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Hydrogen decrepitation as a method of powder preparation of a 2:17-type, $Sm(Co, Cu, Fe, Zr)_{8.92}$ magnetic alloy

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The present work has shown that hydrogen decrepitation of a 2:17-type $Sm(Co_{0.673}Cu_{0.080}Fe_{0.222}Zr_{0.025})_{8.92}$ alloy is a very rapid and convenient means of producing powdered material for the production of polymer-bonded permanent magnets. The magnets made from the hydrogen decrepitated powder (average particle size ~ 100 μm) exhibited improved demagnetization loop shapes, higher intrinsic coercivities and improved elevated temperature stability when compared with the magnets produced from the standard milled powder material (average particle size ~ 40 μm). These differences in properties have been related to the differences in the character of the powders produced by the two methods of decrepitation.

1. Introduction

Many of the rare earth–cobalt (RE–Co) intermetallic compounds are known to form metastable hydrides by an exothermic reaction between the intermetallic compound and hydrogen [1, 2]; this process is always associated with hydrogen decrepitation of the bulk material. Detailed studies have been carried out on the pressure against hydrogen content relationships in a number of $RE\ Co_5$–H_2 systems [1–4] including the $SmCo_5$–H_2 system.

Previous magnetic work [4, 5] on the $SmCo_5$–H_2 system mainly involved a study of the influence of hydrogen absorption on the intrinsic coercivity (iH_c) and remanence ($4\pi M$) values of $SmCo_5$ magnets. It was found that both iH_c and $4\pi M$ are reduced by hydrogen additions and this reduction is particularly pronounced in the case of the iH_c values. The variation of iH_c with hydrogen content at room temperature appeared to mirror the room temperature pressure against hydrogen content isotherm for the $SmCo_5$–H_2 system [4]. It has been proposed that the marked reduction in the iH_c values of $SmCo_5$ magnets by hydrogen absorption can be employed to temporarily reduce the intrinsic coercivity of $SmCo_5$ magnets [6]. The kinetics of the hydrogen absorption/desorption processes in $SmCo_5$ have also been investigated [7, 8].

In view of the decrepitation of the bulk material by hydrogen, work has been carried out in this laboratory [9, 10] to investigate the hydrogen decrepitation process as a means of producing powder of $SmCo_5$ for the manufacture of the polymer-bonded magnets. This work has shown that suitable powder can be produced by a hydrogen decrepitation process in a much shorter time than that employed in the standard milling operation and the polymer-bonded magnets made from this powder material exhibited comparable permanent magnetic properties to those of the magnets made from the standard milled powder.

In the present study, the hydrogen decrepitation characteristics of a $Sm(Co_{0.673}Cu_{0.080}Fe_{0.222}Zr_{0.025})_{8.92}$-type magnetic alloy have been investigated and the possibility of the application of this process as a method of powder production of the present 2:17-type alloy has been examined. The magnetic properties of the hydrogen decrepitated (HD) particles have been assessed by employing these particles to make magnetically aligned polymer-bonded magnets and their magnetic properties have then been compared with those of

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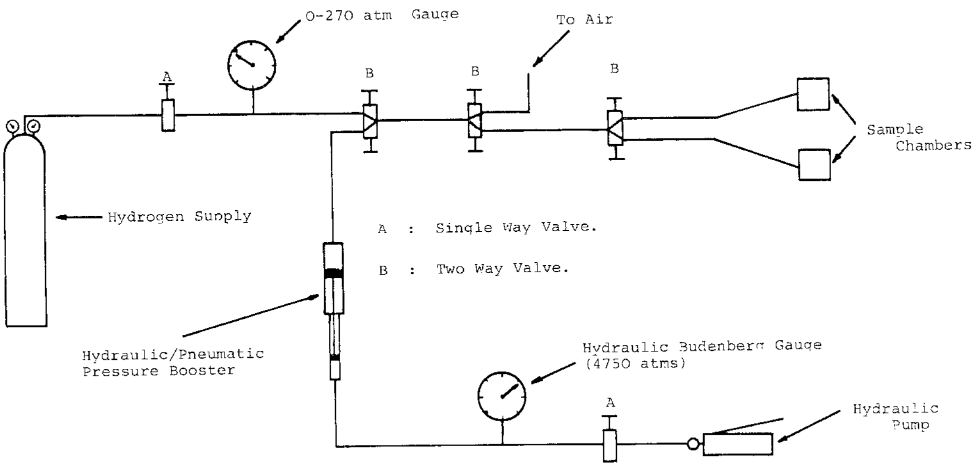

Figure 1 Schematic diagram of a high pressure (0 to 2000 atm) rig.

similar polymer-bonded magnets made from milled (M) powder.

2. Experimental procedure

Magnetically hardened specimens of the present 2:17-type alloy were prepared as follows: The "as-cast" ingots were sealed in previously evacuated silica tubes under 0.5 atm of purified argon, and were then solid solution treated at 1170° C for 4 h, after which they were quenched into water in the argon atmosphere. The solid solution treated alloy was then divided into separate specimens of approximately the same weight which were then subsequently isothermally aged at 800° C from 1 to 50 h in a dynamic vacuum and were then air cooled (in vacuum) to room temperature. From each isothermally aged solid specimen, two types of powder particles were produced:*

(i) by milling and then sieving the powder to produce an average particle size of 40 μm and

(ii) by high pressure hydrogen decrepitation of the specimens at ~300 atm of hydrogen pressure and at about 200° C which produced an average particle size of around 400 μm. To achieve the high pressures employed in this work, a small hydraulic pump was used in order to boost the normal hydrogen cylinder pressure of around 130 atm. A schematic representation of this high pressure rig is shown in Fig. 1. The hydrogenation conditions employed here are broadly similar to those employed to hydrogenate the binary compound of Sm_2Co_{17} [11].

The HD material was scored with intergranular cracks (Fig. 2) which caused the individual particles to be extremely friable. To complete the fracture process therefore, the particles were lightly smeared for a few minutes to produce an average particle size of around 100 μm (Fig. 3). The smeared particles were finally degassed at ~200° C (in a dynamic vacuum of 10^{-6} torr).

To assess the magnetic properties, the magnetically aligned particles were processed into polymer-bonded cylindrical test magnets of an identical size. The magnet production method employed in the present work was very convenient and it has been described elsewhere [12]. The relatively low remanence and energy product $[(BH)_{\max}]$ values obtained in the present work can be attributed to (i) the relatively high average particle sizes (40 and 100 μm for M and HD magnets respectively) and (ii) the factors related to the magnet production procedure [12]. It should however be noted that the iH_c values in the present type of alloys are essentially independent of these factors. The demagnetization curves of the test magnets were characterized by a d.c. magnetic loop tracer in a closed magnetic circuit.

The elevated temperature stability of the magnets was studied by the determination of the permanent deterioration in the magnetic properties as a function of ageing in air at 150° C for periods of up to 1000 h. In this experiment, two polymer-bonded test magnets made from the M and HD particles were utilised. The magnets were magnetically pulsed in a 50 KOe magnetic field, after each stage of the ageing treatment and

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*This ensured the strict comparability of the subsequent magnetic measurements on the HD and M particles in terms of their previous heat treatments.

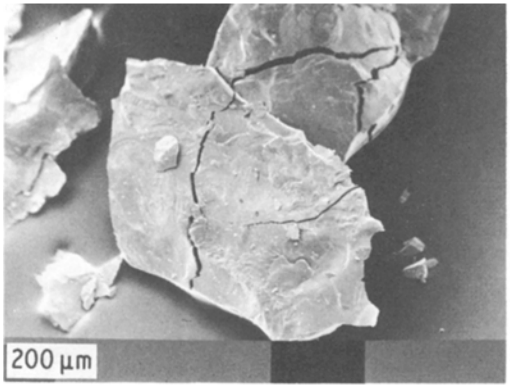

Figure 2 Scanning electron micrograph of a typical HD material.

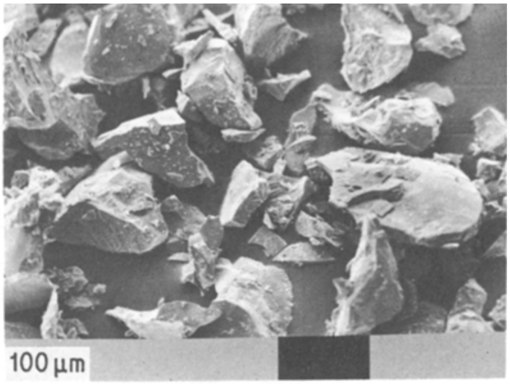

Figure 3 Scanning electron micrograph of a typical HD and smeared material.

their demagnetization curves were then characterized in an identical manner to that described above.

3. Results

The variation shown in Fig. 4 has been reported in a previous paper [13] and illustrates the comparison between the variations of the iH_c values with ageing time for two series of polymer-bonded magnets made from the M and HD particles, respectively. The iH_c curves of both types of magnet exhibit maxima after 38 h of ageing and thus overageing occurs after this time interval in both types of magnet. The iH_c values are always significantly higher in the HD magnets and after the maximum, there appears to be a more pronounced fall in the iH_c values of the M magnets. Typically the iH_c values are 25% higher and the $4\pi M$ values are 4% lower in the HD magnets compared with those of the M magnets. However, it should be noted that the $4\pi M$ value of a polymer-bonded magnet made from the M particles with an average particle size of 100 μm (i.e. identical to that of the HD particles) was

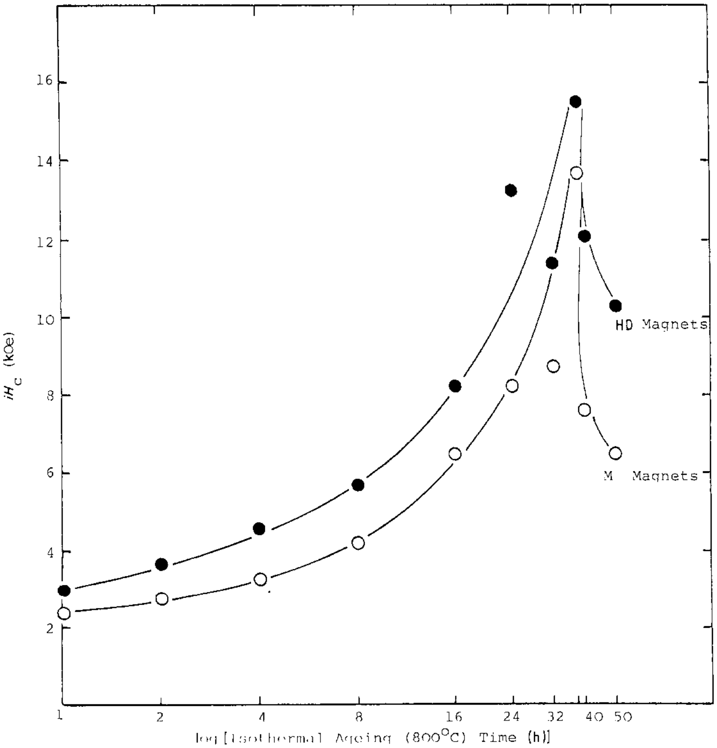

Figure 4 Variation of iH_c values with isothermal (800° C) ageing time for HD and M magnets.

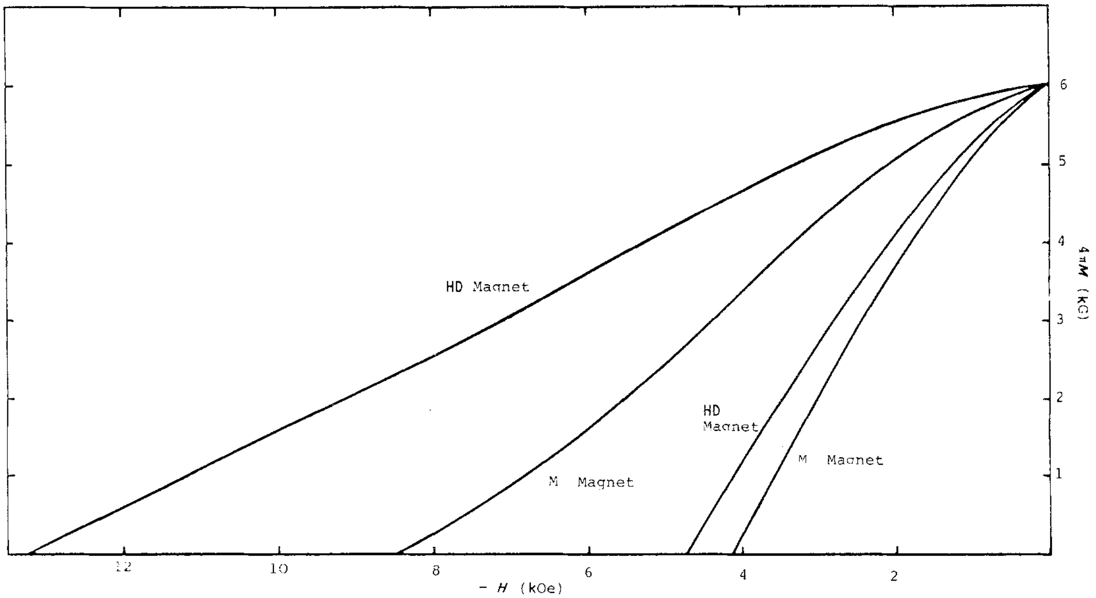

Figure 5 Demagnetization curves of an M and an HD magnet made from material which has been solution treated (1170° C) and isothermally aged (at 800° C for 24 h).

20% lower than that of a magnet produced from the HD material (under identical heat treatment processes).

The demagnetization curves of the HD magnets generally show better loop shapes than those of the similar M magnets. This can clearly be seen in Fig. 5 where the intrinsic ($4\pi M$ against H) and induction (B against H) curves of two identically heat treated (aged at 800° C for 24 h) magnets made from the HD and M powders are compared with one another. In this particular case both magnets exhibited identical values of $4\pi M$ (namely 6 KG). Inspite of the better demagnetization loop shapes and enhanced iH_c values in the HD magnets compared with those of the M magnets, the usual slight reduction $4\pi M$ values of the former magnets generally led to approximately equal $(BH)_{max}$ values for both types of magnet. The highest $(BH)_{max}$ value, corresponding to the iH_c peak, was of the order of 9×10^6 GOe for both types of magnet.

The permanent deterioration in the magnetic properties of two polymer-bonded magnets (produced from the HD and M particles) as a function of the ageing time in air at 150° C are shown in Fig. 6 and Fig. 7 respectively. It can be

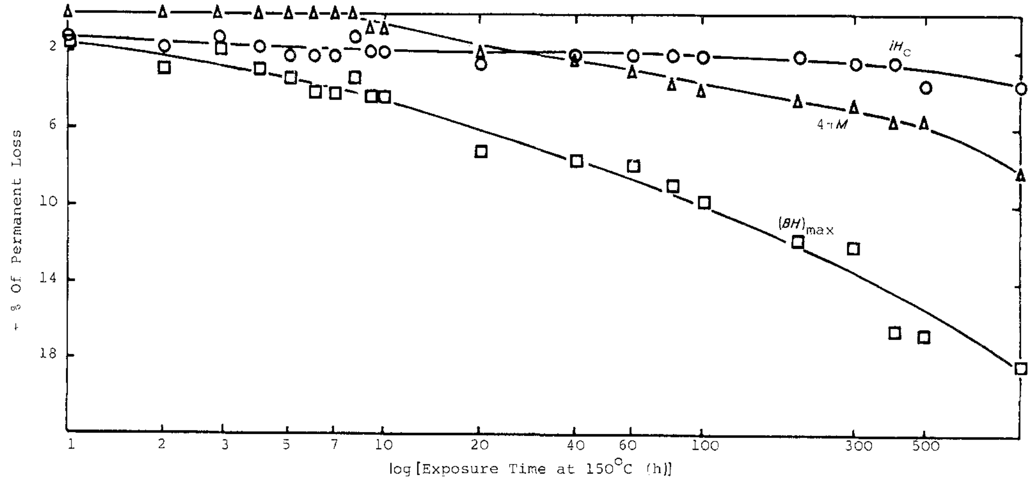

Figure 6 Irrecoverable loss in magnetic properties of a polymer-bonded magnet made from the M material against exposure time in air at 150° C.

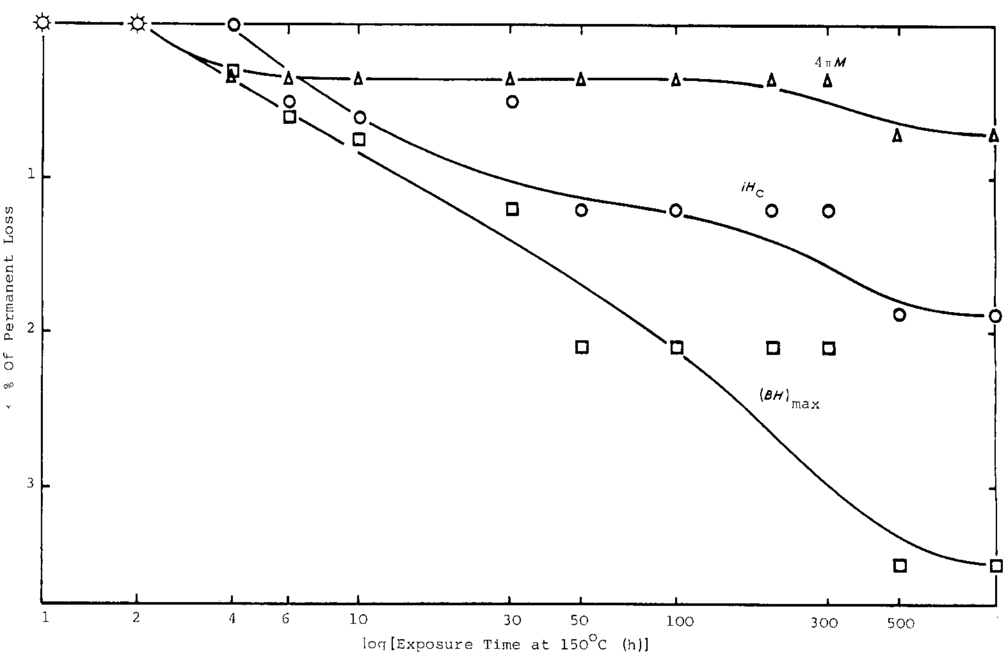

Figure 7 Irrecoverable loss in magnetic properties of a polymer-bonded magnet made from the HD material against exposure time in air at 150° C.

seen from these figures that the irrecoverable losses in the permanent magnet properties are very considerably less in the HD magnet than in the M magnet. For example, after the final ageing period of 100 h, the permanent losses in the iH_c, $4\pi M$ and $(BH)_{\max}$ values in the HD magnet are, respectively, 4, 4 and 7 times less than those of the M magnet.

4. Discussion

We have previously established a correlation between the magnetic and mechanical hardness values in a 2:17-type alloy with the same composition as that examined in the present work [14]. Thus, there were sharp maxima in the curves of hardness and iH_c against ageing time at an ageing period of 38 h at 800° C. This has provided further evidence that the intrinsic coercivity of this type of alloy is predominantly controlled by a general pinning of the domain walls at a critical dispersion of a coherent phase (or phases). On the basis of this correlation between the magnetic and mechanical hardness values, the dependence of the iH_c values of the present 2:17-type alloy on the precise magnetic processing procedure has been investigated [13]. This study revealed that the intrinsic coercivity of the polymer-bonded magnets made from the present alloy is critically dependent on the nature of the mechanical deformation of the powder particles associated with the powder production procedure. Thus, the magnets made from the M powder showed significantly lower iH_c values than those prepared from the HD powder. This difference in iH_c behaviour can be attributed to a lower amount of mechanical deformation being associated with the hydrogen decrepitation process. This would result in a higher proportion of coherent precipitates in the HD powder compared with the M powder because the reduced deformation would result in a lower proportion of the coherent precipitates being converted into semi-coherent or incoherent forms. The proposal that a lower amount of deformation is associated with the production of the HD material is consistent with the intergranular decrepitation process evident from the SEM studies (see Figs. 2 and 3) and with the absence of a significant amount of the fine debris as observed in the milled material (Fig. 8). In addition, crystal defects associated with the heavily deformed particles might provide easy nucleation sites for reverse domain walls and this would also be consistent with lower iH_c values of the M magnets; this is however unlikely to have a dominant influence on the precipitation hardened magnetic alloys.

The sharp fall in iH_c values in both types of

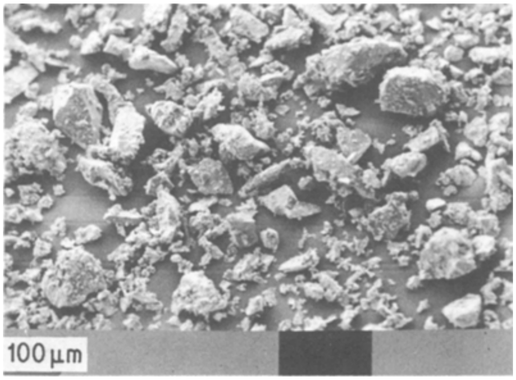

Figure 8 Scanning electron micrograph of a typical M material.

magnet, after the iH_c maximum, has been related to the conversion of a significant proportion of the coherent precipitates into semi-coherent or incoherent particles after the iH_c maximum, since after the maximum, the number of unstable coherent precipitates will be increasingly dominant with increasing ageing time. The less pronounced fall in the case of the HD magnets after the iH_c maximum is again consistent with the proposal that the hydrogen decrepitation process involves a lower amount of mechanical deformation. Thus a smaller proportion of the coherent precipitates would be converted to semi-coherent or incoherent precipitates compared with the M magnets.

The slightly lower values of $4\pi M$ in the HD magnets compared to their M counterparts, could be due to (i) the considerably higher average particle size of the HD particles (which is almost 2.5 times as large as the M powder) leading to difficulty in the alignment of the particles in the polymer matrix, (ii) the effect of heating at ~ 200° C and (iii) retained hydrogen in these particles. Unless the hydrogen is trapped at stable sites within the material, the latter seems unlikely to be the cause of the reduced remanence since, as already mentioned, the material was thoroughly degassed to a vacuum of 10^{-6} torr at around 200° C. The significantly lower $4\pi M$ values of an M magnet with an average particle size of $100\,\mu$m compared with a similar HD magnet (under identical heat treatment processes) is thought to be largely due to the intergranular nature of the HD process and hence the single crystal nature of the HD particles compared with the likely polycrystalline nature of the M powder particularly at this large particle size.

The excellent thermal stability of the present M and HD magnets compared to $SmCo_5$-type polymer-bonded specimens [15] can generally be attributed to (i) the greater intrinsic metallurgical stability of the 2:17-type phases and (ii) the different coercivity mechanism in these materials which involves the pinning of domain walls by fine coherent precipitates; these factors would make these magnets much less susceptible to the deleterious effects of oxidation. The considerably higher thermal stability of the HD magnet in comparison to its M counterpart, could be due to (i) the much greater average particle size of the HD powder, (ii) the absence of the grain boundaries in these particles, (iii) a possible prestabilization process which might have occurred during the outgassing at ~ 200° C, (iv) a lower degree of deformation, (v) the lower amount of fine debris and (iv) the enhanced bonding between clean HD particle surfaces and the polymer matrix.

Studies have also been carried out on the magnetic properties of the HD material obtained from another 2:17-type $Sm(Co_{0.674}Cu_{0.096}Fe_{0.216}Zr_{0.014})_{7.55}$ magnetic alloy. The particle morphology has been found to depend on the alloy composition and this can have a marked effect on the magnetic properties of the HD magnets. Thus, in the case of this alloy poorer magnetic properties have been obtained for HD magnets compared with those of the M magnets and these studies will be the subject of a further publication [16].

Acknowledgements

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