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Hot-pressed polycrystalline yttrium iron garnet

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A simple hot-pressing system is described which enables small volumes of polycrystalline yttrium iron garnet to be routinely produced. The products have high density, very low second phase content and a controlled grain size. Their magnetic properties compare very favourably with similar polycrystalline material produced by conventional sintering. Sample porosity may be varied in a controlled manner by simple changes in pressing conditions.

1. Introduction

The dependence of the spin-wave relaxation process on sample microstructure has been the subject of extensive investigation for a number of years (see, for example, the review of Patton [1]. Relaxation mechanisms within the spin-wave manifold have been reasonably well understood for some time but this is still not the case for relaxation data obtained outside the manifold, in high applied magnetic fields. Investigations in this laboratory [2, 3], using yttrium iron garnet (YIG) have endorsed the view that the physical microstructure plays a dominant part in the relaxation mechanisms, particularly pores and grain size distributions. Much of this work was carried out using conventionally fired materials in which the variation in grain size was large and almost uncontrollable. Furthermore, the results of microwave relaxation measurements obtained from such material were not in agreement with those of others, particularly Patton. The latter used samples produced by hot-pressing; a technique in which grain growth is limited due to the relatively low fabrication temperature. Extensive inquiries revealed that YIG of this type was neither commercially available in the UK, nor had the hot-pressing of YIG been successfully achieved. We, therefore, had to prepare YIG in our own laboratories, using a hot-pressing method, in order to extend our microwave relaxation studies to samples of controlled microstructure.

The production of hot-pressed YIG, though not extensive, is not uncommon; however details of the exact material preparation are rarely quoted. In general the production of a mixed phase system followed by annealing seems necessary for the production of a final single phase product. For example, Blair *et al.* [4] report a reactive hot-pressing method using coprecipitated oxalates of yttrium and iron. This produced samples of a mixture of garnet and orthoferrite and it was necessary to follow the pressing with an anneal in air or oxygen in order to convert the orthoferrite phase to the garnet one. Similarly both Shimeda *et al.* [5] and Koop [6] could only achieve the true garnet phase through an anneal subsequent to hot-pressing.

This paper describes the development of a simple hot-pressing system which enabled laboratory samples of high quality YIG to be produced without additional annealing. These samples had a microstructure, in terms of porosity and grain size, which could be controlled by the simple variation of pressing conditions. Details of the facility are given, together with typical results from the extensive appraisal to which all samples were subjected.

2. Material preparation

2.1. The hot-pressing unit

The hot-pressing system was of the basic uniaxial compaction type and is outlined in Fig. 1. It was constructed using a standard open-face workshop press and a resistance-heated furnace. The walls and lid of the furnace were constructed from fibre board and the furnace base was made from furnace bricks cut to appropiate sizes. Gaskets of fibre blanket minimized heat losses through any gaps at the wall/base and wall/lid contact surfaces.

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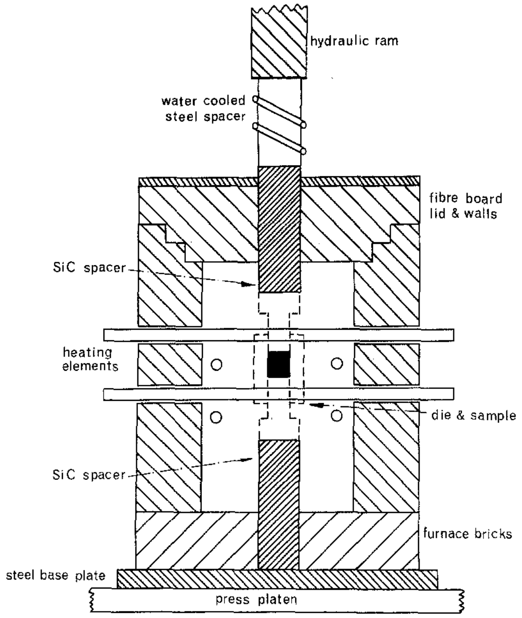

Figure 1 Schematic diagram of hot-pressing unit excluding press frame, gauge etc.

Heating was provided by a cross-hatched arrangement of crusilite elements positioned through holes in the furnace walls. Temperature control was by means of a standard three-term controller using a Pt/13% Pt–Rh thermocouple as a sensor. The actual sample temperature was measured by a similar thermocouple inserted into a pocket in the wall of the die. The necessary pressure (about 3000 psi) was readily provided by a manually operated hydraulic pump with pressures at the sample being determined from oil pressures in the ram as measured by a Bourdon pressure gauge.

2.2. YIG powder preparation

YIG itself was hot-pressed since it was anticipated that pressing the constituent unreacted oxides would not yield a fully reacted product. Stoichiometric amounts of 99.999% Y_2O_3 and 99.99% Fe_2O_3 were mixed in a ball mill for about 20h, using ceramic balls and alcohol to form a slurry. The milled mixture was dried with an infrared lamp, sieved down to 50 μm particle size and small batches presintered to form YIG. The procedure was to prefire for 2 h at 1200°C followed by remilling and to repeat this firing and milling cycle up to five times. By this means, YIG was obtained in which the percentage of second phase (principally yttrium orthoferrite) was less than 0.4%, the limit of our analysis measurements.

2.3. Graphite dies

Early pressings were made using die assemblies constructed of graphite, chosen for its ease of fabrication and availability. These pressings were, however, unsuccessful. X-ray diffraction and X-ray microanalysis indicated that the final products contained only a small amount of YIG, the remainder being mainly $YFeO_3$. There was also a marked graphite loss during each pressing and the die breakage rate was high. Wrapping the YIG powder in platinum foil and other similar preventative measures did not produce any significant increase in the YIG content of the final compacts.

Thomson (private communication) considered that the conversion of YIG to $YFeO_3$ most likely occurred by reduction, due to the formation of carbon monoxide within the die, according to the reaction;

$$Y_3Fe_5O_{12} + \tfrac{1}{3}CO \rightarrow 3YFeO_3 + \tfrac{2}{3}Fe_3O_4 + \tfrac{1}{3}CO_2 \quad (1)$$

The liberated carbon dioxide in turn diffused back to the die to generate more carbon monoxide by reaction with the graphite. A continuous supply of carbon monoxide was thus made available for the reduction process to continue with a consequent high percentage conversion to the orthoferrite phase. The high diffusion rate of CO through platinum at elevated temperatures explained the failure of platinum foil as a protective barrier.

Attempts to prevent the reduction taking place by either using alternative atmospheres within the furnace or by surrounding the compact with various inert powders were only partly successful. The best results were obtained with a compact surrounded by alumina which was then close wrapped in platinum foil. Even so, only 50% of the resulting hot-pressed pellet was YIG.

2.4. Alumina dies

It proved possible to make successful pressings using die sets made from alumina (99.5%). With these a routine was evolved which resulted in good quality YIG products from the powder prepared as indicated above. Undersize precompacts of the powder, pressed at 6 T in^{-2}, were loaded into the alumina die and surrounded by a layer of alumina powder. The latter aided the removal of the final compact and also acted as a lubricant during pressing. Without it, some bonding occurred between the compact and both die and plungers, so that sample removal became a severe problem.

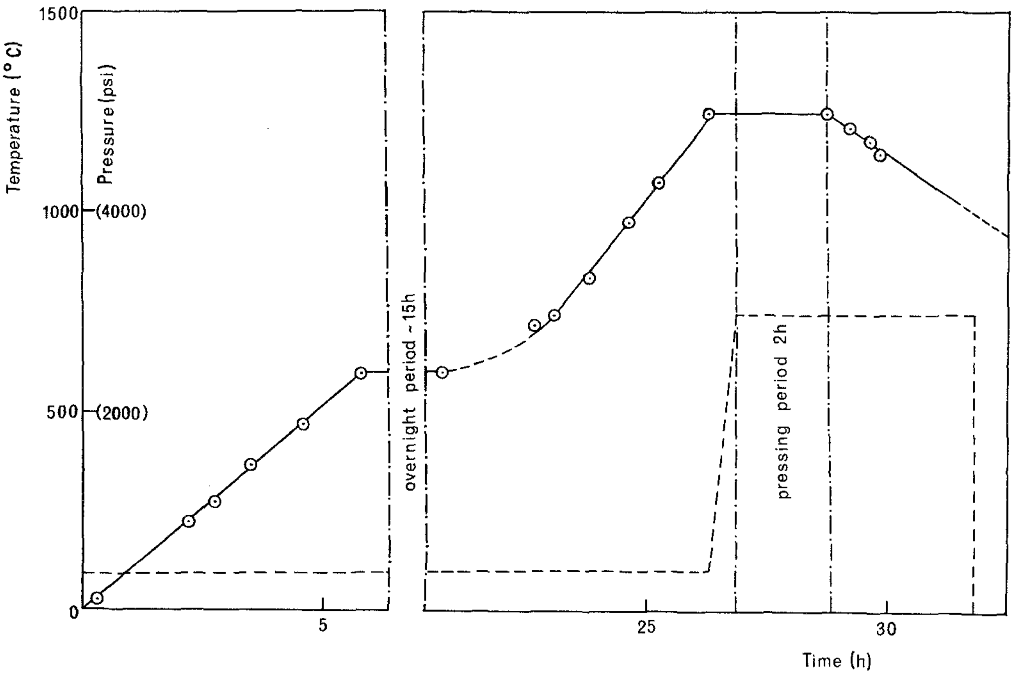

Figure 2 Typical hot-pressing cycle; temperature and pressure variations are shown by full and dashed lines respectively.

2.5. Pressing conditions

A typical pressing cycle is shown in Fig. 2. It was based on the results of a number of trial pressings to check the influence of variations in sintering time, pressure and temperature on the microstructure of the pressed product. Pressings were made which allowed for variations in only one of these parameters at a time. The results are shown in Figs. 3–6.

Fig. 3 shows a variation of the density of the final compact with changes in sintering time. Clearly, a final pressing time of the order of 2 h was sufficient to produce a high density, longer times giving no significant further densification.

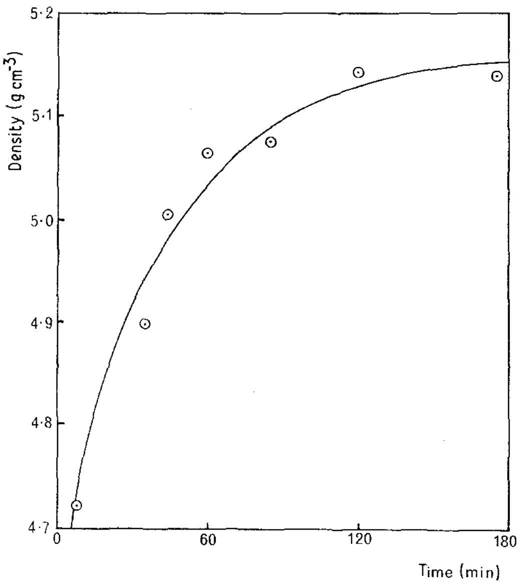

Figure 3 Effect of pressing time on final density at 1250°C.

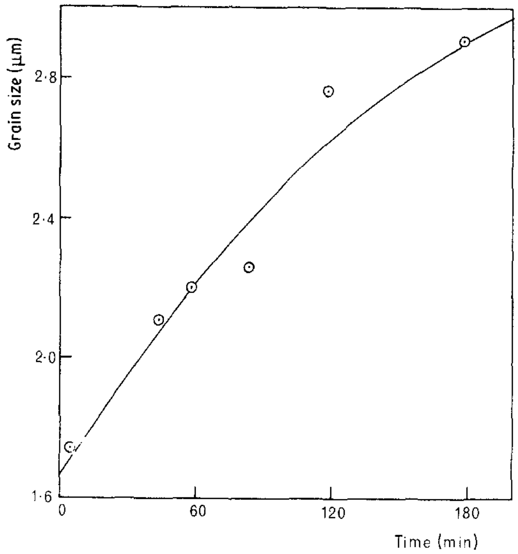

Figure 4 Influence of pressing time on mean grain size at 1250°C.

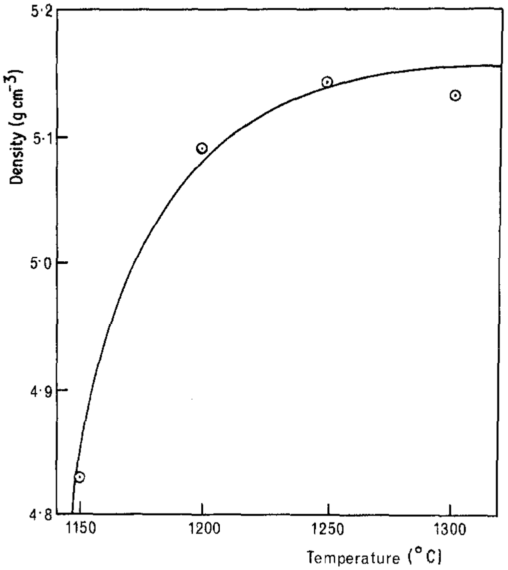

Figure 5 Effect of pressing temperature on final density.

In Fig. 4, the variation in grain size occurring over the same range of pressing time is shown. The significant feature of this figure is the lack of any marked grain growth over the range of sintering time considered. It was therefore possible to produce samples of differing density (and hence porosity) but much the same average grain size, by simple variations in sintering time.

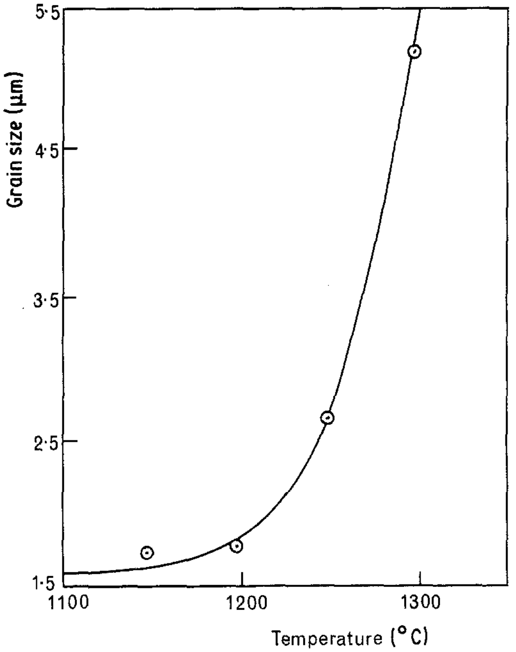

Figure 6 Increase of average grain size with pressing temperature.

Figs. 5 and 6 show the densification and grain growth which occurred as the final pressing temperature was varied. It can be seen that the density and grain size variations produced by temperature changes were much more rapid than those produced by changes in pressing time. Although higher temperatures produced high density samples, the average grain sizes of these were greater, and subject to more rapid variations, than those produced at lower temperatures. The chosen pressing temperature of 1250°C for the cycle of Fig. 2 was selected as a compromise in that it would result in samples which had a high density but still retained a reasonably small and controllable grain size.

An essential feature of the successful pressing was the minimization of thermal shock to the die system. Slow and controlled heating and cooling rates of about 100°C h^{-1} were used with an approximately linear rise and fall. This meant that the system remained in a pressurised and heated state (about 300 psi at 600°C) during an overnight period of the cycle. This occurred at sufficiently low a temperature not to influence the microstructure in any way. The effect on product quality of significant variations in heating and cooling rates was not investigated. Minor variations which did take place did not produce any noticeable changes in final microstructure.

3. Material characterization

Appraisal of the hot-pressed compacts was made using a wide selection of characterization techniques.

3.1. Density

Spheres were prepared from small cubes cut from each pressed pellet and their bulk density and corresponding porosity found from accurate mass and volume determinations.

3.2. Magnetic parameters

Room temperature saturation magnetization ($4\pi M_s$) values were obtained for these same spheres using a Foner vibrating magnetometer and the Curie temperature was determined using a simple oscillation technique.

3.3. X-ray diffraction

Checks on purity and estimations of second phase content were made from X-ray diffraction data obtained from powdered pieces of the pressed products. Quantitative estimations of the orthoferrite content were made, following the procedure of Delf *et al.* [7], by mixing known percentages of pure $YFeO_3$ and $Y_3Fe_5O_{12}$ and comparing the intensity ratios of the lines in the corresponding X-ray diffraction spectra.

Additional checks on quality and impurity content were obtained via Y:Fe ratios available from X-ray microprobe analysis measurements.

3.4. Grain size and distribution

Slices, cut from pressed pellets, were polished to a 0.25 μm finish and then thermally etched (about 1200°C for 30 min) to reveal their grain structure. Grain sizes and distributions were estimated from extensive visual scanning of photomicrographs obtained from transmission and scanning electron microscopes and also by optical microscopy.

3.5. Microwave measurements

Ferrimagnetic resonance (fmr) linewidths and both low and high field effective linewidths (W) were measured for all spheres. The measurements were made using *C*-band (5.7 GHz) and *X*-band (9.3 GHz) spectrometers as described by Duncan *et al.* [3].

4. Results

The analysis of many samples showed that the final hot-pressed compacts were high quality YIG. An indication of this quality may be seen from the properties of a representative sample. These are given below and compared with the results from standard polycrystalline YIG or data quoted in the literature.

Density = 5.11 ± 0.02 $g\,cm^{-3}$ (cf X-ray density = 5.17 $g\,cm^{-3}$)
Porosity = 1.16%
Lattice constant = 1.238(5) ± 0.001 nm (cf 1.2375 ± 0.0005 Gilleo *et al.* [8])
Curie temperature = 277 ± 3°C (cf 275–290°C Lax and Button [9])
$4\pi M_s$ = 1735 G (cf 1740 G single crystal value)
Average grain size = 2.0 μm
Half width of grain size distribution (Fig. 7) = 2.7 μm
Average pore size = 1.1 μm
Estimated second phase content < 0.4% (approximate noise level on X-ray diffractometer output)
fmr linewidth = 52 ± 2 Oe at 5.7 GHz
Low field effective linewidth = 10 Oe at 5.7 GHz
High field effective linewidth = 3 Oe at 5.7 GHz

A photomicrograph of a typical dense compact is shown in Fig. 8 clearly revealing the grain structure and low porosity.

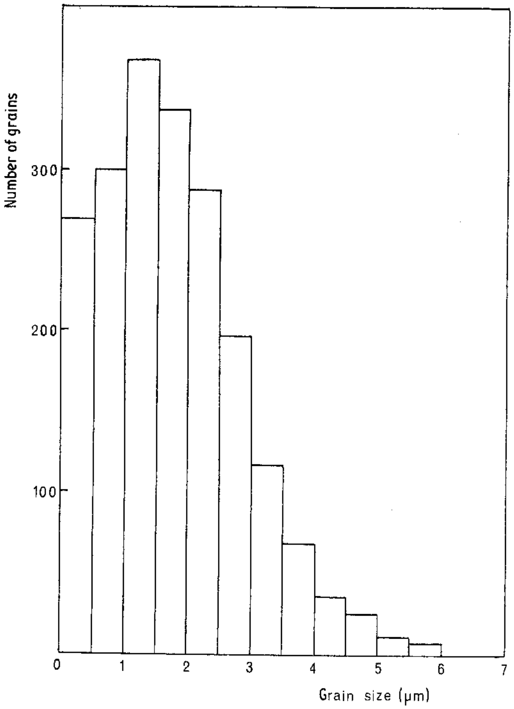

Figure 7 Typical grain distribution for a hot-pressed YIG sample.

5. Conclusions

A simple hot-pressing facility has been developed from which small volumes of good quality YIG may be produced using a routine pressing cycle. The products are of high density, and consequently low porosity, with a controlled grain size. Simple modifications of the pressing cycle enable sample porosity to be varied in a controlled manner.

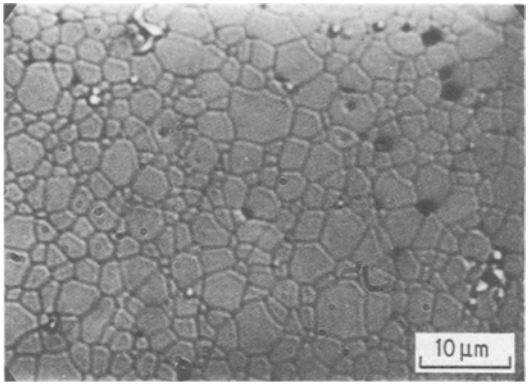

Figure 8 Photomicrograph of typical dense sample. (Thermally etched for 20 min at 1220° C).

Quality appraisal measurements indicate that the second phase content is very low and that the products have properties which compare very favourably with those of polycrystalline YIG produced by conventional sintering.

The system has enabled the production of specimens for a study of microwave loss mechanisms, the details of which will be published elsewhere.

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