

Storing Hydrogen in the Solid State

INTERMETALLICS CONTAIN PLATINUM GROUP METALS

Recent activity in the field of energy research indicates that hydrogen may participate to an ever increasing extent in future energy utilisation. For instance, hydrogen could be piped for domestic consumption, either being converted by fuel cells into electricity for lighting, or used directly as a heating and cooking fuel.

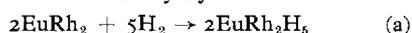
Many of these applications for hydrogen will require it to be stored in a more convenient manner than at present. Solid state hydrogen storage, that is, storing hydrogen in a metal alloy that will absorb and desorb hydrogen to a high level, has attracted much attention in the literature in recent times.

Two new papers (1,2) have been published by workers at the Bell Laboratories, Murray Hill, New Jersey, which shed light on possible degradation mechanisms for storage compounds. The investigations were based on experiments on the properties of EuPd and EuRh₂. It was found that EuPd changed structure during hydrogen absorption although the europium remained divalent. EuRh₂ was found to be particularly interesting because although the initial absorption of hydrogen by the compound indicated a higher reversible capacity than LaNi₅, this reversibility declined during cycling until the material became a stable hydride.

Although deterioration in the hydrogen capacity of other compounds has been observed, it has generally been associated with the presence of water or oxygen, which lead to the production of hydroxides or oxides. This EuRh₂ degradation mechanism appears to be intrinsic to the hydrogen absorption process.

Using Mössbauer spectroscopy the authors were able to characterise the europium environment of the compound before and after cycling. They considered the initial hydriding spectra showed evidence that the europium in hydrided EuRh₂ was in mole-

cular complexes or clusters similar to those found for europium in EuH₂. Further cycling produced a spectra that contained a significant component of unhydrided material. The formation of a rhodium rich phase and a relatively stable EuH₂ phase was postulated to fit the experimental observations. Initial absorption is said to occur via the formation of a metastable ternary hydride:



the reaction being less exothermic than:



It is postulated that reaction (a) occurs initially, with phase separation of the type shown in (b) virtually impossible due to negligible diffusion taking place at the temperature of absorption. After several absorption cycles, however, the lattice is severely strained by the volume changes involved, which enhances diffusion. This is accompanied by the comminution of the sample into a very fine powder, of which not all the particles are in good thermal contact with each other. As reaction (a) is exothermic, local heating can occur, leading to the possibility of diffusion and the formation of EuH₂.

The authors were able to restore the original hydrogen absorption properties by vacuum annealing at 350°C for 5 hours, evidently allowing the rhodium to diffuse into regions of high europium concentration.

Although the degradation effects described above rely on the rapid dissociation of EuRh₂, the authors suggest that the phenomenon may also exist in the LaNi₅ family of intermetallic compounds. The regeneration processes should be equally applicable in other cases where similar mechanisms are operable.

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References

- 1 R. L. Cohen, K. W. West and K. H. J. Buschow, *Solid State Commun.*, 1978, **25**, (5), 293
- 2 K. H. J. Buschow, R. L. Cohen and K. W. West, *J. Appl. Phys.*, 1977, **48**, (12), 5289