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# **Observation of the Interface between Resin and Carbon Fiber** by Scanning Transmission X-ray Microscopy

## T. Harano<sup>1</sup>, R. Murao<sup>1</sup>, Y. Takeichi<sup>2</sup>, M. Kimura<sup>2</sup>, Y. Takahashi<sup>3</sup>

<sup>1</sup> Advanced Technology Research Laboratories, Research and Development, Nippon Steel & Sumitomo Metal Corporation, Futtsu, Chiba 293-8511, Japan

<sup>2</sup> Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

<sup>3</sup> Department of Earth and Planetary Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

E-mail: harano.ya6.takayuki@jp.nssmc.com

Abstract. The sub-micron spatial distribution of chemical states of carbon fiber (CF) and the interface between CF and resin must affect physical properties of carbon-fiber-reinforced plastic (CFRP). In order to evaluate scanning transmission X-ray microscopy (STXM) techniques for application to the chemical-state analysis of CFRP, we performed STXM measurements near C K-edge energies. The results of the spectral deconvolution analysis suggest the presence of another phase at the interface of CF and resin, which may be a coating layer. In addition, the preferred orientation of the stuck of graphene sheets to the fiber axis direction of CF was observed by using linear polarized X-ray beams.

#### 1. Introduction

It is essential to investigate the interface between materials as well as their microstructures to reveal the origins of the physical properties of composite materials. For example, chemical states (valence, functional groups, etc.) around the interface between carbon fiber (CF) and resin in carbon-fiberreinforced plastic (CFRP) gives helpful information in clarifying the enhancement mechanisms of tensile strength and elastic modulus. Conventional techniques for these studies include X-ray photoelectron spectroscopy and X-ray absorption near-edge structure (XANES) spectroscopy. However, their spatial resolutions are in the order from mm to µm. This makes it difficult to observe the interface structures in detail. The spatial resolution of electron energy-loss spectrometry (EELS) is much higher (less than 1 nm) than those of conventional spectroscopy techniques. However, EELS might not be appropriate for organic compounds because the strong electron beams sometimes damage organic materials. On the other hand, X-ray beams are much softer than electron beams. In the past ten years, lithographic fabrication techniques have enabled us to use optical devices such as Fresnel zone plates (FZP) whose spatial resolution is 20-100 nm. Scanning transmission X-ray microscopy (STXM) is a very powerful method for chemical imaging around the interface of composite materials [1]. In this study, we performed C K-edge absorption imaging applied to the analysis of distributions of chemical states in CFRP.

#### 2. Experimental

CFRP thin film was fabricated by focused-ion-beam (FIB) processing and finished by milling using an argon ion beam to remove the damage to surfaces by FIB. The thickness of the film was adjusted to about 80 nm. The CFRP analyzed in this study is a commercial product that consists of CF made from

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polyacrylonitrile and epoxy resin. The estimated tensile strength and elastic modulus of this CFRP are 1760 MPa and 125 GPa, respectively. Fig. 1(a) shows a schematic illustration of a cross section (CS) and a longitudinal section (LS) of the CF. Fig. 1(b) presents a backscattered electron image of the thin film. Note that the angle between the incident direction of electron beams and the normal vector of the thin film is 35 degrees. We collected image stacks of C *K*-edge XANES in the red-dotted square regions ((I) the interface region between CF and resin, and (II) CS of CF) in Fig. 1(b). Fig. 1(c) shows a transmission electron microscope (TEM) image of CF (CS) and resin. An inner-ring texture was observed in CF (CS), and details will be discussed in the next section.

STXM measurements were performed at BL-13A of the Photon Factory, IMSS, KEK, Japan. The compact STXM instrument [2] realizes XANES imaging with a spatial resolution of 40 nm by using FZP, and is especially suited to measuring XANES spectra around C *K*-edges. Moreover, the undulator of BL-13 can generate a radiation light source switched to horizontal and vertical linear by APPLE-II-type undulators [3]. In this study, linear horizontal  $\rho/2$  (LHR) and linear vertical  $\sigma/2$  (LVS) modes of X-rays were used. The aXis2000 software was used for analysis of the image stacks [4].



**Figure 1.** (a) Schematic illustration of a cross section (CS) and a longitudinal section (LS) of CF. (b) BSE image of the thin film. (c) Transmission electron microscope image of CS of CF and resin.

## 3. Results and discussion

Fig. 2(a) shows an X-ray absorption contrast image of (I) in Fig. 1(b) taken at E=286.5 eV of LHR mode of X-rays. The energy corresponds to the transitions from 1s to  $\pi^*$  (phenolic (C\*-OH)). This image consists of  $70 \times 70$  pixels (pixel size:  $40 \times 40$  nm<sup>2</sup>). Around the interface between CF and resin, another absorption contrast accounted for by neither CF nor resin was observed. This suggests the presence of another phase around the interface. We consider that the fact that the absorbance of the interface region is higher than those of CF and resin can be explained by the difference in density among them because we adjusted the entire thickness uniformly by FIB processing and argon milling. Image stack measurements around the C K-edge were carried out in the view shown in Fig. 2(a). Fig. 2(b) shows the C K-edge XANES spectra of resin, CF (LS), and the interface. These are the averaged spectra of the black-dashed square regions of (i) resin, (ii) CF (LS), and (iii) the interface in Fig. 2(a), respectively. These spectra are normalized by the intensity of the peak top of the transitions from 1s to  $\sigma^*$  of C-C at 292 eV. The split peak in the XANES spectra of the regions of (i) and (iii) around 284.8 eV corresponds to the transition from 1s to  $\pi^*$  of C=C, while the other peaks at 286.5 and 288.3 eV correspond to the transitions from 1s to  $\pi^*$  (phenolic (C\*-OH)) and those from 1s to Rydberg/ $\sigma^*$  (O(C\*-H)R), respectively [5]. Moreover, the peak at 285.2 eV of the spectrum of (ii) corresponds to the transitions from 1s to  $\pi^*$  of C=C. These are consistent with the typical chemical structure of epoxy resin [6]. In the case of the spectrum of (ii), only two peaks were observed at 285.2 eV and around 292 eV, which correspond to the transitions from 1s to  $\pi^*$  of C=C and those from 1s to  $\sigma^*$  of C-C, respectively. This result is consistent with the X-ray diffraction (XRD) study of CF [7], which shows XRD peaks originating from graphite. Therefore, this suggests that CF consists of stacks of graphene sheets. On the other hand, the peak positions of the spectrum of (iii) are the same as those of (i). However, the intensity ratio among the peaks is different from those of (i). These observations suggest that the organic material around the interface consists of the same functional groups with different compositional ratios from those of resin. This result is in accordance with the general manufacturing IOP Conf. Series: Journal of Physics: Conf. Series 849 (2017) 012023

process of CFRP, in which CF is coated with organic material before being embedded in resin to improve the affinity between CF and resin.



**Figure 2.** (a) The blackdashed squares show regions of averaged XANES spectra of (i) resin, (ii) CF (LS), and (iii) the interface used for RGB deconvolution. (b) Averaged XANES spectra of resin, CF (LS), and the interface in each region shown in Fig. 2(a).

Firstly, in order to deliberate whether a third phase is present between CF and resin, two types (A and B) of singular-value decomposition (SVD) analyses were carried out: (A) by using (i) and (ii) excluding (iii) shown in Fig. 2(a); and (B) by using the averaged spectra of (i), (ii), and (iii), respectively. These averaged spectra are shown in Fig. 2(b). Residual curves of the three regions after SVD analyses of (A) and (B) are shown in Fig. 3(a) and (b), respectively. Both regions of (i) and (ii) fit in very well in both cases. By contrast, the region of (iii) could fit in only in the case of (B). From the perspective of spectra analysis, it is concluded that a third phase is present in the interface, which is neither CF nor resin. An RGB color-deconvoluted image of the SVD of (B) using three spectra is shown in Fig. 3(c). The thickness of the third phase is about 100 nm. In addition, a transition region of about 300 nm in thickness was observed at the boundary of the resin and the third phase.



**Figure 3.** Residual curves of each region after SVD analyses of (A) resin/CF(LS) and (B) resin/CF(LS)/interface are shown in (a) and (b), respectively. (c) RGB (red: resin, green: CF (LS), blue: the third phase) color-deconvoluted image of the interface between resin and CF (LS). The two-way arrow is the polarization of LHR mode of X-ray beams.

Subsequently, we performed image stack measurements of (II) in Fig. 1(b) to investigate the chemical state of the inner ring observed in CF (CS). C *K*-edge spectra of resin, CF (CS), and inner ring in CF (CS) are shown in Fig. 4(a). These spectra are averages of each region and normalized at 292 eV as well as Fig. 2(b). The configuration of the inner ring is almost the same as that of CF (CS). This means that the chemical state of the inner ring was not different from that of CF. The contrast of the inner ring in CF (CS) observed in the TEM and X-ray absorption contrast images may originate from the difference in density between them.

Finally, the intensity ratio of the transitions from 1s to  $\pi^*$  to those from 1s to  $\sigma^*$  varied in the cases of LS (green spectrum in Fig. 2(b)) and CS (green spectrum in Fig. 4(a)) of CF. It is well known that the XANES peak of a particular electron orbital is sensitive to the relationship between the orientation of its electron orbital and the polarization of incident X-ray beams [8]. The XANES intensity originating from a particular orbital is enhanced when the orientation of its orbital is parallel to the polarization of the X-ray. Fig. 4(c) shows the averaged XANES spectra of CS and LS of CF using LHR and LVS. In

the case of CS, there is no change in the XANES spectra of the C *K*-edge between two polarized Xrays. On the other hand, in the case of LS, the absorption peak intensity originating from the transitions from 1s to  $\pi^*$  using LVS was higher than that using LHR. This indicates that the  $\pi$  orbital in CF is oriented to the central axis of CF. From these results, it is suggested that the graphene sheets almost preferred to orient to the fiber axis direction as schematically illustrated in Fig. 4(d).



**Figure 4.** (a) Averaged XANES spectra of resin (red), CF (CS) (green), and inner ring in CF (CS) (blue) in (II) of Fig. 1(b). (b) RGB (red: resin, green: CF (CS), blue: inner ring in CF (CS)) color-deconvoluted image. The two-way arrow shows the polarization of LHR of X-ray beams. (c) Averaged XANES spectra of CS and LS of CF using two types of polarized X-ray. These spectra are normalized by the intensity at 292 eV. (d) Schematic illustration of the distribution of graphene sheets in CF. The blue and red two-way arrows are the thickness and plane directions of graphene sheets, respectively.

## 4. Conclusion

STXM studies of CFRP were performed to reveal the distributions of the chemical states in CFRP and to evaluate STXM as a characterization technique for chemical imaging of CFRP. From the image stacks of C *K*-edge absorption, the presence of a coating layer between CF and resin is suggested on the basis of the spectral deconvolution analysis of the spectra. The inner region of CF (CS) has the same chemical structure as the outer region of CF. Orientation of the  $\pi$  orbital of C=C in CF could be observed by linear polarized X-rays. STXM is a useful technique for analyzing chemical-state imaging of carbon-bearing multi-composite materials, providing additional and essential information regarding enhancement mechanisms of tensile strength and elastic modulus of CFRP.

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