Kyushu Synchrotron Light Research Center

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Experiment Report for Prefectural Beamline

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Investigation of the Thermal Stability of Graphene in Aluminum Matrix by In-situ Synchrotron Radiation Diffraction

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1. Summary

The thermal stabilities of graphene oxide (GrO) in both aluminum matrix composites with and without alumina interfacial layer, Al-Al_2O_3-GrO and Al-GrO, have been characterized by using in-situ synchrotron radiation diffraction. The results show that GrO is thermally stable in the composite Al-Al_2O_3-GrO in which only the crystallization of amorphous Al_2O_3 was observed, while aluminum was gradually depleted in the composite Al-GrO. The depletion of aluminum might be due to the reaction between aluminium and GrO, but phases are complex and no expected Al_4C_3 phase can be identified.

2. Purpose of experiment and background

Aluminum and its alloys are one of the most widely used materials as the matrix in metal matrix composites (MMCs), both in research and development and in industrial applications.[1] This is mainly due to the low density of aluminum alloys (the first requirement in most applications). Moreover, they are cheap if compared with other low density alloys (such as Mg or Ti). Their excellent behaviour, from different points of view (strength, ductility, corrosion), is very well known and can be modified in order to satisfy different applications. A major shortcoming of aluminum and its alloy is their low Young's modulus (~70 GPa), required in most engineering applications, which could be surmounted by introducing reinforcement.

Graphene, a perfect 2D lattice of sp^2-bonded carbon atoms, has recently attracted tremendous attention in the electronic and composite fields due to its excellent properties, such as high Young's modulus (1100 GPa) and high fracture strength (125 GPa), extremely high thermal conductivity (5000 W/m·K), super charge-carriers mobility (200000 cm^2/V·s) and so on.[2] The research and development of graphene-based composites is an important factor in the practical application of graphene. In the past decade, great efforts had been made in graphene/polymer fields (usually graphene oxide (GrO) is used because of its easy preparation), which immensely improved the mechanical and functional properties of polymer based composites by incorporating only a small amount of GrO. Recently, our results on GrO reinforced metal matrix composites have shown notable reinforcement effect of GrO.[3-4]

In the carbon-Al system, an important issue is the chemical stability of carbon in the Al matrix in fabricating composites at elevated temperatures.[5] In conventional carbon fiber/Al composites, Al carbide (such as Al_4C_3) grows on the prism plane of the carbon fiber. This reaction is serious because the formation of a sharp notch on the fiber by attack of growing Al_4C_3 needles results in a drastic decrease in the composite strength. However, the chemical reaction of the newly reported graphene and Al is rarely reported before. Therefore, study on the reaction condition and mechanism of graphene-Al will provide theoretical guideline for the future researches on the promising graphene reinforced Al matrix composites.

3. Experimental (Note: Description of sample, method of experiment and analysis, etc.)

The composite of Al-Al_2O_3-GrO was with a plate-like shape, and was prepared by absorbing graphene oxide (by Hummers method) onto the surface of Al nano-flakes with Al_2O_3 skins, followed by densifying the mixture powder[3-4], while the composite of Al-GrO was prepared by sputtering Al into the aerogel of GrO. The microstructures of the two composites are shown in Figure 1.

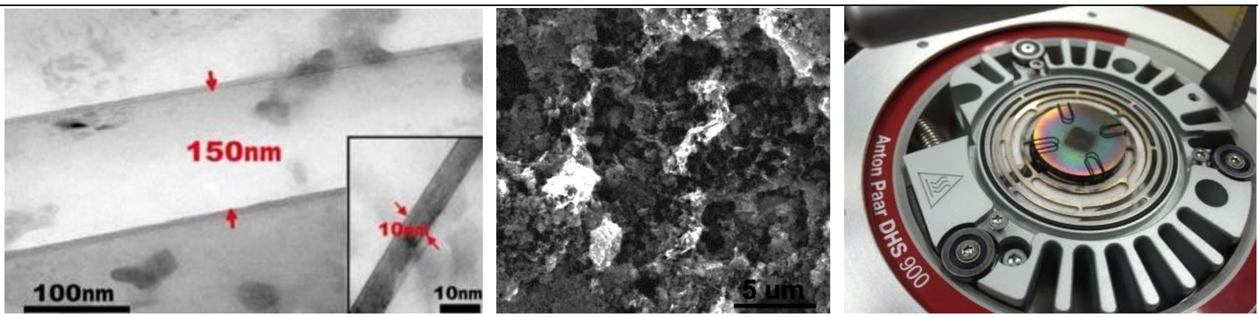

Figure 1. The microstrues of the composites (Left) Al-Al_2O_3-GrO (the inset shows a Al_2O_3-GrO-Al_2O_3 sandwiched layer) and (Middle) Al-GrO. (Right) The furnace used for heating up in in-situ experiments

The in-situ synchrotron radiation diffraction experiments were carried out on the beam line BL15 at Kyushu Synchrotron Light Research Center. The spectra were recorded in the 2θ range from 15 to 70^o at room temperature and then in the range from 573 to 873 K with an interval of 15 or 20 K (heating rate = 10 K/min). The averaged time for data collecting is about 150 seconds) and time to heating up is about 3~4 min for each spectrum. An Anton Paar DHS 900 furnace was used to heat up the samples in a vacuumed atmosphere.

4. Results and Discussions

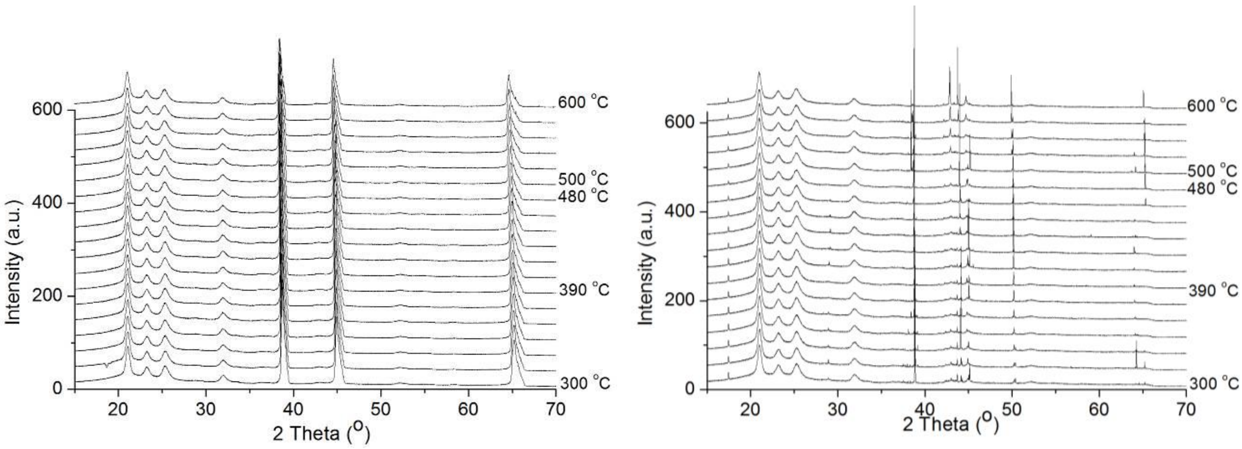

Figure 2. The spectra collected from the in-situ diffraction experiments for the composites of (Left) Al-Al_2O_3-GrO and (Right) Al-GrO.

The whole patterns at all elevated temperatures for the composites Al-Al_2O_3-GrO and Al-GrO are shown in Figure 2. Four broad peaks located in the 2θ range from 20 to 35^o were observed in both samples and kept unchanged at all the elevated temperature. These peaks could not be indexed by possible phases in the Al-C-O system. In the composite Al-Al_2O_3-GrO, three most strong peaks from right to left can be attributed to (111), (200) and (220) of aluminum, and their intensities almost kept unchanged. As shown in the left image of Figure 3, close observation on the peak (111) showed that some small peaks exist on the shoulder, which can be attributed to (311) and (222) of the gamma-Al_2O_3 phase. The intensities of these weak peaks increased with increasing temperature, indicating the gradual crystallization of the amorphous Al_2O_3 in the composite. No any new peak appears in the patterns of the composite Al-Al_2O_3-GrO at all the elevated temperatures, indicating that GrO separated from aluminum matrix by the interfacial layer Al_2O_3 is thermally stable in the composite, at least during the period of two hours for heating up.

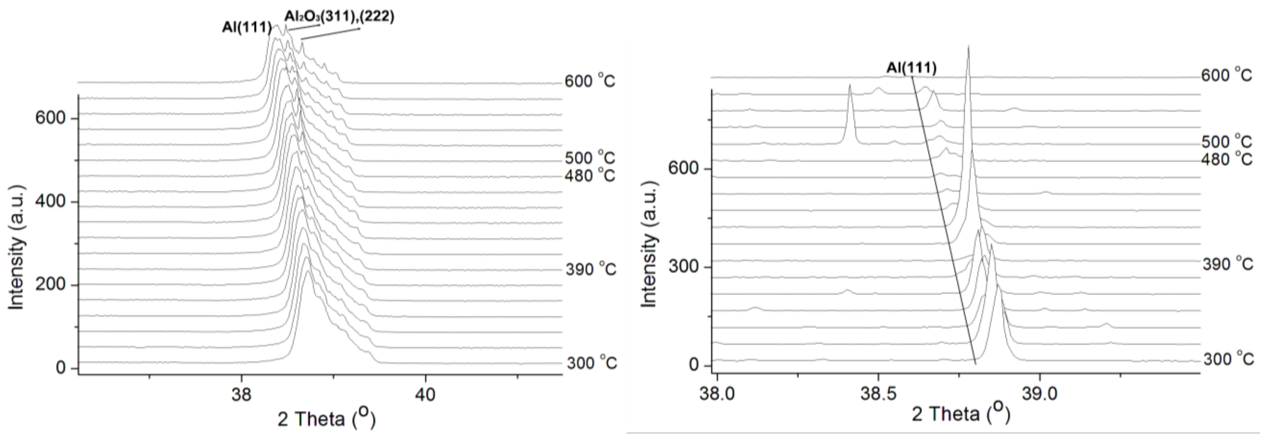

Figure 3. The characterized 2θ range reflecting the phases changes in the composites of (Left) Al-Al_2O_3-GrO and (Right) Al-GrO.

While the case is completely different in the composite Al-Gr prepared by sputtering. The patterns are more complex than that of Al-Al_2O_3-GrO. Except for the main peaks from Al, other unidentified peaks also exist. The reason is not so clear now. One possible reason is the great difference between the amounts of GrO in the two composites. GrO is dispersed in aluminum matrix as reinforcement in composite Al-Al_2O_3-GrO, while aluminum is sputtered on the surface of GrO aerogel in composite Al-GrO. However, as shown in the right image of Figure 3, aluminum was gradually depleted in the composite of Al-GrO. The depletion of aluminum might be due to the reaction between aluminum and GrO, but the phases of products is complex and no expected Al_4C_3 phase can be identified.

In conclusion, GrO is thermally stable in the composite Al-Al_2O_3-GrO because of the existence of Al_2O_3 barrier layer, but interfacial reaction took place in the composite Al-GrO and no Al_4C_3 phase was observed.

5． Future issues

1. The unidentified peaks are needed to be confirmed whether from the samples or from the measuring system;
2. Analysis by transmission electron microscope (TEM) is needed to be identified the interfacial microstructures before and after reaction.

6． References

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7． **Publications, patents** （Note: Typical deliverables related to this proposal.）

The experimental data obtained in this work will be submitted to an international scientific journal.

８．**Keywords**（Note: 2-3 words about samples and experimental methods.）

Aluminum matrix composites; Graphene oxide; Interfacial reaction.

９．**About the publication of research results**

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