Physica C 469 (2009) 2000-2002

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc



High temperature hydrogenation of CaC₆

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ARTICLE INFO

Article history: Received 23 February 2009 Received in revised form 20 May 2009 Accepted 18 August 2009 Available online 22 August 2009

PACS: 74.70.-b 74.25.Ha 61.05.cp 71.20.Tx

Keywords: Graphite intercalation compounds Superconductivity Hydrogenation

1. Introduction

Graphite intercalation compounds (GICs) are known to absorb hydrogen either by physisorption or chemisorption depending on the temperature [1–3]. The hydrogen reaction is found to depend on hydrogenation pressure, temperature, the staging or ratio of the graphite to intercalate, and the given intercalated metal [3]. Furthermore, in some of the alkali-metal-GICs, the pronounced changes in structural and superconducting transitions were observed due to hydrogenation [3-7]. The recently synthesized bulk CaC₆, with a reasonably high superconducting transition temperature, $T_C = 11.5 \text{ K} [8]$ stimulates whether even higher transition temperatures can be achieved by hydrogenation as happened in the case of KC₈H_x [6]. The hydrogenation in partially Ca-intercalated graphite compound synthesized from natural graphite flakes by Ca-metal vapour method has been reported recently [9]. Here we present a systematic and detailed study on the effect of high temperature hydrogenation on the structure and superconducting properties of fully intercalated bulk CaC₆ synthesized from highly oriented pyrolytic graphite (HOPG) and molten Li-Ca alloy. The X-ray diffraction (XRD) and magnetisation measurements demonstrate that the hydrogenation leads to a segregation of the Cametal atoms from the intercalated graphite and produces a mixture of CaH₂ and graphite as final compounds thereby sup-

ABSTRACT

The structure and superconducting properties of high temperature hydrogenated calcium-graphite intercalation compound, CaC_6 have been investigated using room temperature X-ray diffraction, and temperature and field dependence of magnetisation. It is found that the hydrogenation can only decompose the CaC_6 phase, and generate a mixture of CaH_2 and graphite as the final compound. The hydrogenation of CaC_6 also reveals a degradation of its superconducting properties. The experimental results are discussed in detail and it is found that the formation of stable CaH_2 and deintercalation are the main source for observed phase separation and suppression in superconductivity.

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pressing its superconducting properties. The results have been discussed in terms of variations in structural and superconducting properties which are correlated with the stability of individual phases and the deintercalation of Ca-metal.

2. Experimental

The CaC₆ samples were synthesized from molten Li–Ca alloy and HOPG as described in detail elsewhere [8]. The hydrogenation has been carried out in a stainless steel reactor at 500 °C under a 10 bar of high pure hydrogen. In order to avoid possible hydrogen desorption, the sample cell was cooled down to room temperature, then pressure was reduced to the atmospheric value. The structural and phase identification of pristine and hydrogenated CaC₆ samples have been carried out using powder XRD. XRD measurements were performed at room temperature using X'pert Pro, PANalytical diffractometer using Mo K α radiation in an inert atmosphere. Magnetization measurements as a function of temperature and field were performed in a Quantum Design superconducting quantum interference device magnetometer (MPMS7), with the applied field perpendicular to the basal plane.

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns of pristine and hydrogenated CaC₆ samples, the samples are subjected to different



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^{0921-4534/\$ -} see front matter \odot 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.physc.2009.08.004



Fig. 1. The XRD patterns of pristine and hydrogenated CaC₆ samples; the samples subjected to different hydrogen exposure times at 500 °C and 10 bars of hydrogen pressure. Symbol * represents the metastable higher staging compound.

exposure times at 500 °C under 10 bar of hydrogen pressure. The pristine CaC₆ sample (Fig. 1a) shows single phase behaviour of rhombohedral CaC₆ without any identifiable unintercalated graphite phase. The silver coloured pristine CaC₆ sample turned into black upon hydrogen exposure. The hydrogenated CaC₆ samples did not reveal any evidence of formation of ternary hydride-Ca-GIC as seen in some of the hydrogenated alkali-metal-GICs [3]. The only drastic collapse of CaC₆ phase and development of new reflections corresponding to constituent graphite and orthorhombic (space group: Pnma) CaH₂ [10] can be seen (Fig. 1b-f) with increasing the hydrogen exposure time. The fully hydrogenated CaC₆ sample shows only mixture of graphite and CaH₂. The similar phase separation and development of free graphite upon hydrogenation in the GICs was first observed in the stage-1 LiC₆. The hydrogenation of LiC₆ leads to formation of LiH and graphite [3,4,11]. It was also reported that hydrogenation in stage-1 LiC₆ can produce higher staging Li-GICs by removing fraction of Li to form LiH [11]. Thus the existence of extra weak reflections (represented by star) neither belonging to CaC6 nor CaH2 in the intermediate hydrogenation state might be a metastable higher staging compound. With increase in hydrogenation time the reflections become weaker and finally disappear after certain hydrogenation time. Furthermore, the position of peaks also depends on the reaction time. The formation of LiH was attributed to the strong affinity of lithium to hydrogen [3]. However, the hydrogen absorption in stage-1 KC₈ brings about changes of staging, and gives new sec-

ond-stage ternary compound, KC_8H_x (0.1 $\leq x \leq 0.67$) [3]. The distinct structural behaviour of light and heavy alkali-metal-GICs and the present Ca-GIC due to hydrogenation clearly suggest that the stability of alkali/alkaline-earth-hydrides plays major role apart from the strong electronic effects suggested previously in hydrogenated LiC₆. For example, the charge transferred to the graphene layer and the magnitude of enthalpy formation of alkali-hydride are lower in stage-1 KC₈ compared to a stage-1 LiC₆ [12,13]. Thus, in stage-1 KC₈ the potassium remains intercalated in graphite and the hydrogen atoms sit in the interstitial sites among the K atoms in the intercalant layers for hydrogen concentrations up to KC₈H_{0.1}. Further hydrogen uptake leads to a full-scale structural transition to an ordered stage-2 compound $KC_8H_{2/3}$ in which the intercalants reside in a triple layer sandwich formed by two highly electropositive K layers between which is inserted a less electropositive H layer [3]. In CaC₆, Emery et al. [14], have reported the highest electron charge transfer between calcium and graphene layer, 0.106 electrons per carbon atom, which is very high compared to 0.07 electrons per carbon atom in LiC₆ [15]. The enthalpy of formation of CaH_2 (-180 kJ/mol) is twice that of LiH (-90.6 kJ/mol) and even three times than KH (-58 kJ/mol) [13]. Furthermore, the hydrogenation at significantly elevated temperature also provokes the phase separation, because the Ca atoms can move rapidly and rearrangement of Ca atoms can occur with respect to the graphene planes to reduce the total free energy of the compound. Therefore the absorbed hydrogen atoms prefer to interact directly with Ca. Thus the CaC₆ phase is no longer stable in the hydrogenated GIC, and a stable CaH₂ precipitates as happened in some of the hydrogenated intermetallics containing stable hydride forming element [16,17].

Fig. 2 shows the temperature dependence of magnetization in zero-field cooled (ZFC) at 100 Oe for c-axis oriented CaC₆ samples



Fig. 2. The temperature dependent magnetization of pristine and hydrogenated CaC_6 samples at an external applied field of 100 Oe along *c*-axis. Inset shows the expanded view of superconducting transition behaviour. The samples subjected to different hydrogen exposure times at 500 °C and 10 bars of hydrogen pressure.



Fig. 3. The field dependent magnetization along *c*-axis at 5 K for pristine and hydrogenated CaC₆ samples. The samples subjected to different hydrogen exposure times at 500 °C and 10 bars of hydrogen pressure.

as a function of hydrogen exposure time. The pristine CaC₆ sample shows the superconducting onset transition temperature, T_C = 11.5 K consistent with previous reports [8]. Fig. 3 shows the hydrogenation and field dependence of ZFC-magnetization (M-H) plots measured at 5 K with the field oriented along the *c*-axis. Pristine and all the superconducting hydrogenated CaC₆ samples behave type-II superconducting nature [8]. The hydrogenated samples show the gradual suppression of superconductivity with increasing the hydrogenation time. This can be observed by decreased diamagnetic signal strength in both the temperature and field dependence of magnetization plots. This can be directly correlated to the decreased superconducting volume fraction of CaC_6 phase due to the growth of CaH_2 at the expense of CaC_6 phase as indicated by XRD results in Fig. 1. Thus the hydrogen saturated sample did not exhibit superconductivity because of complete deterioration of CaC₆ phase. The closure observation of superconducting transitions in partially hydrogenated samples in inset of Fig. 2 reveals the broader onset of transitions without much appreciable change in onset of T_{C} . The broader transitions can be often seen in non-homogeneous systems [18], since the transition width depends more on the flux pinning properties of the samples. Since hydrogenation usually proceeds from the surface of a material, with most of the reaction nucleates at defects or grain boundaries (or microcracks in the case of metal hydride system), in the hydrogenated system, the fraction of remaining superconducting phases are separated by large regions of normal conducting or insulating material, CaH₂. Further, the field dependence of magnetisation of partially hydrogenated samples reveal the decreased lower critical field (H_{C1} , defined as M(H) minimum). This can be attributed to the increased penetration depth (λ), since the intercalant disorder caused by motion of Ca atoms and inhomogeneous distribution of remaining superconducting CaC₆ phase can bring changes in the penetration depth and in the coherence length (ξ).

4. Conclusion

We report the first detailed study of high temperature hydrogenation in bulk CaC₆ synthesized by molten Li–Ca alloy method. The hydrogenation eventually regenerates the constituent graphite by forming CaH₂ as Ca is deintercalated from CaC₆. The successive suppression of superconductivity of CaC₆ upon increasing hydrogenation time is attributed to the decrease in superconducting CaC₆ phase volume fraction due to the phase separation and formation of CaH₂ at the expense of CaC₆ phase.

Acknowledgements

This work was supported by the EPSRC Grant Nos. EP/F027923/ 1 and EP/E003907/1 and by a Royal Society & Wolfson Foundation Laboratory Refurbishment award. We wish thanks to Arthur Lovell for his help.

References

- A. Lovell, F. Fernandez-Alonso, N.T. Skipper, K. Refson, S.M. Bennington, S.F. Parker, Phys. Rev. Lett. 101 (2008) 126101.
- [2] Y. Kojima, N. Suzuki, Appl. Phys. Lett. 84 (2004) 4113.
- [3] T. Enoki, S. Miyajima, M. Sano, H. Inokuchi, J. Mater. Res. 5 (1990) 435.
- [4] W. Ishida, H. Miyaoka, T. Ichikawa, Y. Kojima, Carbon 46 (2008) 1628.
- [5] M. Sano, H. Inokuchi, M. Kobayashi, S. Kaneiwa, I. Tsujikawa, J. Chem. Phys. 72 (1980) 3840.
- [6] S. Kaneiwa, M. Kobayashi, I. Tsujikawa, J. Phys. Soc. Jpn. 51 (1982) 2375.
- [7] G. Roth, A. Chaiken, T. Enoki, N.C. Yeh, G. Dresselhaus, P.M. Tedrow, Phys. Rev. B 32 (1985) 533.
- [8] N. Emery, C. Herold, J.F. Marache, P. Lagrange, Sci. Technol. Adv. Mater. 9 (2008) 044102.
- [9] G. Srinivas, C.A. Howard, S.M. Bennington, N.T. Skipper, M. Ellerby, J. Mater. Chem. 19 (2009) 5239.
- [10] J. Bergsma, B.O. Loopstra, Acta. Crystallogr. 15 (1962) 92.
- [11] D. Guerard, Ph.D. thesis, University of Nancy France, 1974.
- [12] L. Pietronero, S. Strassler, Phys. Rev. Lett. 47 (1981) 593.
- [13] A. Klaveness, H. Fjellvag, A. Kjekshus, P. Ravindran, O. Swang, J. Alloys. Compd. 469 (2009) 617.
- [14] N. Emery, C. Herold, M. d'Astuto, V. Garcia, C. Bellin, J.F. Mareche, P. Lagrange, G. Loupias, Phys. Rev. Lett. 95 (2005) 087003.
- [15] S. Pruvost, C. Herold, A. Herold, P. Legrange, Carbon 41 (2003) 1281.
- [16] M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy, V. Srinivasan, Mater. Chem. Phys. 20 (1988) 245.
- [17] G. Srinivas, V. Sankaranarayanan, S. Ramaprabhu, J. Phys.: Condens. Matter. 20 (2008) 255224.
- [18] T.E. Weller, M. Ellerby, S.S. Saxena, R.P. Smith, N.T. Skipper, Nat. Phys. 1 (2005) 39.