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In situ high-temperature TEM observation of material escape from a surface of CoFeNi/Cu/ZrAlO composite into the amorphous carbon layer

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ABSTRACT

We observed the moment of material escape from a surface of CoFeNi/Cu/Zr(Al)O_2 composite into the amorphous carbon layer when we studied the phase transformation of the structure using in situ transmission electron microscopy (TEM) technique at 800 °C. To protect the top surface of the TEM specimen against focused-ion beam process damage, the specimen had been coated with an amorphous carbon layer, a thin Pt film and a W protective layer. During our high-temperature experiments at 800 °C, we detected that the CoFeNi nanoparticles moved from the surface of the TEM specimen into the amorphous carbon layer. A porous amorphous carbon layer had a large impact on the visualization of this phenomenon. Liquid-like behavior of the CoFeNi phase, which possessed some crystalline order, was detected before the material escaped from the surface. After heating, the carbon layer became tightly packed with small particles and single atoms. The majority of the particles in the carbon layer were in the size range of 1–4 nm. The particles were assigned to the CoFeNi, FePt, and W phases. The CoFeNi particles escaped directly from the specimen surface, while the FePt and W particles were formed in the carbon layer during heating as a result of atomic reactions. The single atoms observed in the carbon layer were attributed to the heavy elements Pt and W.

1. Introduction

Transmission electron microscopy (TEM) has become an essential tool for exploring the nature of materials and processes [1–4]. Although modern TEM can be used to examine atomic-level structures [4–7] and even individual atoms [8–10], the visualization of some phenomena such as liquid-phase processes at the interface or growth and transport of a substance at high temperature remains a challenging task and requires the development of specific TEM techniques. Despite the design of different types of liquid cells and specimen holders for high-temperature TEM observations [11–16], such investigation of liquid-phase phenomena involving metallic materials are still not ubiquitous because of numerous technical difficulties. Furthermore, the electron-optical conditions for TEM are still incompatible with the vapor phase. Visualization of the high-temperature phenomena occurring at the interfaces is important in many areas such as physics, chemistry, and materials science, as well as in the development of technological processes [17–20]. TEM visualization of phase transitions at high temperature is crucial for developing quantitative models and will provide insight into the nature of atomic-level structural mechanisms, which are still not understood completely.

Using severe plastic deformation, we fabricated a nanolaminated amorphous/crystalline composite structure and studied the thermal stability and phase transformation of this structure using in situ TEM observation [21]. During our high-temperature experiments, we incidentally observed that the metallic nanoparticles moved from the surface into the amorphous carbon layer applied for protection of the TEM specimen against focused-ion beam (FIB) process damage. The carbon layer played a large role in the visualization of this phenomenon because it acted as a trap that caught the particles and single atoms that were removed from the surface. In this paper, we demonstrate in situ TEM observations of material escape from the surface and reactions of the elements in the carbon layer during heating experiments. We expect that these results will have important implications in the development of TEM techniques for the visualization of high-temperature processes, simulations of interface phenomena, and the design of hybrid materials.

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2. Experimental details

The fabrication of the nanolaminated amorphous/crystalline composite structure and the structural transformation during heating were reported in our previous work [21]. The escape of material from the surface was detected during heating experiment conducted at 800 °C. At this temperature, the specimen consisted of branched nanocrystalline grains of $Zr(Al)O_2$ and face-centered cubic (fcc) CoFeNi with Cu inclusions.

We used the following procedure to prepare the TEM specimens, which played a crucial role in the visualization of the described phenomena [22,23]. The TEM specimen was prepared on a molybdenum TEM grid using an FIB instrument (FEI Helios NanoLab DualBeam). The Ga ions used in the FIB process induce damage in the TEM specimen [22–26]. To prevent top surface damage caused by the ion beam, the area of interest was marked with black ink carbon (permanent marker) [23]. Next, a carbon strip was coated with a thin Pt film (around 10 nm) in order to provide conductivity and protection to the carbon strip. Finally, the W protective layer was deposited using FIB (FB-2100, Hitachi), during which the thin Pt film was subjected to high-energy ion bombardment to break the Pt film into nanosized fragments [22,23]. The layer structure on the TEM specimen after FIB processing before heating is shown in Fig. 1a. The FIB-deposited W layer had an amorphous-like structure (Fig. 1b) and contained C and Ga [25,27]. The black ink carbon layer was amorphous and appeared to be porous (Fig. 1c) [23]. The pores intersected and formed a connected network (Fig. 1c). Pore features had a wide range of sizes. The distribution of pore sizes is given in the supplementary material (Fig. S1). The distribution of pore sizes was determined from atomic force microscopy images taken from different areas on the surface. The average size of the pores was approximately 14 nm. The carbon layer is supposed to have a sponge-like structure.

In situ heating observations were conducted using a TEM Jeol JEM-3011 operating at 300 kV and 800 °C. JEM-3011 was equipped with thermionic LaB6 gun. We conducted our heating in situ experiments when the electron beam was switched on. In addition, a series of the experiments were performed when the electron beam was switched off. In that case, we also detected the particles in carbon layer after heating at 800 °C. Therefore, we think that the beam current in LaB6 gun was not so high to have an influence on the escape of materials. The specimen was heated with a Jeol high-temperature holder (EM-31050) that had a heating temperature up to 800 °C. The heating element was heated by direct electric current. The temperature was measured by using temperature-thermolectromotive force relation curve. In order to calibrate the curve, we observed the magnetic domain walls of a pure Fe at room temperature and at Curie point using Lorentz mode. At temperatures above 770 °C, the magnetic domain wall disappeared. Sample drifting rate may indicate a temperature gradient. We could obtain clear TEM images in 10 min after increasing temperature. There could be a temperature gradient but it was not severe in this system. Furthermore, the thickness of the carbon layer was around 100 nm. We think that a temperature gradient between surface of the specimen and carbon layer was negligible and it did not greatly influence the escape of material. Videos were recorded during the heating experiments using an SC 1000 CCD camera (Gatan Inc.). The video files provided in the present work provide real-time observations.

After the heating experiments, the specimen structure and chemical composition were evaluated using an atomic-resolution analytical electron microscope (Jeol JEM-ARM200F) operated at 200 kV and equipped with a Quantax (Bruker) energy-dispersive X-ray spectroscopy (EDS) microanalysis system. For the high-angle annular dark field scanning TEM (HAADF-STEM) images, a 22 mrad convergence semi-angle was used with an inner collection semi-angle of 67 mrad and an outer collection semi-angle of 170 mrad. The HAADF images had a spatial resolution of 0.08 nm. The high-resolution TEM (HRTEM) and HAADF-STEM images were analyzed using GATAN digital micrograph software. No image processing was applied to the TEM images. HAADF STEM image simulation was performed by applying a fast Fourier transformation (FFT) multi-slice algorithm using xHREM (v 3.6, HREM Research Inc.).

Elemental X-ray maps, in which a complete spectrum was stored for every pixel, were acquired in the STEM mode with a probe size of 0.2 nm. Quantax processing tools were used to extract, quantify, and compare the EDS spectra of selected regions in the map. The combinations of the elements and colors in the mixing element images in the present work were chosen to provide general information of the phase composition. It should be noted that it is difficult to accurately measure the concentration of light-weight elements (i.e., O and C) using EDS analysis. Furthermore, the analyzed carbon layer was not uniform at the nanoscale level and contained different phases and elements, which had peaks that overlapped in the EDS spectrum. In the present work, the chemical composition data quantified from the EDS spectra represent average and approximate values and are provided for comparison.

3. Experimental results

The escape of material from the surface was detected after around 20 min of heating at 800 °C. Selected images from the video sequence are given in Fig. 2. These images show some features of material escape at 800 °C, but we recommend viewing the original video files (Supplementary Videos (SVs)), as they provide more detailed information.

Fig. 2a–d (SV 1) shows the moment of material escape. The particle appears and grows on the surface (Fig. 2a), where its behavior resembles that of a droplet. Next, it moves away from the surface, changing its shape several times (Fig. 2b). Then, it is stretched, a neck begins to form (Fig. 2c), and the particle ultimately escapes from the surface (Fig. 2d). It seems that the carbon layer, which is supposed to be porous (Fig. 1c), creates obstacles that hinder particle movement. The particle changes shape and slides across the surface as it searches for free spaces in the carbon layer from which to escape. While the particle is moving, it demonstrates liquid-like behavior, but the diffraction contrast of the moving substance suggests that the material possesses some crystalline order. Fig. 3 shows the moment of particle detachment. This image was obtained after the in situ heating experiment. The particle, which was attributed to the CoFeNi phase [21], escaped from the surface and was trapped by the carbon layer.

Fig. 2d–f (SV 2) shows the coalescence and absorption of the particle by surface material. The substance from the surface moves toward and eventually merges with the particle (Fig. 2e). Then, surprisingly, the material from the surface absorbs the particle, resulting in its disappearance, as shown clearly in Fig. 2f. Despite the fact that the particle appears again momentarily, as can be seen in Fig. 2g, the disappearance suggests that the surface may absorb particles that are close to the interface.

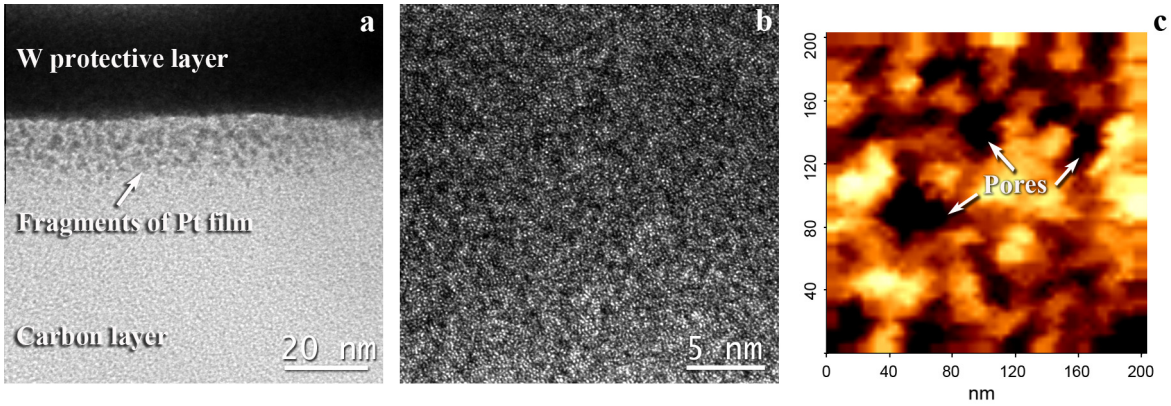

Fig. 1. HRTEM images of the (a) carbon layer and the (b) W protective layer on the TEM specimen after FIB processing before heating. (c) Atomic force microscopy image of the black ink carbon layer, illustrating its porosity.