ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 698–703

Journal of ALLOYS AND COMPOUNDS

# Preparation and Properties of metal matrix hydride compacts via the rotary forging compaction route

D.B. Willey*, A.J. Williams, I.R. Harris

*School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK*

## Abstract

Metal matrix hydride compacts have been produced by the rotary forging compaction route using aluminium and titanium hydride in various ratios as the matrix and hydride components respectively. The compaction process was found to produce high density compacts, achieving >90% density at loads of <7 MPa. The samples were hydrogen cycled in a dilatometer to assess the linear changes associated with hydride formation–decomposition. An intermetallic reaction between the aluminium and degassed titanium was found to reduce the mechanical stability and hydrogen capacity.

*Keywords:* Metallic hydrides; Rotary forging; Metal matrix hydride compacts

## 1. Introduction

The hydrogen storage intermetallics have been found to have many important applications. However, intrinsic properties of metallic hydrides such as decrepitation, poor thermal conductivity and the pyrophoric nature of some hydride powders have adversely affected the applicability of these materials to everyday applications.

Past work [1–4] has shown that mixing (or coating) the hydride with a metallic non-hydride former and pressing into a pellet or ‘‘compact’’ increases the effectiveness of these hydrides particularly with respect to the thermal conductivity and the handling. In the present work, an alternative method for the production of metal matrix hydride compacts (MMHCs) via the rotary forging compaction route has been investigated, as this process has been shown to produce compacts of high density and good mechanical strength, which may prove vital when cycling the compacts in hydrogen. The process is performed at room temperature which provides further advantages over techniques such as hot pressing. Rotary forging has been employed successfully to produce a variety of pressed products such as metal or polymer bonded permanent magnetic materials [5,6]. In the present studies, this technique has been employed to produce aluminium–titanium hydride composites and the hydrogen absorption–desorption behaviour of these compacts has been assessed.

## 2. Experimental

The rotary forging machine used in the production of the MMHCs is based on a design by Penny and Slater [7,8] and is described in more detail elsewhere [5]. The basic principle of this process, however, is that a small overall load is applied, which produces a very high local load, making the compaction process very energy efficient compared to other methods, such as uniaxial pressing. The overall load is applied in the range of 0–60 bars, and this is converted to a local pressing load of approximately 0–13 MPa. Fig. 1 shows a schematic diagram of the rotary forging process and Fig. 2 shows the lower tooling die arrangement. The matrix–hydride powder mix is loaded into the lower die and then raised to the upper tooling to produce a pseudo-closed system. The motor is then started and this rotates the tooling at high velocity and the lower die is raised to commence the compaction process. Forging is completed when the displacement reading approaches a constant value.

Bulk quantities of titanium hydride were produced by the hydrogenation of titanium sponge powder (average particle size 100 μm) at 500°C and 10 bar hydrogen pressure. The titanium hydride produced was mixed with

---

*Corresponding author.

*PII* S0925-8388(96)02990-8

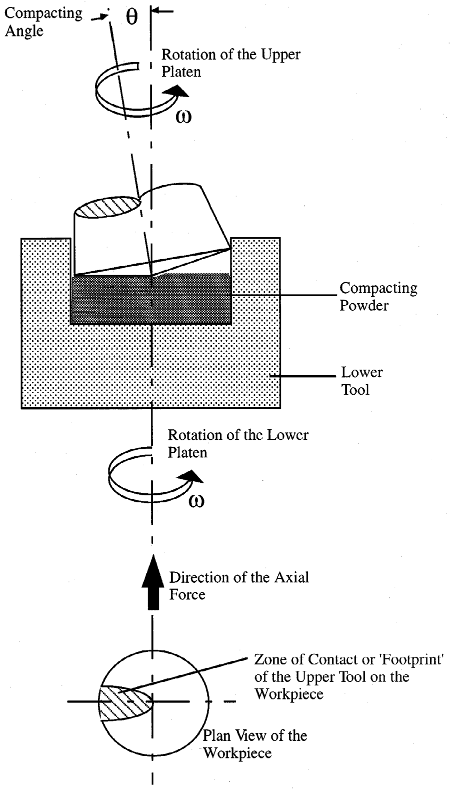

Fig. 1. Schematic of rotary forging process.

aluminium powder (Goodfellows 99.9% purity, average particle size ~20 μm) and rotary forged to produce the compacts. The powders were forged using a range of pressures to assess the densities of the compacts as a function of forge pressure, as well as investigating any effects the forging process may have on the microstructure. The densities of the as-forged compacts were measured by means of the liquid displacement method, after which the samples forged at 30 bar were mounted for microstructural examination.

The hydrogen absorption–desorption temperatures of the titanium were assessed by differential thermal analysis (DTA). The titanium sponge was heated under 1 bar hydrogen and in a rotary vacuum atmosphere i.e. $<2.0\times 10^{-5}$ bar and the relative hydrogen sorption temperatures identified. The dilatometer samples were prepared by machining the compacts into 20×5×5 mm rectangular specimens and then heated to appropriate temperatures (as observed in the DTA) to enable hydrogen sorption to take place. The samples were then cycled in ~1 bar hydrogen, supplied from a $LaNi_5$ hydrogen store. After these studies, the samples were mounted for metallographic examination.

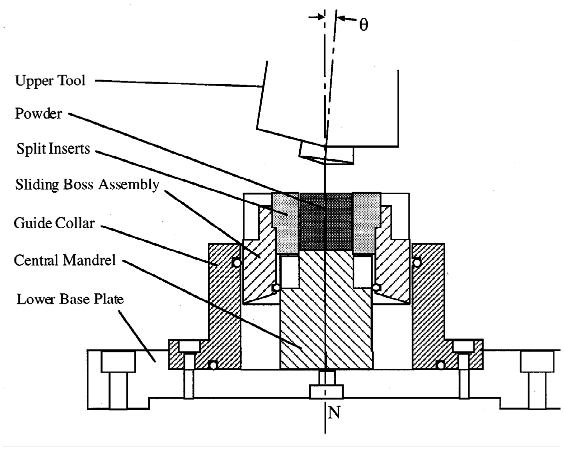

Fig. 2. Floating die arrangement.

## 3. Results and discussion

The stoichiometry of the titanium hydride produced in bulk was determined by X-ray diffraction to be face centred cubic $TiH_x$, $x=1.97$, with the X-ray diffraction peaks correlating with those published by Sidhu et al. [9]. Fig. 3 shows the densities of the aluminium–titanium hydride compacts produced. The aluminium 10% titanium hydride appears to approach 100% density at 40 bar pressure, while the 25 and 50% compositions attain a maximum density of 98 and 95.5% respectively, with no further increase, even at 60 bar forge pressure. The densities of the aluminium 75% titanium hydride compacts continue to increase over the whole pressure range, achieving >99.5% density at 60 bar.

Fig. 4 shows a macroscopic picture of 20 mm diameter as-forged compacts, both parallel and perpendicular to the plane of forging. The surface of the as-forged compact

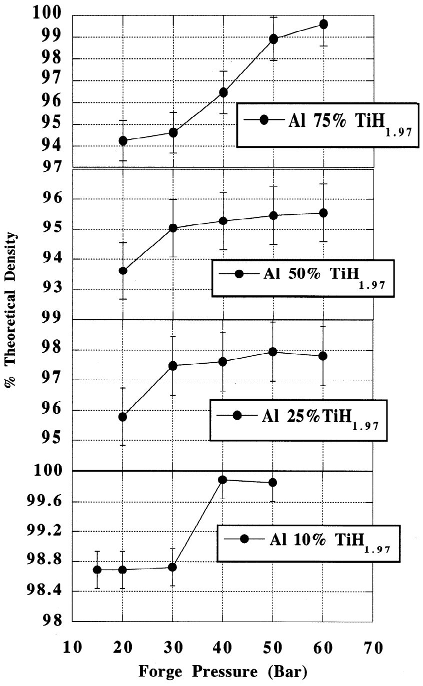

Fig. 3. % Theoretical densities of aluminium–titanium hydride compacts, as a function of forge pressure.

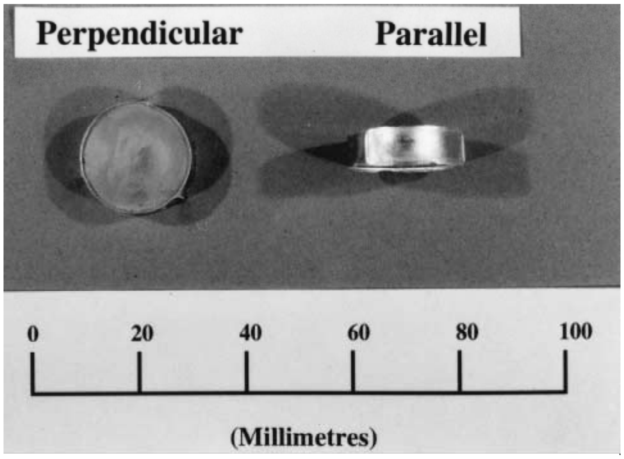

Fig. 4. Macroscopic picture of an as-forged metal matrix hydride compact, perpendicular and parallel to forging direction (20 mm diameter die).

perpendicular to the plane of forging is very smooth, with evidence of ''flash'' on the edges where the powder has been ''back extruded''. The appearance of the compact parallel to the plane of forging is also very smooth, showing that the aluminium component of the powder mix produces dense, mechanically stable compacts.

Fig. 5(a–d) show the microstructures of the as-forged compacts pressed at 30 bar. The titanium hydride (A) is fairly evenly distributed throughout the aluminium matrix (B). The 10 and 25% hydride compositions have no discernible porosity within the structure, while the 50 and 75% hydride compositions start to display some porosity (C), particularly within the 75% compact.

Fig. 6 shows the hydrogen sorption temperatures of the titanium measured by DTA in 1 bar hydrogen. The hydrogen DTA trace (A) shows hydrogen absorption occurring at 420–440°C and partial desorption at 660°C. Fig. 6 also shows a rotary vacuum desorption DTA trace (B) of the hydrogenated titanium, with desorption occurring at 500–550°C. It was therefore established that cycling the dilatometer specimens at approximately 550°C would enable both hydrogenation and vacuum desorption to occur.

The hydrogen absorption–desorption properties of the aluminium 50% titanium hydride compact were assessed in the dilatometer. The sample was heated to ~550°C (ramp rate 5 °C min$^{-1}$) under rotary vacuum to enable the

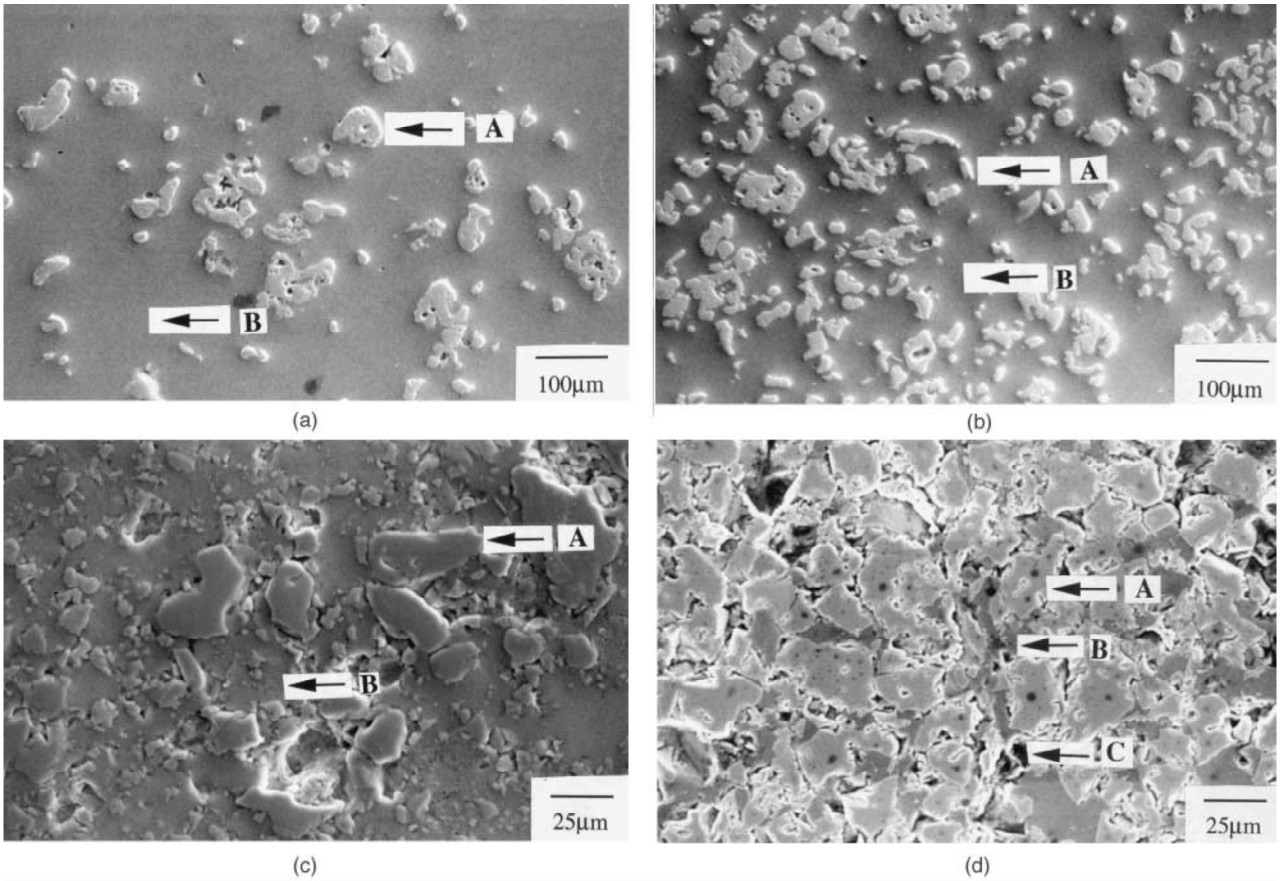

Fig. 5. (a) Microstructure of the as-forged aluminium 10% titanium hydride compacts, forged at 30 bar. Titanium hydride=(A); aluminium =(B). (b) Microstructure of the as-forged aluminium 25% titanium hydride compacts, forged at 30 bar. Titanium hydride=(A); aluminium=(B). (c) Microstructure of the as-forged aluminium 50% titanium hydride compacts, forged at 30 bar. Titanium hydride=(A); aluminium=(B). (d) Microstructure of the as-forged aluminium 75% titanium hydride compacts, forged at 30 bar. Titanium hydride=(A); aluminium=(B); porosity=(C).

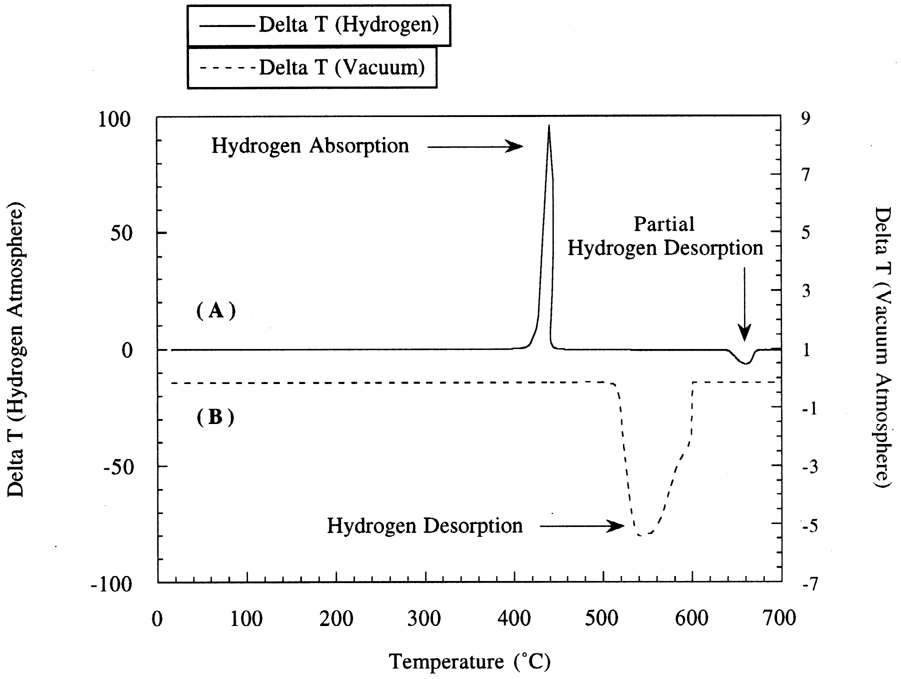

Fig. 6. Hydrogen (A) and vacuum (B) DTA plots of hydrogen sorption of titanium.

titanium to initially desorb hydrogen. Fig. 7(a) shows the first desorption trace of the sample during heating to temperature. Hydrogen desorption commences under rotary vacuum at 390–400°C, inducing a contraction of ~1%, this being >100°C lower than the DTA desorption trace of the titanium. As the desorption continues, plastic deformation of the sample occurs inducing a linear expansion of >5%, this taking ~100 min to reach completion, Fig. 7(b). It appears that the production of very clean titanium due to the desorption process promotes the expansion reaction. Diffusion mechanisms between the titanium and the aluminium, such as the Kirkendall effect, may also contribute to the observed expansion. However, a detailed investigation into the mechanism of the reaction is required.

Once the expansion reaction had completed, isothermal hydrogen sorption was performed. Fig. 8 shows the relative linear changes of the subsequent isothermal hydrogen absorption–desorption reactions. It is observed that the % linear expansion due to hydrogenation is larger than the % linear contraction associated with desorption with the average linear expansion associated with subsequent hydrogen sorption cycles being 0.63% on hydrogenation and the average linear contraction on desorption being 0.46%. This difference in values of absorption–desorption suggests that further plastic deformation maybe occurring during cycling. Over the test period, however, the difference in the values of absorption–desorption decrease with cycle number. At the end of testing, the sample appeared to show little or no mechanical strength as well as exhibiting large surface cracks. This suggests that during hydrogen cycling a reaction (or reactions) occur which reduces the mechanical strength.

Figs. 9 and 10 show the cycled aluminium 50% titanium hydride dilatometer sample. Fig. 9 shows that the edge of the sample is a dense structure containing the aluminium and the titanium (D), while the centre of the sample, (Fig. 10), shows evidence that a large pore forming reaction (E) had occurred within the sample, accounting for the large linear expansion.

Fig. 11 shows a back scattered electron image of the particles within the sample and it can be seen that there is a two phase region present within the structure. The light phase (Phase F) was identified to be titanium, while the dark phase (Phase G) was found to be $\gamma$-titanium aluminide, TiAl. The presence of the free titanium would account for the ability of the compact to continue cycling hydrogen, even after the titanium aluminide/pore forming reaction had occurred. The subsequent absorption–desorption data, Fig. 8, shows that the % linear expansion is consistently larger than the measured % contraction during hydrogen sorption. This suggests that further reactions between the aluminium and the titanium are occurring, producing more of the titanium aluminide intermetallic and/or more porosity, which would also continue to reduce the mechanical stability of the compact.

The presence of reaction by-products between the matrix and the hydride former has been reported previously [2,10], and it has been shown that these by-products contribute to a decrease in the mechanical strength and hydrogen capacity of the compacts. A possible solution to the problem is to use a less stable hydride in the compacts, so that a lower temperature could be used for hydrogen sorption, thus reducing the driving force for the production of such reaction by-products.

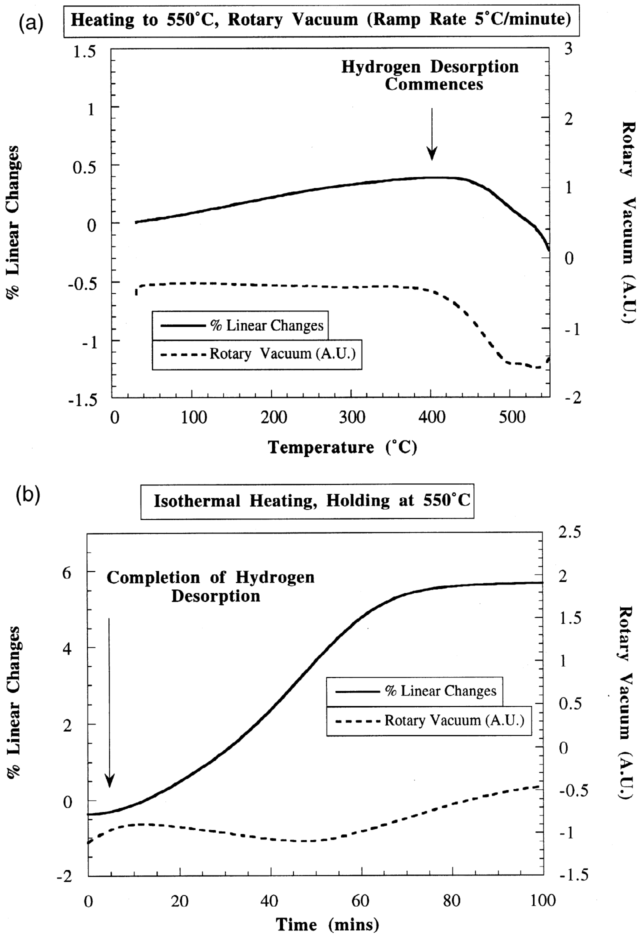

Fig. 7. (a) First hydrogen desorption of aluminium 50% titanium hydride compact, heating to 550°C, rotary vacuum atmosphere. (b) First hydrogen desorption of aluminium 50% titanium hydride compact, isothermal heating at 550°C, rotary vacuum atmosphere.

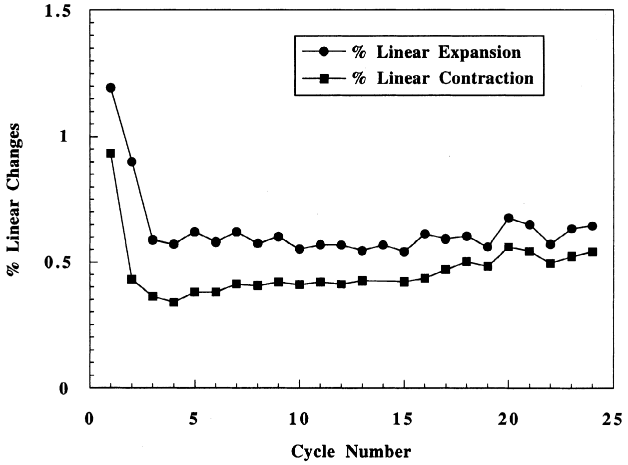

Fig. 8. Linear changes associated with subsequent hydrogen sorption cycles of aluminium 50% titanium hydride.

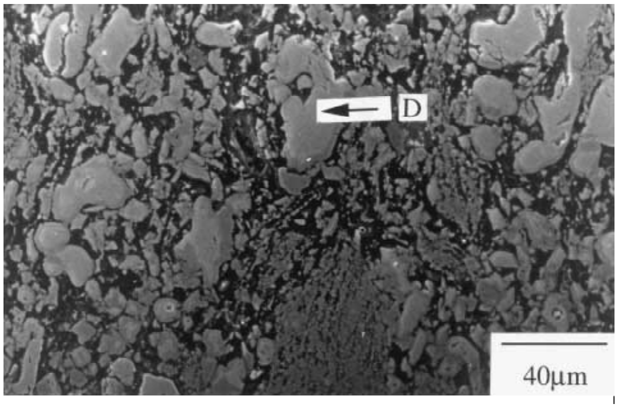

Fig. 9. Micrograph of the edge section of a cycled aluminium 50% titanium hydride specimen, D=titanium and aluminium.

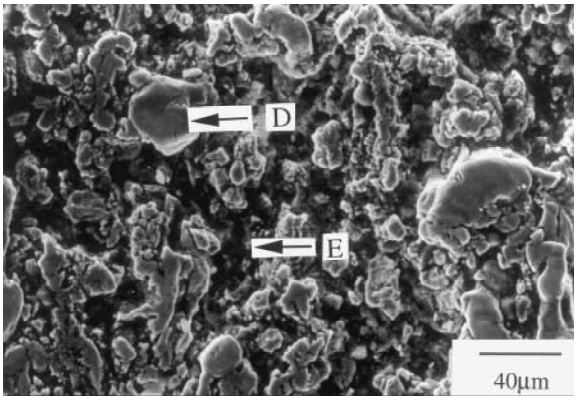

Fig. 10. Micrograph of the centre section of a cycled aluminium 50% titanium hydride specimen, D=titanium and aluminium, E=porosity.

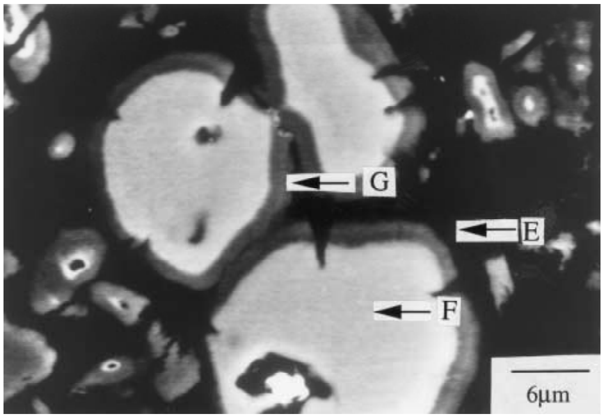

Fig. 11. Back scattered electron imaging micrograph of a section of a cycled aluminium 50% titanium hydride specimen, E=porosity, phase F=titanium, phase G=titanium aluminide, TiAl.

## 4. Conclusions

It has been shown that rotary forging produces high density MMHC, which are mechanically stable in the as-forged state, even at low matrix compositions. The compacts show a level of stability when cycled in hydrogen, however, the intermetallic/pore forming reaction that occurred within the sample while testing may have contributed to the decrease in mechanical stability and hydrogen capacity. Dilatometry has been found to be a good method for monitoring the hydrogen absorption–desorption behaviour of the compacts, together with the formation of TiAl and its effects on the absorption–desorption characteristics. The present investigation indicates promising features of the rotary forged compacts. Therefore, further studies on rotary forged matrix–hydride compacts, with different binders and hydrides will be studied.

## Acknowledgments

Thanks are due to Colin Tattam for helpful discussions and to Penny and Giles (Blackwood) for providing access to their Rotary Forging Machine.

## References

[1] M. Ron and M. Elemelach, *Hydrides for Energy Storage*, Pergamom, 1978, p. 417.

[2] M. Ron, D. Gruen, M. Mendelsohn and I. Sheft, *J. Less-Comm. Metals, 74* (1980) 445.

[3] E. Tuscher, P. Weinzierl and O.J. Eder, *Int. J. Hydrogen Energy, 8(3)* (1983) 199.

[4] H. Ishikawa, K. Ogura, A. Kato, H. Suzuki and E. Ishii, *J. Less-Comm. Metals, 120* (1986) 123.

[5] N. Rowlinson, *PhD Thesis*, University of Birmingham, 1989.

[6] C. Tattam, A.J. Williams, J.S. Hay, S.F. Tedstone, M.M. Ashraf and I.R. Harris, *J. Appl. Phys., 76* (1994) 6831.

[7] W.A. Penny, (1979), *PhD Thesis*, The City University, London, 1981.

[8] W.A. Penny and R.A.C. Slater, UK Patent Application No. 7 903 561, Published No. 2 041 268, 1979.

[9] S.S. Sidhu, L. Heaton and D.D. Zauberis, *Acta Crystallogr., 9* (1956) 612.

[10] Q.D. Wang, J Wu and H. Gao, *Z. Phys. Chem. NFB, 164* (1989) 1367.