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Improvement in the cast structure of Sm_2Fe_{17} alloys by niobium additions

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Abstract

A technique for producing Sm_2Fe_{17} from cast ingots without the presence of free iron has been developed which involves the addition of between 4 and 5% Nb to the melt. The free iron is thereby replaced by paramagnetic $NbFe_2$. A nitriding procedure for this material in N_2 gas to produce $Sm_2Fe_{17}N_{3-\delta}$ with $\delta \approx 0.3$ is described.

1. Introduction

A novel interstitial magnetic compound, $Sm_2Fe_{17}N_{3-\delta}$, was discovered by Coey and Sun in 1990 [1]. The material possesses a *c*-axis anisotropy field which has recently been estimated to be in excess of 20 T [2] and has a Curie temperature in excess of 450 °C. These properties make the material an excellent candidate for permanent-magnet applications.

Unfortunately Sm_2Fe_{17} forms through a peritectic reaction between solid iron and a samarium-rich liquid. This leads to considerable amounts of free iron when cooling from the melt [3] which, unless removed by a subsequent homogenization treatment, reduces the coercivity of the subsequent nitrides. Some groups have had success in achieving good coercive properties in isotropic nanocrystalline material produced by melt spinning [4] or mechanical alloying [5], but these procedures lead to a low saturation magnetization and energy product.

Methods of creating a single-phase material include either annealing a samarium-rich alloy or annealing under a samarium atmosphere, for up to 2 weeks at 1000 °C. However, these energy-intensive and time-consuming production techniques would make the material industrially unattractive.

The aim of the present work has been to develop a technique which produces material free of α-Fe relatively cheaply and preferably in the as-cast state. Our previous studies [6] have shown that small niobium additions are very effective in removing free iron from the $Nd_2Fe_{14}B$ cast alloy and

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produce a microstructure exhibiting a majority $Nd_2Fe_{14}B$ phase together with a fine eutectic mixture of $Nd_2Fe_{14}B$ and the stable Laves phase $NbFe_2$. In view of these observations we decided to investigate the effect of niobium additions on the constitution of cast Sm_2Fe_{17} in the hope that similar behaviour would be obtained in these alloys.

2. Experimental techniques

The 0.5, 1 and 2% Nb casts were arc melted using Rare Earth Products Sm_2Fe_{17} and Goodfellow Metals 99.9% pure niobium wire. The 4, 5 and 10% Nb alloys were melted in an induction furnace operating at 1400 °C. The compositions of the casts are recorded in Table 1 and all have a majority phase Sm_2Fe_{17}. The microstructures of these alloys were investigated both optically and by scanning electron microscopy on a JEOL 5200 and an ISI 100A. The JEOL 5200 was fitted with an energy-dispersive X-ray (EDX) analyser which provided phase composition analysis. X-ray diffraction (XRD) data were obtained using a modified Philips diffractometer using a Hilton Brooks signal processor and Cr $K\alpha$ radiation or on a Siemens diffractometer using Co $K\alpha$ radiation. ^{57}Fe Mössbauer spectroscopy was carried out with a ^{57}Co-in-rhodium source and thermomagnetic analysis (TMA) was performed on a Sucksmith balance.

In order to nitride the alloys, they were powdered by crushing followed by grinding for 30 min under nitrogen before milling under cyclohexane in a rotary ball mill for 6 h. Nitrogen absorption studies were then carried out on a thermopiezic analyser designed and built at Trinity College Dublin [7]. This provided data on the nitrogen absorption characteristics of the alloys over a range of temperatures and pressures. Based on this information, bulk nitrogenation was performed in a conventional furnace using purified nitrogen (less than 5 ppm O_2). These powders were then analysed by XRD and TMA.

3. Results

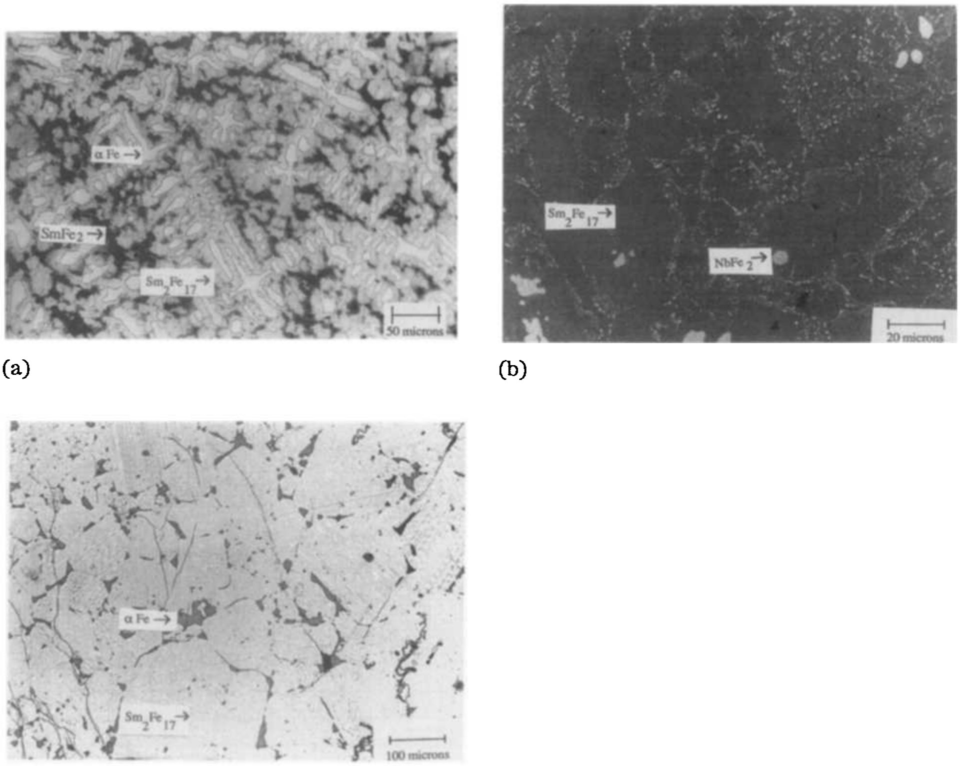
The niobium-free and niobium-containing cast alloys were examined with metallographic microscopy to determine their microstructure. Dendrites of

TABLE 1

Nominal composition (at.%) of various cast alloys

Nb	Sm	Fe
0	10.52	89.48
0.5	10.5	89
1	10.4	88.6
2	10.3	87.7
4	10.2	85.8
5	10	85
10	9.5	80.5

free iron were clearly visible in the niobium-free material. The degree of iron segregation caused by this dendritic growth resulted in the formation of $SmFe_2$ as well as Sm_2Fe_{17}, as can be seen in Fig. 1(a). The metallographic studies indicate that the proportion of α-Fe dendrites diminishes progressively with increasing niobium content with the corresponding appearance of faceted crystals of the Laves phase $NbFe_2$. At the 4% Nb composition, no α-Fe was observed and the microstructure shows the presence of Sm_2Fe_{17} and $NbFe_2$ as part of a eutectic mixture of Sm_2Fe_{17} and $NbFe_2$ or as primary crystals. The form of the $NbFe_2$ appears to depend on the cooling rate and this could determine whether there is a fine eutectic or a divorced eutectic. The present observations of the removal of free iron from the 2–17 alloy by the addition of niobium can be understood in terms of the presence of a deep eutectic in the Sm_2Fe_{17}–$NbFe_2$ system such that the α-Fe + liquid peritectic isotherm is avoided by small niobium additions. If this is the case then it should be possible to produce single-phase Sm_2Fe_{17} by controlled solidification of the 4% Nb alloy.



(a)

(b)

(c)

Fig. 1. Optical micrographs of (a) cast niobium-free material, (b) 2–17 as cast with 4% Nb showing light regions of $NbFe_2$ and a finely divided eutectic mixture of $NbFe_2$ and Sm_2Fe_{17} and (c) homogenized 2–17 showing twinning and small amounts of free iron (dark phase).

XRD analysis revealed no characteristic α-Fe lines in materials with niobium concentrations between 4 and 10%. Additional reflections were found in these alloys which corresponded to those characteristic of $NbFe_2$ [8]. The diffraction pattern of the 5% Nb material was analysed, and the Sm_2Fe_{17} lines were fitted to a rhombohedral structure. The resulting lattice parameters agree with previously published values [1]. The correspondence of these parameters to those of Sm_2Fe_{17} indicates that there is no significant substitution of iron by niobium in the 2–17 phase.

The difference between the niobium-free and 5% Nb materials can be seen clearly on the thermomagnetic curves of Fig. 2 (see also Table 2). No ferromagnetic phase except Sm_2Fe_{17} is apparent in the latter case, whereas in the former the ferromagnetic phases $SmFe_2$ and iron are observed, consistent with the metallographic observations (Fig. 1). The close correspondence of the Curie points of the Sm_2Fe_{17} phase in both alloys agrees with the XRD results which indicate no significant niobium substitution in the 2–17 phase.

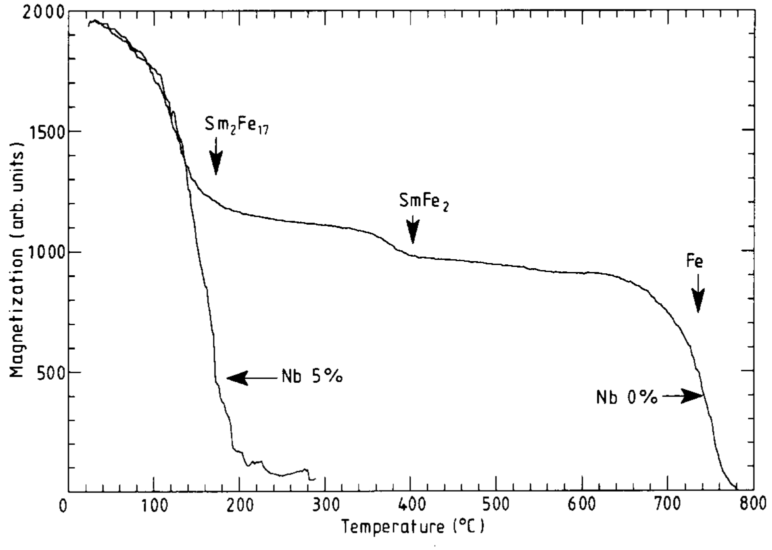


Fig. 2. TMA of Sm–Fe and cast Sm–Fe–Nb showing removal of free iron by niobium additions.

TABLE 2

EDX analysis of the phases found in Fig. 2(b), showing material composition (at.%)

Phase	Content		
	Sm (±1%)	Fe (±1%)	Nb (±1%)
Matrix	12.4	87.6	–
Light	–	64.4	35.6

Mössbauer spectroscopy [9, 10] was used to look for small amounts of α-Fe that might have been missed by TMA or XRD. Figure 3 shows the room temperature Mössbauer spectrum of the 5% Nb material and demonstrates the absence of α-Fe lines. An upper limit on the iron content is 0.5 wt.%; the percentage of free iron in the other alloys is presented in Table 3. The fitted curve in Fig. 3 includes a quadrupole doublet in the centre of the spectrum (9% of the total absorption) corresponding to paramagnetic $NbFe_2$.

The subsequent nitriding properties of the material were evaluated by thermopiezic analysis (TPA) of the sieved powder (Table 4). For a particle radius of 5 μm and a nitriding temperature of 450 °C, optimum nitrogenation is expected to occur after 10 h [11]. Analysis of the powders by TPA led to a maximum nitrogen content of 2.7 atoms per formula unit. The magnetic properties were comparable with those obtained from nitrogenated powder

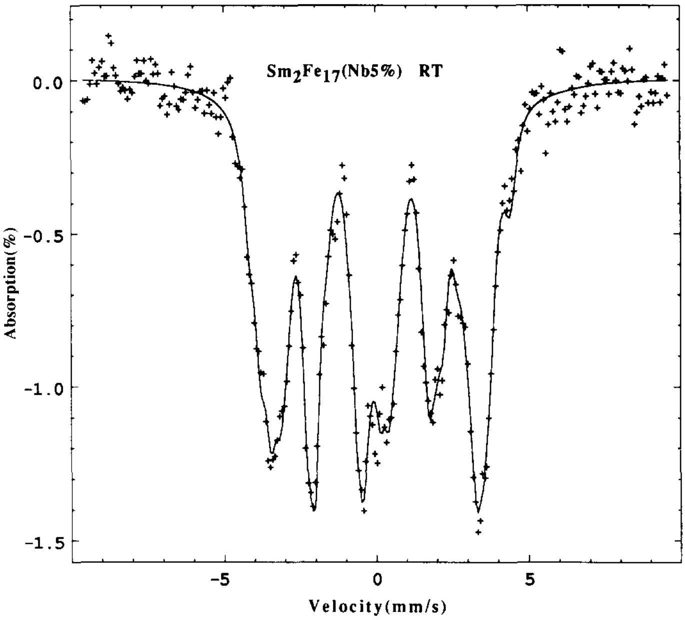


Fig. 3. Mössbauer data (+) and fitted curve (−) for the Sm_2Fe_{17} compound with 5% Nb (room temperature). The absence of peaks at ±5.1 mm s^{-1} shows that no free iron is present.

TABLE 3

Percentage iron found in casts from fittings made to Mössbauer data

Nb (%)	Fe (%)
0	>25
1	21
3	13
5	<0.5

TABLE 4

Optical microanalysis of particle size distribution[a]

Size[b] (μm)	Number	Volume (%)
$0.5<d<1.5$	33	39
$1.5<d<3$	32	38
$3<d<6$	12	14
$6<d<10$	3	4
$10<d<20$	4	5

[a] The powder was sieved through a 15 μm sieve.
[b] $\langle d\rangle_N=2.7$ μm; $\langle d\rangle_A=11.1$ μm; $\langle d\rangle_V=13.5$ μm.

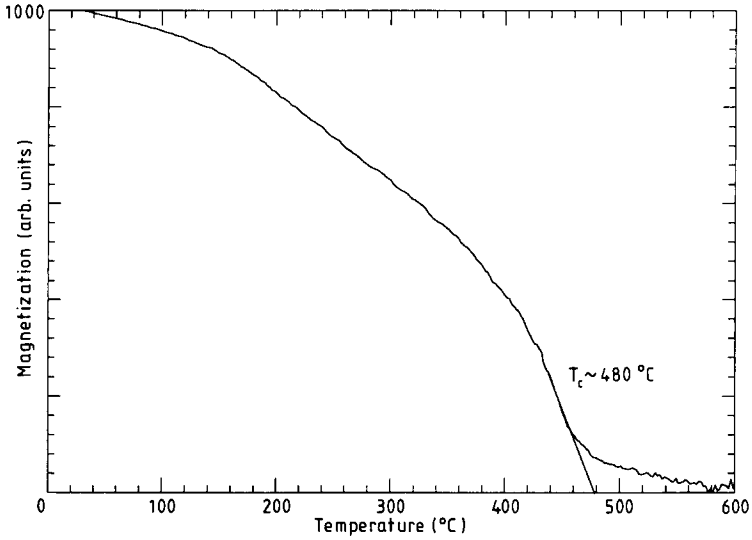


Fig. 4. TMA of nitrided powder showing a Curie temperature of 480 °C.

of homogenized materials, and TMA (Fig. 4) indicated a Curie temperature of 480 °C, in agreement with the measured nitrogen content.

X-ray investigation of the nitrided powder revealed that, if the reaction with nitrogen gas was overextended, the powder formed α-Fe predominantly at its surface. The intensity of the iron lines was reduced (Fig. 5) when the powder was subsequently ground, which is consistent with the presence of a surface layer.

Coercivities of around 0.2 T were observed in unbonded powders of the 5% Nb alloy, which are close to those observed in similar powders made from homogenized Sm_2Fe_{17}. The powders were subsequently mixed with up to 15% Zn in powder form. This mixture was then compacted and sintered under a nitrogen atmosphere around the melting point of zinc. An increase in the coercivity was produced, and these results will be discussed elsewhere.

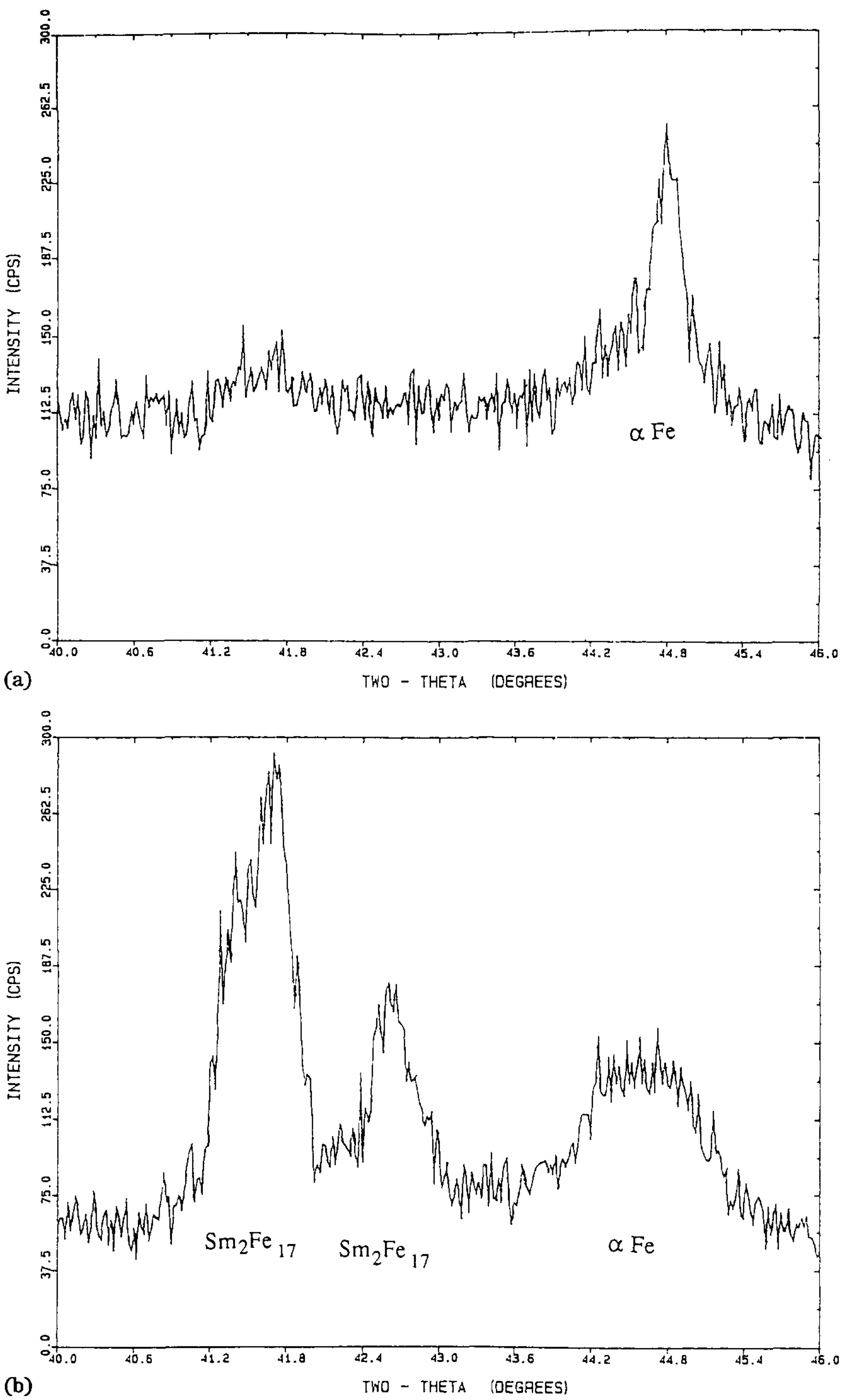


Fig. 5. X-ray data showing nitrogenated powder (a) before regrinding, with a sharp iron peak visible, and (b) after regrinding, with strong 2–17 lines visible and a broader iron peak.

4. Conclusions

We have described a process by which α-Fe-free Sm_2Fe_{17} may be obtained from a cast alloy by the addition of small amounts of niobium. It is probable that, in view of the stabilities of the TFe_2-type Laves phases (where $T \equiv Ti$, V, Zr, Nb, Hf, Ta) such a process could be achieved through the addition of other light transition elements. Preliminary data suggest that this material is in no way inferior to the alloy obtained by a long anneal at 1000 °C. We believe that this work represents a significant step towards developing an efficient processing route for the nitrogenated powder.

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