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Solid-state crystal growth of rare earth metals and alloys adopting the h.c.p. crystal structure

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Abstract

The results of 34 solid-state recrystallization crystal growth attempts on rare earth metal elements and rare earth–rare earth alloys which adopt the hexagonal close-packed crystal structure are presented. Following a procedure which involved annealing ingots which had been strained by fast cooling from the melt, a heat treatment recipe of annealing for at least 40–60 h at a temperature equivalent to 85% of the absolute melting temperature or 95% of any h.c.p.–b.c.c. transformation temperature, whichever was the lower, was deduced to lead to the most extensive grain growth. The potential advantages of solid-state crystal growth over melt growth for these materials were found to be experimental simplicity, the preparation of crystals with improved crystal quality and lower volatilization losses for higher vapour pressure materials.

1. Introduction

Much of the current research into the physical properties of the rare earth metals and their alloys, particularly their complex magnetic properties, is dependent upon the availability of high-quality single-crystal samples. The growth of single crystals of those rare earth elements which adopt the hexagonal close-packed (h.c.p.) structure at room temperature can be achieved in a number of ways. Growth from the melt is possible even with those elements which show a high-temperature phase transformation to the body-centred cubic (b.c.c.) structure; indeed, seeded crystal growth (for example using float zoning) is possible in spite of such phase changes [1]. Melt-grown crystals, however, often require a subsequent anneal to reduce the level of crystal defects if good crystalline quality is required; furthermore, melt growth techniques are not useful for many alloys because of the possibility of segregation of components as a result of what is most easily labelled the zone refining effect. For the very highest purity, high-quality crystals, solid-state electrotransport (SSE) is probably the ultimate technique for many of the rare earth metals, possibly in conjunction with float zoning if a seeded crystal is required [2, 3]. The major drawbacks to SSE are the time required, typically hundreds if not thousands of hours, and the fact that only a relatively small proportion of the sample will be refined to the highest purities.

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Solid-state recrystallization crystal growths have been practised with the rare earths for many years. While difficulties have been experienced in preparing consistently high quality crystals of the double hexagonal close packed (d.h.c.p.) and samarium-type rhombohedral metals, many of the reported attempts involving h.c.p. metals and alloys have proved relatively successful, particularly after it became recognized that start metal purity was a critical factor. ("Solid-state recrystallization crystal growth" and "solid-state crystal growth" are used here as general terms intended to encompass a number of techniques including those variously called strain annealing, grain growth, growth from cast metal and recrystallization annealing.) As is well known, the driving force for the crystallographic changes which result in the solid-state growth of large grains is the reduction upon heat treatment of strain energy within the lattice, although where a phase transformation occurs this can have an additional influence. The strain energy may be introduced precisely and deliberately, in which case the technique qualifies for the definition of strain annealing [4], or it may be present as a by-product of the specimen consolidation or fabrication processes. During annealing after the introduction of strain, a number of processes are initiated, namely recovery, primary recrystallization, grain growth, and possibly secondary recrystallization or exaggerated grain growth. The distinctions between these phenomena have been described in detail by Cahn [5]. With the rare earth metals, however, the choice of straining and annealing conditions is likely to be influenced by more than just crystallographic factors, as sample vapour pressure and reactivity also have to be considered. With high vapour pressure rare earths, the use of the lowest annealing temperature which will give significant grain growth is clearly desirable so as to prevent excessive loss of material by volatilization, while contamination of the sample from any container or the environment must be avoided.

The potential advantages of solid-state recrystallization crystal growths as applied to the h.c.p. rare earth metals and alloys can be listed as:

(1) Experimental simplicity. It is relatively easy to perform crystal growths under the ultra-low contamination conditions necessary to retain purity when working with these notoriously reactive metals.

(2) As processing temperatures are lower than for melt growth, the technique is more suitable for many of the higher vapour pressure rare earth metals.

(3) The crystalline perfection of the crystals prepared is potentially better than for melt-grown crystals, where macroscopic evidence of polygonization effects and sub-grain formation can be extensive.

(4) The method can be applied to many solid solution alloys as well as elements.

(5) There are few limitations as to sample shape (*i.e.* a rod-shaped sample does not have to be prepared as in float zoning or SSE).

(6) If start metals are expensive or scarce, crystal growth can be attempted with smaller volumes of material than would be required for many melt growth techniques.

The main disadvantages are:

(1) Seeding for a particular crystal orientation is not trivial.

(2) There exists no general formula for the determination of heat treatment programmes. Partly as a result of this, results can be unpredictable.

This latter point is central to the applicability of solid-state crystal growth techniques to rare earth metals and requires further explanation. There are obviously many experimental variables which can affect the grain size during solid-state crystal growth; however, a study of the literature relevant to rare earth metals does not yield readily much in the way of a guide either to an experimental technique or a generalized thermal recipe for crystal growth. Beaudry and Gschneidner [6] and Abell [7] have reviewed the previously published work but it is worth giving a brief outline of a few selected papers to illustrate this point. Nigh [8] reported attempts to grow large grains of several h.c.p. rare earth elements by annealing as-arc-melted buttons in a resistance furnace. For gadolinium, the recipe was to anneal at 1050 °C for 12 h and then to increase the temperature by 50 °C increments every 12 h to a maximum of 1200–1225 °C, the best results coming from a part of the furnace which exhibited a temperature gradient of approximately 25 °C cm^{-1}. For yttrium, an anneal at 1100 °C for 8 h then an increase in the temperature by 50 °C increments every 8 h to a maximum of 1350 °C was said to give the best results. The logic behind these recipes was not explained. Peterson *et al.* [9] annealed extrinsically strained gadolinium samples at 1150 °C for 3 days and reported that samples strained by about 1% gave the largest grains, whereas samples strained by only 0.66% did not recrystallize. Whittaker [10], working on yttrium and holmium, melted ingots in a cold boat using radiofrequency heating, and then annealed the samples *in situ* at about 100–200 °C below their melting points. With holmium a 15 mm^3 grain grew in an ingot 20 mm × 20 mm × 30 mm after annealing at 1300 °C for 30 h; Abell [7] speculated that the presumed temperature gradient within the sample due to the presence of the cold boat probably contributed towards the success of this technique. Crystals have been prepared at the Ames Laboratory, Iowa State University, by solid-state methods [11] using a technique which involves sealing a polycrystalline button into a tantalum crucible and annealing for 24 h at approximately 150 °C below the melting point, or 10–20 °C below any polymorphic transformation if this is lower.

Two factors contribute towards the apparent diversity of procedures described above. Firstly, because solid-state crystal growth is not an exact science (indeed, the actual mechanism often is not fully understood) there is a natural tendency towards believing that each step of a successful recipe is necessary, even though some may be superfluous, simply because time is not available to perform the control experiments which would be needed to determine which factors really are vital. Secondly, luck can play a large part in such crystal growth. It is largely a matter of luck, for example, whether the orientations of recrystallized grains within a sample are such that one or two grains will grow to consume all others or whether, say, four or five grains will form a stable configuration which will inhibit further growth.

Thus it is only when a large number of crystal growth experiments are compared that trends can be detected.

The main aim of the present paper is not to make any claims that the procedures used are the best or most efficient possible, although certain conclusions are drawn from the work described, but to document the results of 34 solid-state crystal growth attempts in order that the database of available evidence for the h.c.p. rare earth metals and alloys can be extended. It is important to emphasize again that the work described here applies only to those rare earth metals and intra-rare earth alloys which adopt the h.c.p. structure; similar procedures applied to d.h.c.p., cubic or rhombohedral metals and alloys are unlikely to succeed.

2. Experimental procedures

Although the general philosophy of solid-state crystal growth of annealing a strained sample is well documented, there are a number of ways of both straining and annealing samples, as is evident from the brief review of the previous work on rare earths. The methods used in this work, together with other experimental procedures, are described below. The specific treatments given (*e.g.* annealing times and temperatures) are listed in the results section.

2.1. Straining method

Several straining methods were evaluated in the early stages of the work; these included bending samples, simple deformation in a vice and fast cooling from high temperature. The overriding consideration at all times was the need to maintain clean conditions to prevent contamination of the samples. The application of a precise, measured degree of mechanical strain, necessary for a technique to qualify as true strain annealing, was deliberately avoided because of the limitations placed upon sample shapes. The straining method settled upon, and used for all the work described here, was to introduce strain thermally by melting the sample and then cooling quickly to room temperature by turning off the heating power. This procedure was tried at first because of its speed and simplicity (it carries no risk of contaminating the samples as a result of excessive handling or machining operations) and was perpetuated as it appeared to be relatively successful so long as it was followed by the correct annealing process. The disadvantage was that, because a precisely known degree of strain was not administered, it was somewhat difficult to analyse the results scientifically.

2.2. Annealing methods

Most of the early experiments involved annealing in a cold boat while, more recently, most samples were heat treated by hanging them within an induction heating coil. Two samples were sealed in tantalum to evaluate this commonly used technique.

2.2.1. Cold boat using induction heating

This apparatus, which has been described fully elsewhere [13], contained the sample in a copper boat which was made of six rectangular-section copper tubes arranged in a semicircle to give a container 15 cm long and 1 cm wide. There was a gap of about 1 mm between the segments, which allowed some estimate of the temperature of the bottom of the ingot, a helpful feature for solid-state anneals. The boat was enclosed within a silica vacuum tube, around which a radiofrequency coil was placed. Extremely clean environmental conditions were attainable with this equipment, the base vacuum being about 1×10^{-10} Torr, although several of the materials studied did not have sufficiently low vapour pressures to permit prolonged annealing in vacuum.

An advantage to annealing samples in the cold boat was that, normally, the sample could be prepared (*i.e.* melted into a suitable ingot as described in section 2.5.) and annealed *in situ*, so saving time and reducing contamination risks. The principal disadvantage was that long-term temperature control was relatively poor, as the sample temperature was critically dependent upon the degree of contact made with the cold boat (levitation is at best minimal during solid-state annealing). The contact, and hence the temperature, was found to change with time as a result of both vibration and volatilization of material from the sample (if of sufficiently high vapour pressure), which tended to form a bridge between the sample and the boat. Temperature measurement was also difficult; we used an optical pyrometer which viewed the sample through the silica vacuum tube. Readings became increasingly unreliable if the sample vapour pressure was high enough for material to sublime onto the vacuum tube. Sometimes, as-annealed ingots were found to have a smaller grain size at their bottoms than their tops, presumably indicating either that the bottoms were cooler owing to the proximity of the boat, or that the points of contact with the boat acted as nucleation sites during recrystallization.

2.2.2. Sample hanging vertically, induction heating

As an alternative to cold boat annealing, a technique was developed whereby a sample was hung within a vertical silica vacuum tube which was itself within a radiofrequency coil. Initially, samples were held in tungsten wire cradles, although this method was soon superseded by drilling a small hole at the end of the sample and hanging it on a tungsten wire hook. Although slight bonding to the tungsten hook sometimes occurred, the amount of contamination in the bulk of the sample was believed to be negligible. Vacua of the order of 1×10^{-10} Torr were attainable within the system.

This arrangement allowed very good temperature control with long-term stability. Although temperature measurement depended upon the use of an optical pyrometer placed outside the vacuum tube, problems caused by clouding of the tube were not so critical as with the cold boat because the good temperature stability meant that repeated temperature measurements, with corresponding adjustments to the power to maintain a constant temperature, were unnecessary. Further, the sample could be viewed *via* a mirror through the bottom of the tube (some 25 cm below the sample) which normally remained relatively unclouded.

2.2.3. *Sample sealed in tantalum, resistance furnace*

The sealing of samples in small tantalum capsules is a commonly used technique for annealing the higher vapour pressure metals, as it allows the use of higher temperatures (or longer times) than would otherwise be attainable. In addition, the oxidation risk resulting from annealing in a slightly contaminated environment is reduced, although it should be noted that hydrogen readily diffuses through tantalum at elevated temperatures. The disadvantages of the method are the cost and complication involved in sealing the samples in tantalum and the possibility of the sample reacting with the capsule.

In the present work, only two samples were annealed in this manner. They were placed in small tantalum buckets and sealed in by arcwelding on a tantalum lid. Annealing was performed by placing the capsules in an evacuated alumina furnace tube within a resistance furnace, a procedure which gave very good temperature accuracy and control.

2.3. *Temperature measurement*

For the two annealing techniques which used induction heating, indirect means of temperature measurement were needed, with either a disappearing filament optical pyrometer or a remote infrared thermometer being used. Both of these instruments rely for their accuracy upon correct emissivity calibration. As the apparent emissivity of a material can vary with sample purity and shape, and is also influenced by the silica tube in the viewing path, it was felt that it would be unwise to rely too heavily upon previously published emissivity values (where they exist), so the instruments were recalibrated, where possible, before each run with a "new" material. This was performed by melting some of the relevant material in a cold boat, cooling until it was just molten, and adjusting the emissivity control of the measuring instrument until the correct melting temperature was obtained. This procedure was not possible with dysprosium, holmium and erbium, however, because volatilization of the sample onto the cold boat vacuum tube was too rapid to allow temperature measurement; for these elements, emissivity values similar to those measured for gadolinium were assumed. The emissivity value measured or assumed for each material is given in the results section. As a result of the uncertainties inherent in this type of temperature measurement, it would be unrealistic to claim an accuracy better than ± 20 °C in the quoted temperatures. This error would be further increased if sample volatilization led to clouding of the silica vacuum tubes.

2.4. *Start metals*

Start metals were obtained either from the Materials Preparation Center of Iowa State University (Ames, IA, U.S.A.) or from Rare Earth Products Ltd. (U.K.) It is impractical to give analyses for each metal investigated, but typical analyses of the Ames metals have been published by Beaudry and Gschneidner [6]. Almost invariably the major contaminants were the interstitial impurities oxygen, hydrogen, carbon and nitrogen; typically the sum of these four contaminants would be in the range 500–2000 ppm at., the variation being largely dependent upon the hydrogen content.

Comprehensive analyses for the Rare Earth Products (REP) metals ("High Purity" grade material was always bought) were not supplied, but the evidence of previous purification studies would indicate that the impurity levels were somewhat higher than the Ames metals [2, 12].

2.5. *Initial melting*

Samples were melted into a suitable shape (and strained by quick cooling) either by arc melting on a water-cooled copper hearth or by induction melting in the copper cold boat described earlier. The arc furnace, which used a non-consumable tungsten electrode, was operated under 0.5 bar argon, which was purified by melting a titanium getter button prior to melting the sample. Although the cold boat system was UHV rated, most melting was performed under 0.5 bar purified argon to limit volatilization losses. Alloy samples were remelted several times to ensure homogeneity.

2.6. *Sample sizes and shapes*

The size of grains produced by solid-state methods depends not only upon the straining and annealing programmes but also upon the sample size and shape. In general, the larger the sample, the better is the chance of preparing a large crystal, but sample sizes were often limited by material cost or availability. In the results section, the sample weight and volume are noted for each growth attempt. The sample shape also plays a part in determining the attainable grain size. The best samples would be approaching spherical in shape, but these are difficult to hold when using the vertical hanging method of annealing, so a compromise sample shape approximating to that of an elongated pear was eventually used when employing this method, the sample being hung from the thinner top. It is worth noting, although the effect was not systematically investigated in this work, that the sample shape also influences cooling rates (and thus the amount of strain introduced into the sample) when employing thermal straining methods.

2.7. *Inert gas operation*

Many of the anneals in the cold boat and using the hanging sample technique were performed under argon, rather than under vacuum, the choice between the two being made after consideration of the vapour pressure characteristics of the metal(s) concerned. Clearly the volatilization suppressing effects of the inert gas were required for the higher vapour pressure materials unless annealing times were very short.

Even when an argon environment was used it was still considered necessary to first pump the systems to UHV levels to ensure leak-tightness and to minimize any degassing from the system walls during the anneal.

Argon was admitted to the pumped and baked system (a low-temperature bake was usually applied during pumpdown) via a British Oxygen Company inert gas purifier specified to reduce the total of all gaseous impurities to below 1 ppm vol. Argon pressures of between 0.5 and 0.7 bar were used in most cases.

3. Results and discussion

The results of the crystal growth attempts are presented in Table 1 and are listed in an order intended to reflect the relative successes of the individual experiments. Hence the runs which showed the most pronounced grain growth, as judged by the percentage of the sample occupied by the largest grain, are at the top of the list, with the least successful runs at the bottom. In a few cases a two-temperature anneal was given; the reason for the reduction in temperature from the higher initial value was normally to reduce the possibility of volatilization losses. The approximate vapour pressure of the element concerned at the annealing temperature (or the highest vapour pressure component, assuming elemental values, in the case of alloys) is given in column 12, these data being taken from standard vapour pressure/ temperature tables. In column 13 an estimate of the volume of the largest grain formed in the sample is given; for many samples, especially those with large grains, it was relatively easy to measure this volume, although for some samples only a rough estimate could be made. Finally, in an attempt to equate the results from sample of different sizes, column 14 gives the approximate volume of the largest grain as a percentage of the volume of the whole sample, this being the value used to determine the order of this table.

Having listed the crystal growth results it is natural to ask whether it is possible to deduce from them an ideal heat treatment recipe for the growth of large crystals of h.c.p. rare earth metals and alloys. It may be possible to arrive at such a formula by seeing whether there are any similarities in procedure which are common to the more successful runs, but it must first be decided whether it is intrinsically much easier to induce the growth of large grains with some of the materials than with others. If this is the case (perhaps because one material has a more favourable activation energy for recovery or recrystallization) it would be unfair to compare the success of a grain growth recipe used for such an "easy" material with one used for a "more difficult" material. It is proposed that the results in Table 1 give no indication that grain growth was obviously easier with some of the material types than with others. Inspection of this table does not reveal any obvious indication of any species-sensitive order; for example, it cannot be said that growth was clearly more successful, and therefore easier, with gadolinium alloys than with yttrium alloys, or that elements always gave bigger grains than alloys. Neither is there any clear evidence to suggest that the presence of a transformation to the b.c.c. structure at high temperatures seriously influenced growth. (Although there are probably a disproportionate number of Gd–Tb alloys in the lower regions of the list, this is almost certainly because these were the first materials to be investigated, when techniques were still being developed, rather than because of any inherent difficulties.) If it can be accepted from this evidence that the "success ratings" of these solid-state crystal growth attempts on rare earth metals and alloys adopting the h.c.p. structure were primarily a function of the various straining and annealing treatments, rather than the specific element(s) present, it is then possible to compare the relative merits of the differing grain growth procedures despite the fact that they were applied to different, albeit closely related, materials.

In any comparative analysis of the results, the relative contributions of the various experimental variables have to be separated. The main variables can be listed as the melting/straining method, the annealing technique, the annealing temperature and the annealing time. One assumption made in the following comparisons is that the annealing temperatures for the different materials can be normalized by considering them as a proportion of the absolute melting point of the relevant sample. Unfortunately, it is not possible to consider rigorously the effects of the experimental variables wholly independently, as they tend to be interrelated, but one factor which does become apparent from inspection of the table is that there is no one technique/temperature/time combination which alone gives good results. While the probability of growing large grains does appear to be greater when using some recipes, other recipes can also give good results, albeit less consistently. This contrasts with the conventional wisdom concerning true strain/anneal crystal growth, whereby an exact and critical amount of strain is presumed to be required, followed by annealing at a precise temperature, if grain growth is to be significant.

A crude analysis of the data, aimed at finding the most influential experimental variables, involves taking the ten most successful and the ten least successful grain growth attempts and averaging the annealing temperatures, times, grain sizes etc. to see if any trends were evident. Table 2 presents this analysis, the top part of the table referring to the ten best and ten worst growths as judged by the percentage of the sample occupied by the largest grain, while the bottom section of the table shows the best and worst ten attempts as judged by the size of the largest grain in a particular sample. In both cases, the overall data for all 34 growths are given alongside. Probably the most striking feature shown is the clear difference in average annealing times between the best and worst runs, the best runs showing an average annealing time more than twice that of the worst runs. To further illustrate this point, the run length data for the best and worst ten runs in Table 1 are plotted on a bar graph in Fig. 1. While it cannot be stated categorically that a short annealing time (*e.g.* 24 h) will inevitably result in smaller grains, the evidence does seem to point to the conclusion that the probability of obtaining a large grain increases if the annealing time is at

TABLE 1

Results of crystal growth in order of percentage of sample occupied by the largest grain

	Initial melting technique[a]	Sample volume (cm^3)	Start metal source[b]	Annealing technique[c]	Environment[d]	Assumed emissivity
Er	Arc	2.2	A	VRF	Ar	0.37
Gd–31%Sc	CBM	2.1	A	VRF	Ar	0.37
Gd–36%Sc	Arc	1.7	A	VRF	Ar	0.37
Gd–50%Tb	CBM	1.8	A	CBA	Vac	0.37
Gd–29.5%Sc	CBM	1.4	A	VRF	Ar	0.37
Y	Arc	8.5	A	VRF	Ar	0.38
Er	CBM	1.5	A	VRF	Ar	0.37
Y–1%Ce	Arc	2.7	R	CBA	Vac	0.38
Y–5%Ce	Arc	2.7	R	CBA	Vac	0.38
Ho	Arc	2.3	A	VRF	Ar	0.37
Gd–25%Sc	CBM	2.0	A	VRF	Ar	0.37
Gd–30%Tb	CBM	2.7	A	CBA	Vac	0.37
Gd–28%Sc	CBM	2.4	A	VRF	Ar	0.37
Gd–23.7%Lu	CBM	1.9	R	VRF	Ar	0.37
Er	CBM	1.5	A	VRF	Ar	0.37
Sc–23%Er	Arc	1.6	A/R	ST		
Y–22%Tb	Arc	4.2	A/R	CBA	Ar	0.37
Gd–32%Sc	CBM	2.5	A	CBA	Ar	0.37
Sc	Arc	1.7	R	VRF	Ar	0.38
Y	Arc	2.7	R	CBA	Vac	0.38
Ho	Arc	2.8	R	CBA	Ar	0.37
Tb–25%Gd	CBM	2.0	A	CBA	Vac	0.34
Y–15%Er	Arc	3.9	R	VRF	Ar	0.38
Gd–24%Lu	CBM	3.1	R	VRF	Vac	0.37
Gd–50%Tb	CBM	2.5	A	CBA	Vac	0.37
Gd–10%Tb	CBM	2.5	A	CBA	Vac	0.37
Sc–25%Er	Arc	1.4	A/R	ST		
Sc–5%Tb	Arc	0.7	R	CBA	Ar	0.37
Y–30%Gd	Arc	6.4	R	CBA	Ar	0.37
Gd	CBM	2.5	A	CBA	Vac	0.37
Dy	Arc	3.5	R	CBA	Ar	0.37
Gd–32%Sc	Arc	2.5	A	VRF	Ar	0.37
Gd–10%Tb	CBM	1.9	A	CBA	Vac	0.37
Tb–10%Gd	CBM	2.4	R/A	CBA	Vac	0.34

[a] Arc, in arc furnace; CBM, in cold boat.

[b] A, Ames Laboratory; R, REP "High Purity".

[c] CBA, in cold boat using r.f. heating; VRF, hung vertically, r.f. heating; ST, sealed in tantalum.

[d] Vac, vacuum; Ar, argon.

All compositions are atomic percent.

Annealing temperature (°C)	Annealing temperature as percentage of melting point	Annealing temperature as percentage of h.c.p.–b.c.c. transformation temperature	Annealing time (h)	Vapour pressure (Torr)	Largest grain volume (cm^3)	Largest grain as percentage of sample volume
1255	85	–	3}	1×10^{-2}		
1170	80	–	42}	4×10^{-3}	1.5	70
1085	87	95	61	4×10^{-5}	1.3	60
1110	89	97	96	8×10^{-5}	1.0	60
1170	89	94	24	4×10^{-5}	1.0	60
1060	86	93	73	3×10^{-5}	0.8	60
1190	81	84	240	8×10^{-6}	4.5	50
1200	82	–	72	5×10^{-3}	0.8	50
1165	80	83	240	4×10^{-6}	1.1	40
1165	83	84	240	4×10^{-6}	1.0	40
1140	81	–	24}	8×10^{-3}		
1100	79	–	72}	4×10^{-3}	1.0	40
1090	88	94	75	5×10^{-5}	0.8	40
1225	94	98	24	1×10^{-4}	0.9	35
1080	87	94	76	4×10^{-5}	0.8	35
1140	84	88	72	8×10^{-6}	0.6	35
1250	85	–	24	1×10^{-2}	0.5	35
1180	81	87	264	4×10^{-3}	0.5	35
1070	77	80	120	4×10^{-6}	1.3	30
1160	92	99	48	3×10^{-4}	0.8	30
1220	82	93	94	8×10^{-4}	0.5	30
1165	80	82	240	4×10^{-6}	0.7	25
1280	89	–	26	7×10^{-2}	0.7	25
1250	88	98	20	1×10^{-4}	0.5	25
1390	93	94	5}	9×10^{-2}		
1090	76	77	20}	8×10^{-4}	0.8	20
1050	79	82	3}	9×10^{-7}		
900	70	73	23}	1×10^{-8}	0.6	20
1180	90	95	24	5×10^{-5}	0.5	20
1235	95	99	25	1×10^{-4}	0.5	20
1180	81	87	264	4×10^{-3}	0.3	20
1280	86	99	72	3×10^{-3}	0.15	20
1130	81	90	4}	7×10^{-6}		
1060	77	85	120}	1×10^{-6}	1.0	15
1220	94	99	26	4×10^{-5}	0.4	15
1230	89	96	24	8×10^{-2}	0.3	10
1145	91	99	72	1×10^{-4}	0.25	10
1170	91	95	24	4×10^{-5}	0.2	10
1230	92	96	25	1×10^{-4}	0.03	1

TABLE 2

Summary of best 10 and worst 10 runs

As judged by percentage of sample occupied by largest grain

	Best 10	Worst 10	Overall (34)
Start material	8A, 2R	5A, 3R, 2A/R	56%A, 32%R, 12%A/R
Melting technique	6Arc, 4CBM	5Arc, 5CBM	50%Arc, 50%CBM
Average sample volume (cm^3)	2.7	2.6	2.6
Annealing technique	7VRF, 3CBA	1VRF, 1ST, 8CBA	44%VRF, 50%CBA 6%ST
Average annealing temperature	84%MP 90%TT	89%MP 96%TT	86%MP 92%TT
Average annealing time (h)	119	58	88
Average percentage occupied by largest grain	53	14	32

As judged by size of the largest grain

	Best 10	Worst 10	Overall (34)
Start material	6A, 3R, 1A/R	6A, 2R, 2A/R	56%A, 32%R, 12%A/R
Melting technique	8Arc, 2CBM	4Arc, 6CBM	50%Arc, 50%CBM
Average sample volume (cm^3)	3.5	2.2	2.6
Annealing technique	5VRF, 5CBA	1VRF, 1ST, 8CBA	44%VRF, 50%CBA 6%ST
Average annealing temperature	83%MP 88%TT	90%MP 96%TT	86%MP 92%TT
Average annealing time (h)	129	58	88
Average volume of largest grain (cm^3)	1.5	0.3	0.8

Key to abbreviations as in Table 1.

least 40–60 h, although there does not seem to be much additional advantage in adopting significantly longer annealing time (e.g. greater than 200 h).

In addition to the marked differences in annealing times between the best and worst runs, it would also appear from Table 2 that lower annealing temperatures, say 83–84% of the melting point, would be preferable to higher temperatures in the range 89–90%. Bar graphs (Fig. 2) of the annealing temperatures, both as a proportion of the melting points and of h.c.p. to b.c.c. transition temperatures (where applicable) for the best and worst runs partly reinforce this deduction although the evidence is not entirely conclusive. One complication is that many of the worst runs had short annealing times as well as higher annealing temperatures, making it difficult to decide whether the time or temperature factor was the more influential. (For some of the materials the choices of temperature and time were linked by vapour pressure considerations — if a material has a high vapour pressure, high annealing temperatures and long annealing times are clearly incompatible if volatilization losses are to be controlled.) The poor results obtained from some runs where the annealing temperature was close to the transformation temperature may well have resulted from errors in experimental procedure which allowed the

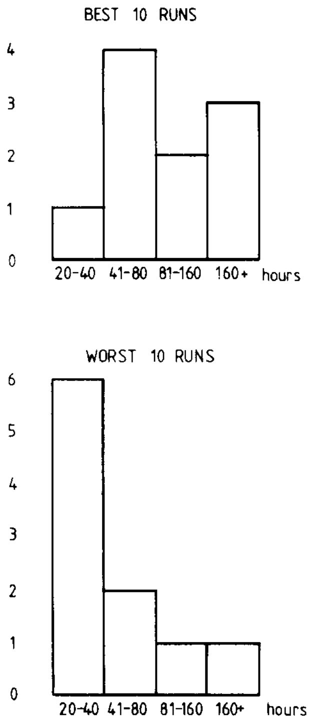

Fig. 1. Bar graphs showing the annealing times of the best ten and worst ten runs in Table 1. The results are split into four timebands, with the height of each column indicating the number of runs which fell into a particular timeband. The high incidence of worst runs in the 20–40 h timeband is clearly shown.

sample (or part of the sample) to stray into the b.c.c. phase field. Such errors can come from several sources, the most obvious of which are inaccurate phase diagrams or a wrongly assumed emissivity value for the material. Overall there would not seem to be any advantage to be gained from adopting annealing temperatures which are higher than about 85% of the melting point or 95% of the transformation temperature, whichever is the lower.

From Table 2 it is evident that eight of the ten largest crystals resulted from samples which had been initially arc melted rather than melted in the cold boat. It could be assumed that this indicates that arc melting was a better method for introducing the correct amount of strain for the subsequent annealing stage, but this assumption may be misleading, as most of the larger samples were arc melted and, clearly, the larger the sample the greater the chance of preparing a large grain. Overall, however, arc melting may well be preferable as an initial melting method if only because weight losses tend to be lower when working with high vapour pressure metals.

Of the annealing techniques employed, hanging the sample vertically in the radiofrequency coil was found to be by far the easiest, most reliable and successful, and was preferred to the cold boat method even though a combined melt/anneal in the cold boat took less time. The speculation by

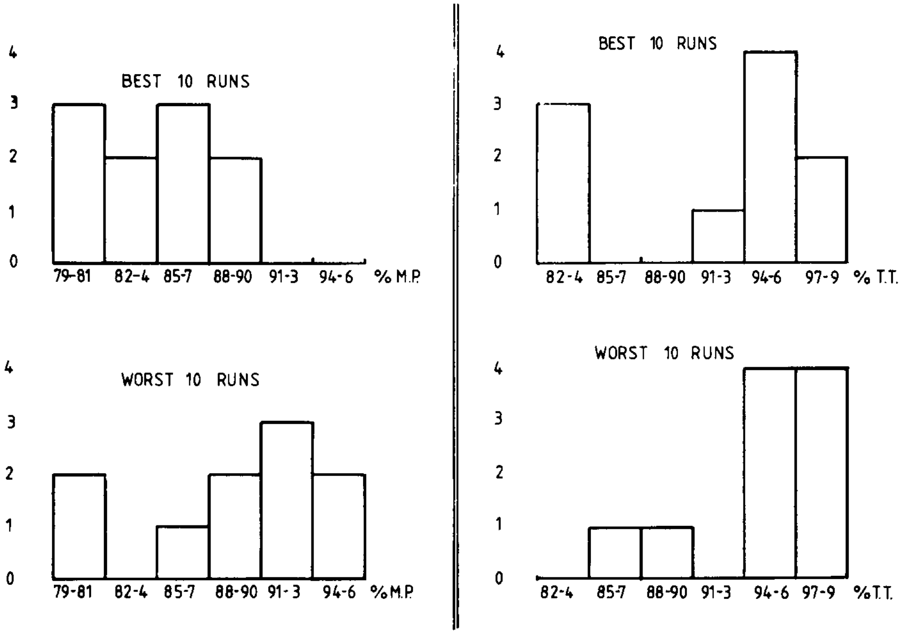

Fig. 2. Bar graphs showing the annealing temperatures used for the best and worst runs in Table 1. On the left, the annealing temperature is taken as a percentage of the absolute melting point for the best ten and worst ten runs, while on the right the annealing temperature is taken as a percentage of the h.c.p.–b.c.c. transition temperature for the best ten and worst ten runs from materials which showed such a transformation. In both cases the results are split into percentage (*i.e.* temperature) bands, with the height of column indicating the number of runs which fell into a particular band.

Abell [7] that the presumed temperature gradient induced in a sample when annealing in a cold boat could contribute towards any success from this technique would appear invalid, as the hanging method was no less successful, and here no such temperature gradient exists. Despite the preference expressed here for simple annealing techniques, sealing samples in tantalum would clearly be necessary to reduce weight losses with some metals (*e.g.* thulium) or, more particularly, alloys with a high vapour pressure component. For the majority of h.c.p. rare earths, however, the complication of sealing samples in tantalum before annealing would appear to be unnecessary. On the subject of volatilization losses, it is difficult to state at which level these become excessive. For an element this occurs if the volatilized material interferes with the annealing process, or if the metal is too expensive or too scarce to allow losses. For alloys, compositional accuracy is normally the limiting factor. Table 3 lists the losses from a selection of the annealing runs (not including losses during melting) to give an indication of the scale of the problem.

In a paper of this type it is obviously not possible to give extensive details of the characterization of each crystal prepared, but it is necessary to make a few general observations. The qualities of the larger grains from

TABLE 3

Weight losses during annealing as a result of volatilization (selected runs only)

	Annealing temperature (°C)	Vapour pressure (Torr)	Technique	Environment	Weight loss (% h^{-1})
Er	1200	5×10^{-3}	VRF	0.7 bar Ar	0.03
Gd–24Lu	1050	9×10^{-7} (Gd) 1×10^{-7} (Lu)	VRF	Vacuum	0.09
Gd–23.7Lu	1140	8×10^{-6} (Gd) 1×10^{-6} (Lu)	VRF	0.7 bar Ar	0.0003
Gd–32Sc	1160	3×10^{-4} (Sc) 1×10^{-5} (Gd)	CBA	0.4 bar Ar	0.008
Gd–31Sc	1085	4×10^{-5} (Sc) 1×10^{-6} (Gd)	VRF	0.5 bar Ar	Not detectable

Key to abbreviations as in Table 1.

most samples (*i.e.* those used for specimens in further experiments) were assessed using back reflection X-ray Laue techniques, note being taken of both the shape of the "spots" on individual films, and of any "wander" between successive films as the sample was moved in a plane parallel to the film. In the vast majority of cases, the Laue photographs showed sharp spots without any of the spot splitting characteristic of the polygonization defects often found in float-zoned h.c.p. rare earth metals (especially those with a polymorphic transformation where spots can be split over several degrees). In addition, it was uncommon to detect any misalignment of the orientation along the length of grains indicating a mosaic spread within the grain, although the resolution of the X-ray technique in this respect could not be claimed to be greater than one degree.

Although the procedures used in this work were relatively simple, the task of determining exactly what was happening on a microstructural level is much more complicated. To understand and evaluate the processes involved fully it would first be necessary to correlate the final grain size distribution within a sample with the degree of strain in the as-cast ingot and the subsequent annealing temperature. In an attempt to gain some insight into the structure of as-cast ingots, samples of two elements, yttrium and erbium, were examined in some detail, these elements being chosen as yttrium exhibits a phase change to the b.c.c. structure at high temperature, while erbium does not. Samples of yttrium were prepared by both arc and induction melting to give a comparison between the two techniques, the erbium sample being arc melted alone; in each case the heating power was turned off while the sample was still molten to give a rapid cool. The microstructures of all three samples were remarkably similar, revealing mixed grain sizes, often columnar in shape, from less than 1 mm^3 up to a maximum of about 30 mm^3 in volume with significant numbers of twins. No obvious metallographic differences could be detected between the arc melted yttrium and erbium samples despite the presence of the h.c.p.–b.c.c. transformation in yttrium but not erbium; however, the cold boat melted yttrium did appear to contain more twins than the arc melted metals, especially in grains which had been at the surface adjacent to the boat. Back-reflection Laue X-ray pictures from the surfaces of as-melted samples showed ill-defined, split spots as would be expected from the microstructures. The apparent similarities between these microstructures would appear to reinforce the point that the annealing temperatures and times, rather than the precise straining procedure, were the more critical experimental variables in determining the eventual grain size.

Further X-ray examination of the erbium ingot revealed differences in lattice spacings as a function of position (*i.e.* top, bottom, sides and internal faces exposed by sectioning) of 0.12% in the a spacing, 0.08% in the c spacing and 0.14% in the c:a ratio. These results, together with the metallography, strongly suggest that the samples were not uniformly strained during the quick cooling processes, a conclusion which fits in with the visual observation of the metals cooling on cold hearths/boats whereby different parts of the ingots appeared to cool at different rates, although no realistic estimate could be made of the actual cooling rates involved. Thus the residual strain map of an as-melted sample is likely to be a complex function of sample position, shape, size, melting method and melt temperature and would be expected to vary from sample to sample.

Prior to any attempts to correlate strain levels with grain size, it may first be necessary to determine what effect a strain gradient has upon the recrystallization and grain growth processes in these materials. It could be argued that the recrystallization processes which lead to the nucleation of new grains are initiated in a region, or regions, of a sample which happen to contain the ideal level of strain leading to the growth of grains which then envelop other, less ideally strained, areas (the grain size distributions of as-annealed samples were representative of normal grain growth rather than secondary recrystallization). This would have some similarities to the common strain/anneal practice whereby uniformly strained samples are annealed in a temperature gradient. Alternatively, it could be that the strain gradient itself plays a more fundamental part in the migration of grain boundaries, or that any texture within the matrix is the key component. One way of resolving these questions may be to investigate one material using samples of different sizes for, given similar shapes, smaller samples would be expected to cool more quickly than larger samples with higher overall strain levels, but possibly with less of a strain variation within a sample. The role of twins in the as-cast ingots is also deserving of study, as twins are generally assumed to be good nucleation sites for grains in h.c.p. metals and hence to detract from a large eventual grain size, if twinning is pronounced, by initiating the simultaneous nucleation of a large number of grains. These details, however, fall outside the scope of this paper, the first priority of which is to report an empirical recipe for the solid-state growth of large grains in h.c.p. rare earth metals.

4. Conclusions

(1) Solid-state recrystallization-type crystal growths have been attempted with 34 rare earth elements and rare earth–rare earth alloys adopting the h.c.p. structure. In all cases initial strain was applied by cooling quickly from the melt during initial sample preparation, although a variety of annealing techniques and treatments were tried.

(2) Within this group of closely related materials, the final grain sizes achieved appeared to be primarily dependent upon the annealing conditions employed rather than the exact species of element(s) present.

(3) The suggested annealing condition for maximizing grain growth is annealing for at least 40–60 h at a temperature of 85% of the absolute melting temperature or 95% of any h.c.p.–b.c.c. transformation temperature, whichever is the lower.

(4) The most successful experimental techniques were found to be arc melting for the initial sample preparation and hanging the sample vertically within a radiofrequency coil for annealing, although for the highest vapour pressure h.c.p. rare earths, sealing samples in tantalum containers would be necessary.

Acknowledgments

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