# Communications

## Discussion of "Diffusion Reaction in the Zirconium-Copper System"*

RISHI P. SINGH and ALAN LAWLEY

Bhanumurthy *et al.*[1] recently published results and observations on diffusion reaction in the Cu-Zr system over the temperature range of 873 to 977 K. From this study, it was concluded that only two intermetallic compounds form: $CuZr_2$ followed by $Cu_4Zr$, with incubation times of 1.03 and 1.07 hours, respectively. The authors also stated that in the only other previous work on this system, Kimura *et al.*[2] confirm the existence of $Cu_4Zr$ and $Cu_3Zr$ in the diffusion zone after isothermal annealing.

The purpose of this note is to give a complete documentation of previous work on the Cu-Zr system, with particular reference to the identification of the phases that form. These studies have utilized diffusion couples,[2,3,4] the melting of stoichiometric compositions corresponding to various phases,[5–11] and thermomechanical processing including precipitation reactions.[12–16]

From these studies, the phases identified are: $Cu_5Zr$, $Cu_{51}Zr_{14}$, $Cu_8Zr_3$, $Cu_2Zr$, $Cu_{24}Zr_{13}$, $Cu_{10}Zr_7$, CuZr, $Cu_5Zr_8$, and $CuZr_2$, and the phase diagram is well established.[11]

For the first phase to form, four compositions have been postulated: $Cu_3Zr$,[2,3,4] $Cu_4Zr$,[2,3,6–8] $Cu_9Zr_2$,[7] and $Cu_5Zr$.[3–5,8,13–16] From these studies, it is our opinion that the first phase is $Cu_5Zr$. Compelling factors are the X-ray diffraction studies on residue extracted from aged alloys by Lou and Grant[13] and electron diffraction and energy dispersive spectrometry (by the authors of this note) on spray-cast Cu-Zr.[16] The compositions of the postulated phases are similar, except for $Cu_3Zr$. Thus, minor errors in the determination of composition could lead to erroneous conclusions.

It is also noted by Bhanumurthy *et al.*[1] that, in principle, diffusion reaction between the two metals should lead to the formation of all compounds, as depicted in the equilibrium phase diagram.[11] Bhanumurthy *et al.*[1] cite $Cu_{51}Zr_{14}$, ($Cu_4Zr$) $Cu_{23}Zr_{13}$, $Cu_{10}Zr_7$, CuZr, $Cu_5Zr_8$, and $CuZr_2$. They do not list $Cu_5Zr$, even though this compound appears in the phase diagram.

In the context of these previous studies on the Cu-Zr system, we conclude that the results/observations offered by Bhanumurthy *et al.*[1] are not new. Also, they do not offer further insight into the details of phase formation in the Cu-Zr system.

### REFERENCES


1. K. Bhanumurthy, G.B. Kale, and S.K. Khera: *Metall. Trans. A*, 1992, vol. 23A, pp. 1373-75.
2. H. Kimura, Y. Minobe, S. Uehera, K. Honma, and N.K. Gakkaishi: *J. Jpn. Inst. Met.*, 1973, vol. 37, pp. 552-57.
3. G. Hillman and W. Hoffman: *Z. Metallkd.*, 1965, vol. 56, pp. 279-86.
4. L. Meny, M. Champigny, R. Beltrando, and P. Salaun: *J. Microsc.*, 1967, vol. 6, pp. 111-15.
5. P. Forey, J.-L. Glimois, J.-L. Feron, G. Develey, and C. Becle: *C.R. Acad. Sci. Paris*, 1980, vol. 291, Serie C, pp. 177-78.
6. M.J. Donachie, Jr.: *J. Inst. Met.*, 1963–64, vol. 92, pp. 180-83.
7. J.M. Vitek: *Z. Metallkd.*, 1967, vol. 67, pp. 559-63.
8. A.J. Perry and W. Hugi: *J. Inst. Met.*, 1972, vol. 100, pp. 378-80.
9. J.-P. Gabathuler, P. White, and E. Parthe: *Acta Crystallogr.*, 1975, vol. B31, pp. 608-10.
10. L. Bsenko: *J. Less-Common Met.*, 1975, vol. 40, pp. 365-66.
11. E. Kneller, Y. Khan, and U. Gorres: *Z. Metallkd.*, 1986, vol. 77 (1), pp. 43-48.
12. I. Kawakatsu, H. Suzuki, and H. Kitano: *J. Jpn. Inst. Met.*, 1967, vol. 31, pp. 1253-57.
13. M.Y.-W. Lou and N.J. Grant: *Metall. Trans. A*, 1984, vol. 15A, pp. 1491-93.
14. V.A. Philips: *Metallography*, 1974, vol. 7, pp. 137-55.
15. L. Arnberg, U. Backmark, N. Backstrom, and J. Lange: *Mater. Sci. Eng.*, 1986, vol. 83, pp. 115-21.
16. R.P. Singh, A. Lawley, S. Freidman, and Y.V. Murthy: *Mater. Sci. Eng.*, 1991, vol. A145, pp. 243-55.


*K. Bhanumurthy, G.B. Kale, and S.K. Khera: *Metall. Trans. A*, 1992, vol. 23A, pp. 1373-75.

RISHI P. SINGH, Senior Engineer, is with the Turbine Materials Power Generation Business Unit, Westinghouse Electric Corporation, Orlando, FL 32826-2399. ALAN LAWLEY, Professor of Materials Engineering, is with the Department of Materials Engineering, LeBow Engineering Center, Drexel University, Philadelphia, PA 19104.

Discussion submitted June 4, 1992.

## Authors' Reply

K. BHANUMURTHY, G.B. KALE, and S.K. KHERA

Singh and Lawley seem to have missed the objective of the communication which is mentioned in the introductory paragraph. We would also like to point out that the aim of the communication was not to comment on the different equilibrium intermetallic phases present in the zirconium-copper system but to identify the intermetallic phases formed in the diffusion zone, to evalute the incubation periods for their formation, and to present diffusion data on the chemical diffusion coefficients and the activation energies in these intermetallic phases.

In the absence of any established phase diagram, we have referred to a recent phase diagram,[1] which shows the intermetallic phases $Cu_5Zr$, $Cu_4Zr(Cu_{51}Zr_{14})$, $Cu_8Zr_3$, $Cu_2Zr$, $Cu_{24}Zr_{13}$, $Cu_{10}Zr_7$, CuZr, $Cu_5Zr_8$, and $CuZr_2$. Though the equilibrium phase diagram indicates several phases, the present study confirms the formation of only $Cu_4Zr$ and $CuZr_2$ in the diffusion zone. This is not unexpected in view of the fact that equilibrium is not established in the diffusion zone as long as a concentration gradient across the phase interfaces exists. We admit that the equilibrium phases, namely, $Cu_5Zr$, $Cu_8Zr_3$, and $Cu_2Zr$ (?), have been inadvertently omitted in our communication. However, this omission does not modify the conclusions drawn. The copper-rich phase formed in the diffusion zone is $Cu_4Zr$ and not $Cu_5Zr$, as has been confirmed from the composition estimated by electron probe microanalysis and also from X-ray diffraction studies.

Singh and Lawley have pointed out that different equilibrium intermetallic compounds have been synthesized earlier. Our communication does not claim that $Cu_4Zr$