

SURFACE STRUCTURE INVESTIGATIONS OF TANTALUM(V) CHLORIDE-GRAPHITE BY SCANNING TUNNELING MICROSCOPY

J. Walter¹, H. Shioyama¹, Y. Sawada¹, and S. Hara²

¹Osaka National Research Institute, AIST, MITI

1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan

²Department of Materials Science & Processing

Osaka University, 2-1 Yamada-Oka, Suita 565, Japan

Introduction

Tantalum(V) chloride forms with natural graphite flakes, intercalation compounds which are relatively stable against environmental conditions [1-3]. After air exposing for few days is no change in the X-ray diffraction (XRD) pattern detected [1]. TaCl₅-graphite flakes which are immersed for 2 h at 90°C in water, shows a beginning of stage conversions [1]. Electronmicroprobe studys on such samples, show a hydrolysis of the guests between the host lattice [2]. Intercalated flakes which are stored for one year after this procedure shows coatings of tantalum oxide on the surface. But analysing with particle induced X-ray emission (PIXE) on such long time exposed samples, gives evidence, that tantalum chloride is encapsulated in few micrometers depth [3].

Experimental

Highly oriented pyrolytic graphite (HOPG) from Union Carbide (Type ZYA) and natural graphite flakes of >99.8% purity from Kropfmühl (Bavaria) were used as host materials. The graphite samples were mixed with anhydrous TaCl₅ from Kanto Chemical Co. Inc. in a one bulb in the presence of chlorine gas. After sealing of the ampoules, the intercalation reactions were performed for four days at 400°C.

The stage was estimated by XRD. The samples were studied with a Nanoscope III and measured at 25°C in air. Commercially available Pt-Ir tips from Digital Instruments were used. The images were obtained by a set-point current of 1.0 to 2.3 nA and by a bias voltage of ±10 to ±100 mV. All samples were freshly cleaved along the basal planes before the measuring starts.

After studying the fresh compound by scanning tunneling microscopy (STM), the intercalation

compounds were exposed in water for two hours at room temperature and dried for 1.5 days at 100°C in air. After this procedure, the XRD pattern was observed again. STM investigations on these samples are also repeated under the same conditions as before.

A fresh and water exposed sample of TaCl₅-graphite, with HOPG as host material, was investigated by electron diffraction. The measurements were performed with an Hitachi HF-2000 FE-TEM, with an accelerating voltage of 200 kV.

Results and Discussion

X-ray diffraction pattern of the fresh HOPG sample, shows that a pure second stage was formed ($I_c = 1253 \pm 25$ pm). No sign of unreacted graphite was observed. The selected area electron diffraction (SAED) image, shows a super-lattice of 0.56 nm ($\sqrt{5} \cdot a_0$), which is rotated to the carbon host lattice of $\pm 19.2^\circ$. Lager super-lattices can not be estimated from the SAED image.

XRD measurements on the intercalation compound with S40 flakes as host materials, showed that a mixture of a second stage ($I_c = 1330 \pm 38$ pm) and a third stage ($I_c = 1610 \pm 9$ pm) was formed.

The surface structure of TaCl₅ graphite intercalation compounds (GICs) estimated with STM, shows some long-periodical structures. One of those structures, is a Moiré pattern (Figure 1), it was observed on flakes of S40 graphite. This structure show a horizontal distance of $4 \cdot a_0$. TaCl₅-GIC with HOPG as host material shows another long periodical structure. In most of the investigated areas are ribbons observalable. The distance between the ribbons is of 0.90 nm ($\approx \sqrt{13} \cdot a_0$). The distance between bright spots on a ribbon was estimated of 0.56 nm to each other bright spot in the same ribbon.

STM images with higher magnifications shows completely different surface structures (Figure 2). Observable are bright spots and spots of lower intensities. The bright spots forms a $(\sqrt{5}) \times 3$ super-lattice, which is rotated to the carbon host lattice of approximately $\pm 19^\circ$. After Fourier transformation of Figure 2, an image with the hexagonal carbon lattice and one additional structure was obtained. This additional structure fits with the bright spots observed in Figure 2. Some weaker spots are visible in Figure 2, but it is not possible to verify this spots in the Fourier transformed image. The structure of the weak spots are rotated to the carbon host lattice and to the super-lattice. Further investigations are necessary to understand the nature of the weak spots.

After immersion in water for two hours, it was no surface structure of the intercalate observable by STM. X-ray diffraction studys give evidence, that TaCl_5 is intercalated. Electron diffractions study on a water exposed sample, give evidence that the super-lattice disappear, only a diffuse spot was observed.

Long periodical structures are observed by some metal chloride GICs [e.g. 4,5]. The occurrence of a Moiré pattern can be attributed to the existence of charge density waves (CDW) [6]. The structure with bright spots in Figure 2 can be verified through Fourier transformation and it is in good agreement with the results from electron diffraction.

All surface structures of the GIC disappear by contact with water at room temperature. Only the carbon surface was detected.

Conclusion

TaCl_5 -graphite is realtively stable against environmental conditions, but not for long time. In contact with water, disappear the surface structure of the intercalant.

Acknowledgments

Jürgen Walter is grateful to the Alexander von Humboldt-foundation and the Science and Technology Agency for his Japan fellowship.

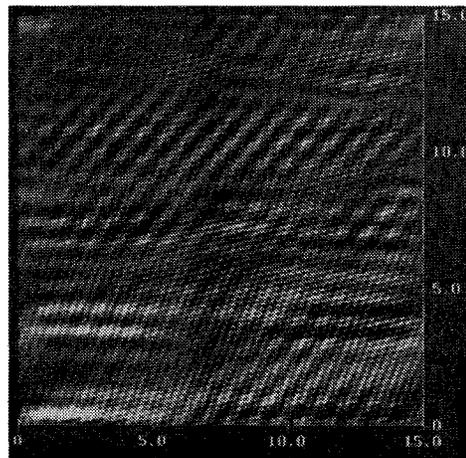


Figure 1. STM image of TaCl_5 intercalated S40 flakes. A long periodical Moiré pattern is observed.

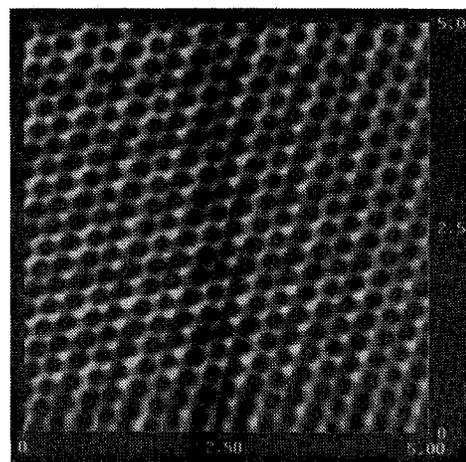


Figure 2. STM image of TaCl_5 intercalated HOPG, with a $(\sqrt{5}) \times 3$ superlattice (bright spots), which is rotated of $\pm 19^\circ$ in regard to the carbon lattice.

References

1. Walter, J. and Boehm, H.P., Carbon, 1995, 33(8), 1121.
2. Walter, J. Synthetic Metals, 1997, in press.
3. Walter, J. and Maetz, M., Mikrochimica Acta, 1997, in press.
4. Ikemiya, N., Okazaki, Y., Hara, S., and Nakajima, T., Carbon 1994, 34(7), 1191.
5. Ikemiya, N., Shimazu, E., Hara, S., Shioyama, H., and Sawada, Y., Carbon 1996, 34(2), 277.
6. Kelty, S.P., Lu, Z., and Lieber, C.M., Physical Review B, 1991, 44(8), 4064.