Journal of Alloys and Compounds 515 (2012) 20–21

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Letter

Comment on “Preparation of transition metal phosphides using the facile solid state synthesis”

Sudhish Kumar*

Department of Physics, University College of Science, MB Campus, M. L. Sukhadia University, Udaipur 313002, Rajasthan, India

ARTICLE INFO

Article history:
Received 31 October 2011
Received in revised form
21 November 2011
Accepted 23 November 2011
Available online 2 December 2011

Keywords:
Solid state diffusion
Transition metal phosphides
Vacuum sealing

ABSTRACT

Most recently an article entitled as “Co_2P: A facile solid state synthesis and its applications in alkaline rechargeable batteries” was published by W. Peng et al. in this Journal. In the article the authors have stated that in solid state diffusion technique “it is difficult to obtain stoichiometric materials due to the volatilization and sublimation of red phosphorous”. However, we state that stoichiometric transition metal phosphides can be easily synthesized using the solid state diffusion technique and also the problem of volatilization and sublimation of red phosphorous can be easily tackled by, initially covering the red phosphorous flakes with metal powders in the quartz ampoule and keeping the temperature of the furnace at 250 °C for the first 72 h.

1. Introduction

Recently an article entitled as “Co_2P: A facile solid state synthesis and its applications in alkaline rechargeable batteries” was published by W. Peng et al. in this Journal. The authors have synthesized the stoichiometric Co_2P crystals using the facile solid-state method and investigated the electrochemical performance of Co_2P. The authors have mentioned in the introduction section that the traditional solid-state reaction has the advantages of high yield and easy operation, which is also introduced in the synthesis of Co–P compounds. The solid state methods to synthesize Co–P compounds could be divided into two types: one is to calcine Co metal and red phosphorous under inner atmospheres and the other one is to reduce Co-based and phosphorus-based compounds under reducing atmospheres. However, the author’s have raised comments on the above two methods: the first one is difficult to obtain stoichiometric materials due to the volatilization and sublimation of red phosphorous, and the second one has potential safety hazard because of the adoption of H_2 [1].

My comment focuses on the first preparation method: calcine Co metal and red phosphorous under inner atmospheres and the author’s statement that “it is difficult to obtain stoichiometric materials due to the volatilization and sublimation of red phosphorous”. As I think that such a statement might be misleading, there is the need to describe the methodology for the synthesis of stoichiometric transition metal phosphides using the solid state reaction technique, in which the problem of the volatilization and sublimation of red phosphorous can be easily tackled. The detailed methodology for the preparation of stoichiometric transition metal phosphides in the series $(Co_{1-x}Fe_x)_2P$ is described in the following section.

2. Experimental details, results and discussion

The technique of solid-state diffusion was used at ~1000 °C as described in Refs. [2–6]. The Fe powder (purity better than 4 N), Co powder (purity better than 4 N) and red phosphorous lumps (purity better than 5 N) were the starting materials. Initially, the surfaces of Fe and Co powders were reduced by heating them in hydrogen atmosphere at ~700 °C for 24 h. A specially designed tubular furnace was used for the reduction, initially the furnace was flushed with N_2 gas for an hour and then continuous flow of H_2 gas was maintained in the furnace. X-ray diffraction (XRD) patterns were recorded of these powders for ensuring reduction of any oxide formation on their surface. The elements were weighed in stoichiometric proportions and filled in the quartz ampoules. Firstly the red phosphorous flakes were filled in the ampoule and then the Co and Fe powder were filled, so that the red phosphorous flakes were fully covered by the metal powders. The ampoules were then vacuum (better than 10^{-3} Torr) sealed and placed in a resistance furnace wound of Kanthel wire. Since the melting temperature of red phosphorous is ~280 °C and due to the high vapour pressure of phosphorous, rapid heating around melting temperature may induce an abrupt explosion. Therefore, the temperature of the furnace was kept at 250 °C for the first 72 h and then the temperature was raised in steps over a period of 7 days to 1000 °C and this temperature was then maintained for 15 days. After this, finally the ampoules were rapidly quenched in distilled water at room temperature. The obtained products were grounded for 5 h to fine powders for perfect homogenization and resealed in evacuated ampoules for the first annealing at 1000 °C for another 15 days.

---

* Corresponding Author. Tel.:+91 294 2413955x245.
E-mail address: skmlsu@gmail.com

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.11.123

It must be emphasized that, when red phosphorous flakes were kept above the metal powders (not fully covered by metal powders) in the quartz ampoule then, some part of the phosphorous vapour may not get diffused in the metal lattice. Because during the heating, firstly a part of the phosphorous vapour will move up and may get deposited on the inner walls of the upper half of the quartz ampoule and, secondly large vapour pressure of the phosphorous vapours inside the ampoule may cause an abrupt explosion inside the ampoule, which results in breaking of the ampoule. The resulting products will not be stoichiometric due to phosphorous deficiency. Therefore it is essential to keep the red phosphorous flakes below the metal powders (i.e. phosphorous flakes situated at the bottom of the ampoule, and fully covered by metal powders), so that phosphorous flakes will get diffused easily in the metal lattice and the problem of phosphorous deficiency in the sample as well as the possibility of explosion inside the quartz ampoule be avoided.

In order to get good quality samples, the annealing and quenching process can be repeated two to three times. XRD patterns were recorded after each heat treatment and every time close inspection of the diffraction profile was done for checking of formation of any impurity phase. Since the nuclear scattering lengths of Co, Fe and P were neither far away nor close to each other, therefore in neutron diffraction studies, these elements can be easily distinguished and their site occupancies can be varied in the Rietveld profile refinements and their stoichiometric proportions can be checked. Number of single phase stoichiometric transition metal phosphides in the series $(Co_{1-x}Fe_x)_2P$ have been successfully synthesized using the solid state diffusion technique [7–9].

3. Conclusion

In conclusion, single phase stoichiometric transition metal phosphides can be easily synthesized using the solid state diffusion technique.

References

[1] W. Peng, L. Jiao, Q. Huan, L. Li, J. Yang, Q. Zhao, Q. Wang, H. Du, G. Liu, Y. Si, Y. Wang, H. Yuan, J. Alloys Compd. 511 (2012) 198.
[2] R. Fruchart, A. Roger, J.P. Senateur, J. Appl. Phys. 40 (1969) 1250.
[3] D. Bellavance, J. Mikkelsen, A. Wold, J. Solid State Chem. 2 (1970) 285.
[4] H. Fujii, T. Hokabe, T. Kamiguichi, T. Okamoto, J. Phys. Soc. Japan 43 (1977) 41.
[5] S.N. Dolia, A. Krishnamurthy, B.K. Srivastava, J. Phys. C 21 (1988) 6005.
[6] V. Ghose, N. Sivayogan, A. Krishnamurthy, B.K. Srivastava, S.N. Dolia, J. Appl. Phys. 73 (1993) 5701.
[7] S. Kumar, S. Chander, A. Krishnamurthy, B.K. Srivastava, J. Magn. Magn. Mater. 237 (2001) 135.
[8] S. Kumar, A. Krishnamurthy, B.K. Srivastava, J. Phys. D: Appl. Phys. 41 (2008) 055001.
[9] S.K. Jain, S. Kumar, P.S.R. Krishna, A.B. Shinde, A. Krishnamurthy, B.K. Srivastava, J. Alloys Compd. 439 (2007) 13.