and local amplification were shown in Figures 5(b) and 5(c). TEM photo showed that interplanar spacing was about 0.25 nm, so it was preferential growth plane ({111}), which proved that SiC nanowire belongs to 3C-SiC structure [18].

4. Conclusion

A more effective method was adopted to produce C_w/SiC composites toughened with *in situ* β-SiC nanowire by hot press sinter and annealed treatment. From the TEM and high resolution image of AM60 specimen, it can be proved that the *in situ* SiC nanowire belonged to 3C-SiC crystal structure.

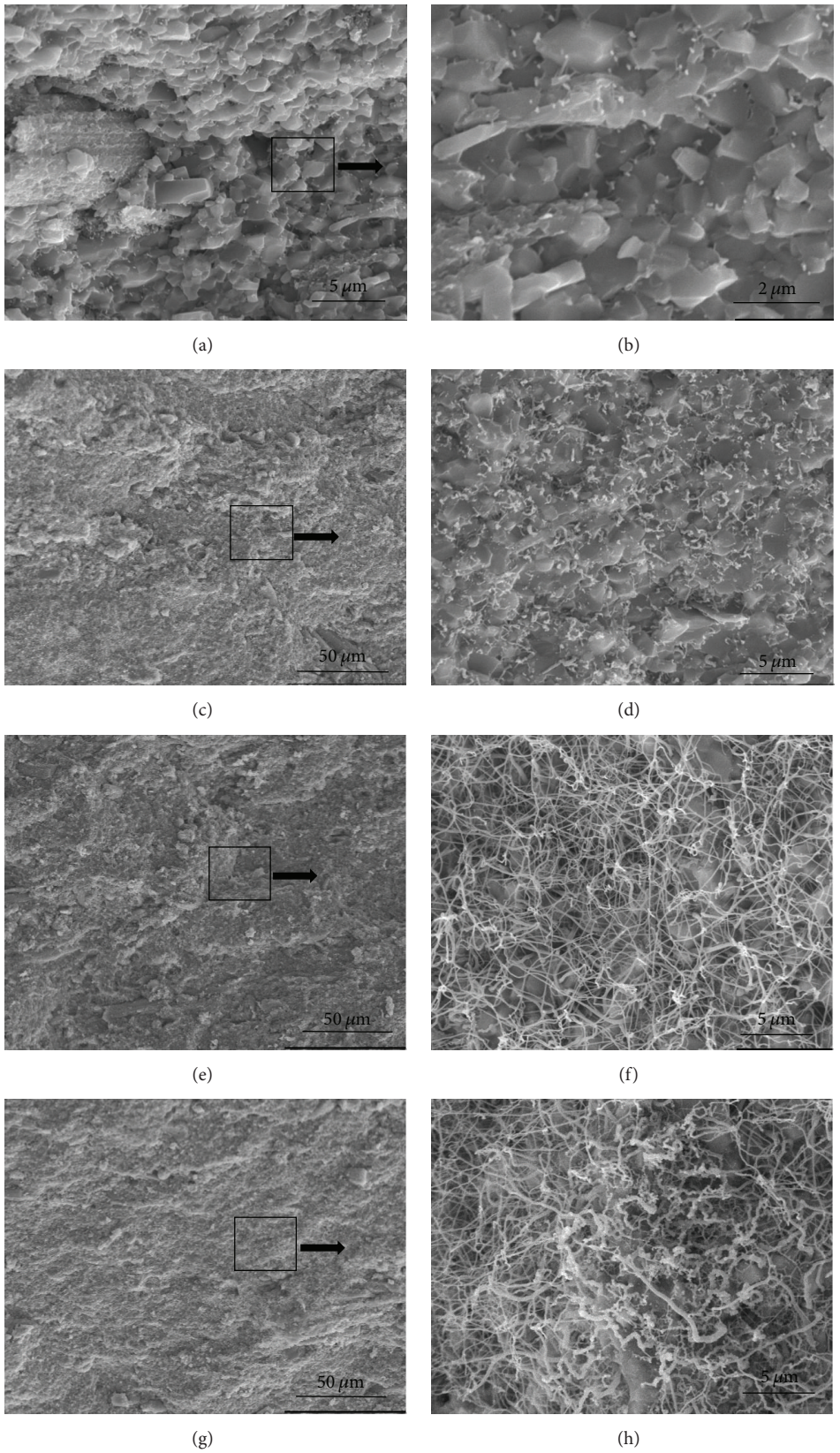


Figure 3: Fracture morphology of annealed specimens, (a) and (b), (c) and (d), (e) and (f), and (g) and (h) for AM10, AM30, AM60, and AM90.

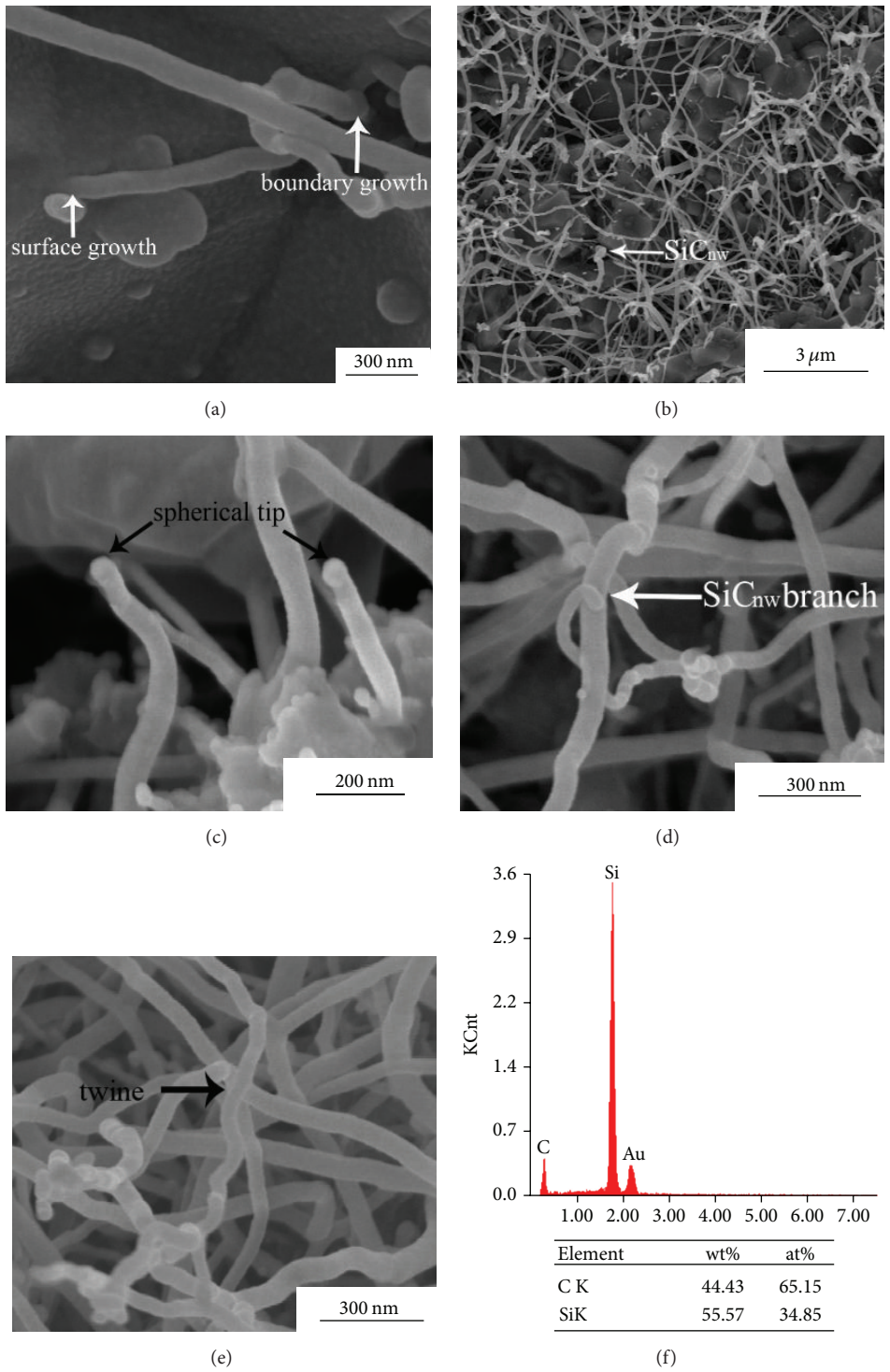


Figure 4: SEM of fracture surface for AM60 specimen, (a), (b), (c), (d), and (e) represented fracture surface and (f) represented the spot energy spectrum.

The growth of *in situ* 3C-SiC nanowire improved mechanical properties of C_w/SiC composites after appropriate annealed treatment. VS mechanisms were proposed as the main growth mechanisms for *in situ* β-SiC nanowire. Synergistic toughening mechanics including debonding and pull-out of carbon whisker and bridge of nanowires were responsible for improvement of fracture toughness for β-SiC nanowire toughened C_w/SiC composites.

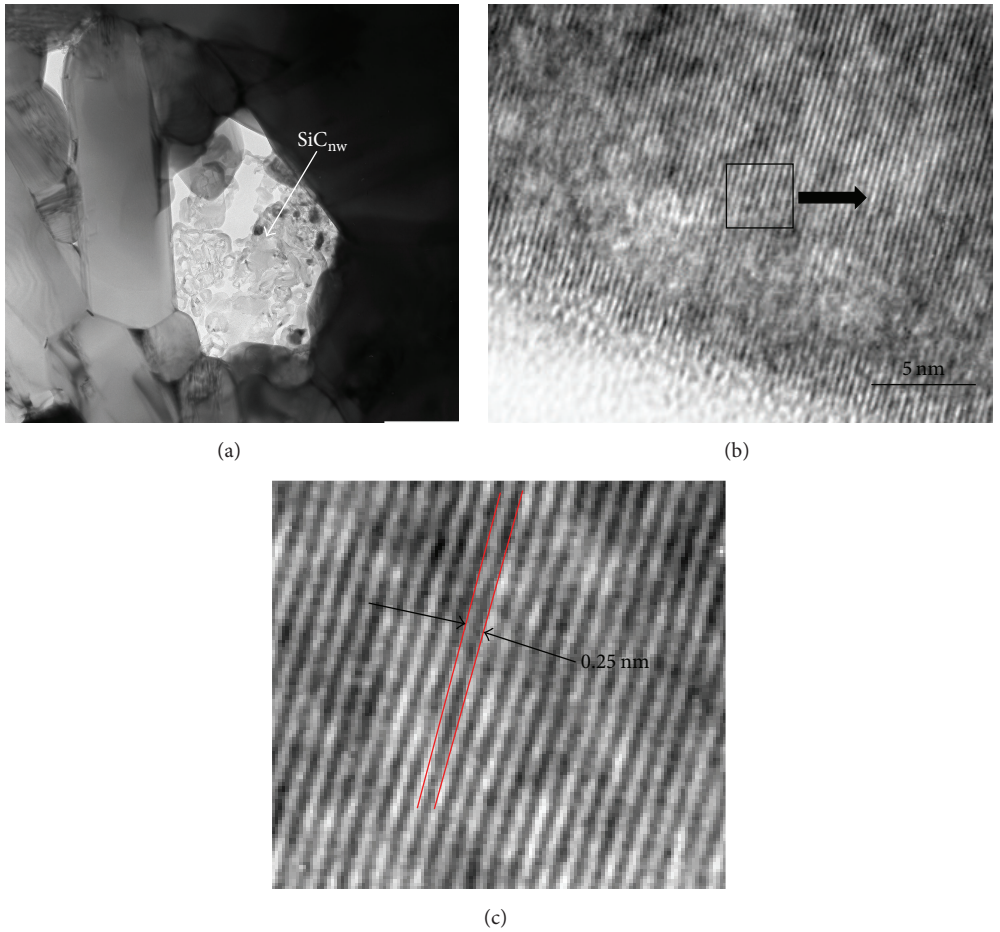


Figure 5: TEM photos of AM60 specimen, (a) and (b) high resolution image and (c) local amplification.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The authors gratefully acknowledge the support by Chinese Postdoctoral Science Foundation (no. 2012M520754).

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