NITROGENATION OF Sm_2Fe_{17} ALLOY WITH Ta ADDITION

B. Saje[a,b], B. Reinsch[c], S. Kobe-Beseničar[b], D. Kolar[b], I.R. Harris[d]
[a] Magneti Ljubljana d.d., Ljubljana, Slovenia
[b] Jožef Stefan Institute, Ljubljana, Slovenia
[c] Max Planck Institute for Metals Research, PML, Stuttgart, Germany*,
[d] School of Metallurgy and Materials, University of Birmingham, United Kingdom

Key words: permanent magnets, nitrogenation, nitrides, Ta, Tantalum, Sm-Fe-Ta alloys, Sm-Fe-Ta powders, TPA ThermoPiezic Analyzers, SEM, Scanning Electron Microscopy, XRD, X-Ray Diffraction, TMA, Thermomagnetic Analysis

Abstract: The nitrogenation behaviour of a Sm-Fe-Ta based alloy which can be used for the preparation of Sm-Fe-N based permanent magnets has been described. Diffusion experiments on thin polished plates provided the nitrogenation processing parameters. Thermomagnetic analysis of partially and fully nitrided powders showed that the required nitrogenation times are somewhat lower than the calculated values which was attributed to the powder condition.

Nitriranje Sm_2Fe_{17} zlitine z dodatkom tantala

Ključne besede: magneti trajni, nitriranje, nitridi, Ta tantal, Sm-Fe-Ta zlitine, Sm-Fe-Ta prahovi, TPA analizatorji termopiezo, SEM mikroskopija elektronska skenirna, XRD uklon Rentgen žarkov, TMA analiza termomagnetna

Povzetek: Opisan je postopek nitriranja zlitine Sm_2Fe_{17} z dodatkom tantala, ki je primerna za izdelavo trajnih magnetov na osnovi Sm-Fe-N. Procesne parametre smo določili s pomočjo difuzijskih eksperimentov. Za te eksperimente smo uporabili tanke polirane ploščice.

Termomagnetna analiza delno in v celoti nitriranih prahov je pokazala, da so časi potrebni za nitriranje nekoliko krajši od izračunanih. To pripisujemo morfologiji prahov.

Introduction and experimental work

Permanent magnets based on the $Sm_2Fe_{17}N_{3-\delta}$ (δ=0.3) interstitial ternary phase are considered to be an attractive proposition for bonded magnets /1/. Unfortunately the binary Sm_2Fe_{17} phase is formed through a peritectic reaction between primarily crystallised iron and Sm-rich liquid. Free iron especially, unless removed by a subsequent isothermal homogenisation treatment, reduces the coercivity of the subsequent nitride when used for permanent magnets. Known methods for creating an alloy without free iron are either high temperature-long term annealing or addition of up to 5 at.% of Nb /2/ or Ta /3/.

There is much theoretical and experimental evidence of the nitrogenation of as-cast and homogenised alloys, but the diffusion parameters such as activation energy (E_a) and preexponential frequency factor (D_o) appear quite inconsistent. The activation energy for nitrogenation in pure nitrogen ranges from 66 to 133 kJ/mole and frequency factor (D_o) from $1.02*10^{-6}$ to $1.95*10^{-10}$ m^2/s /4-7/. There are no data for Ta modified alloys. Therefore it was the aim of this work to study comparatively the nitrogenation of as cast and annealed standard and Ta modified alloy to obtain diffusion parameters which would help to predict optimal processing parameters.

The nitrogenation was carried out on induction melted Sm_2Fe_{17} and $Sm_2Fe_{16}Ta_1$ alloys in pure nitrogen. The stoichiometric composition of cast Sm_2Fe_{17} was additionally homogenised for one week at 1100°C in argon to obtain nearly single phase material. The approximate nitrogenation temperature was determined by means of a thermopiezic analyser (TPA). Alloys were nitrided in 1 bar of pure nitrogen at temperatures from 350 to 550°C for different times (from 1 to 16 h) and examined with optical (Zeiss) and scanning electron microscopy (SEM Jeol EPMA 840 A). From the depth of the nitrogenated layer, activation energy and frequency factor were calculated. The $Sm_2Fe_{16}Ta_1$ alloy was also milled in a ball mill to study the nitrogenation behaviour of powder. Powder was nitrogenated for different times at 1 bar of pure nitrogen at 450 °C. The nitrogenated powder was then characterised by means of scanning electron microscopy (SEM, Jeol EPMA 840 A), X-ray diffraction (XRD Philips, Cu Kα source, step scan mode, step 0.02°, time/step 10 s, Ag as a standard) and thermomagnetic analysis (TMA, Manics DSM 8, horizontal Faraday principle, H_{ext} = 100).

Results and discussion

The results of the diffusion experiments are shown on Fig.1. The square of the average depth of the nitrided layer (and therefore the nitrogen diffusion) in the stoichiometric alloy is slightly larger than that in the Ta

* present address: Robert BOSCH GmbH, FV/FLW, POB 106050, D-70049 Stuttgart

modified alloy. From the measurement the activation energy for Sm_2Fe_{17} alloy was determined to be 82.32±8.97 kJ/mole with frequency factor of $1.7*10^{-10}$ m^2/s and activation energy for Sm-Fe-Ta alloy 92.82±11.96 kJ/mole with frequency factor of $5.3*10^{-10}$ m^2/s. From the data obtained it was possible to calculate that sufficient nitrogenation time for spherical particles of 10 μm diameter would be around 10 hours, according to the equation published in /7/.

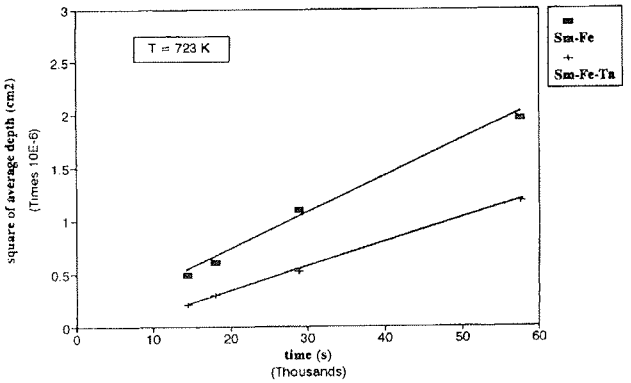

Fig. 1: Square of the average nitrogen layer depth vs. time at 723 K

For the nitrogenation and magnetic properties measurements the milled powder was used. The average particle size of the powder was about 10 μm (as determined with Cilas Alcatel Laser particle sizer) but its irregular morphology has to be noted as well as the broad particle size distribution. Due to these features slightly different nitrogenation behaviour was anticipated as predicted in theoretical modelling /7/. XRD diffraction of the Sm-Fe-Ta powder nitrided for 10 hours showed characteristic peak shifts due to lattice expansion of the Sm_2Fe_{17} phase (Fig. 2a) when compared with the XRD trace of the non nitrided Sm-Fe powder (Fig 2b). The $TaFe_2$ phase didn't change upon nitrogenation and there is no free Fe detectable in the Ta modified non nitrided alloy (see Fig 2c). There was also a small peak attributed to free Fe observed in the nitrided powder (Fig. 2a). Since the average nitrogenation temperature was too low to induce the overall decomposition of the nitride this was attributed to the combined effect of the decomposition of the $Sm_2Fe_{17}N_x$ into SmN and secondary Fe during nitrogenation due to surface effects as reported in /2/ and possible presence of the remanent primary Fe from the cast material.

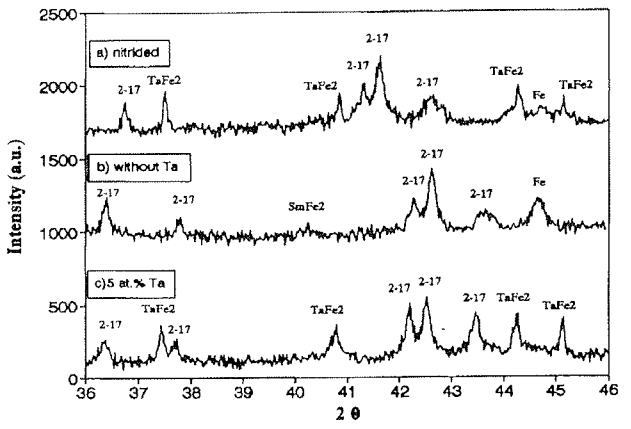

Fig. 2: XRD traces of
a) nitrided Sm-Fe-Ta alloy,
b) as-cast Sm_2Fe_{17} alloy, and
c) as-cast Sm-Fe-Ta alloy.

Several features are apparent from the thermomagnetic scans of fully, partially and non nitrided Sm_2Fe_{17} alloy which are shown on Fig. 3. Only the magnetisation curves of non nitrided and the alloy nitrided for 6 hours exhibit one Curie point corresponding to Sm_2Fe_{17} and $Sm_2Fe_{17}N_{3-\delta}$ phase respectively.

The other traces exhibit contribution from both the nitrided shell and the core. The Curie point of the $Sm_2Fe_{17}N_{3-\delta}$ shell (470°C) remains virtually unchanged irrespective of the nitrogenation times. This shows, that, even after a short nitrogenation time, a layer of nitrogen saturated shell is formed. The Tc of the core increases with nitrogenation time over the range of 100°C. This shift may be caused by the expansion of the core, due to the strain caused by the volume expansion of the nitrogenated shell. Another possibility is that it is due to a combination of this factor together with the presence of regions of intermediate nitrogen concentration, as shown in the Sm-Fe-Nb system /8/.

The Sm-Fe-Ta powder appeared to be fully nitrided even after 6 hours of nitrogenation (for the given processing parameters) which is not in agreement with calculations in which temperature, time, N2 pressure and average particle size were used as the defined values. This difference was therefore attributed to the state of the milled powder i.e. irregular morphology, possible cracks or even anisotropic diffusion through the lattice, geometrical factor, particle size distribution and the surface condition which were omitted from the calculation.

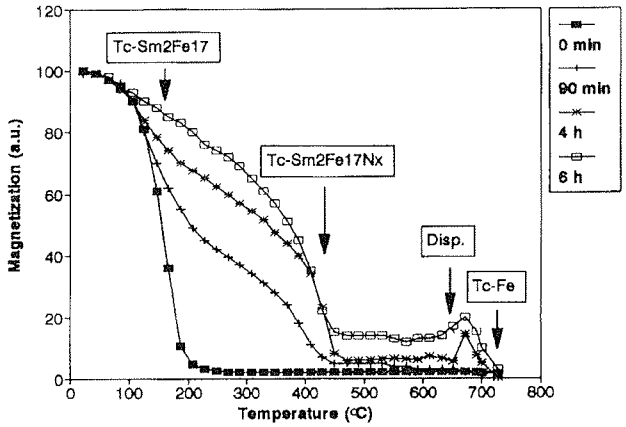

Fig. 3: TMA traces of Sm-Fe-Ta powders nitrided for various times.

Another feature apparent from the graphs on Fig. 3 is the increase of the magnetisation after the Curie temperature of the $Sm_2Fe_{17}N_3$ which was attributed to secondary free Fe formation due to decomposition of the nitride.

Activation energy for Sm_2Fe_{17} alloy was determined to be 82.32±8.97 kJ/mole with frequency factor of $1.7*10^{-10}$ m^2/s and activation energy for Sm-Fe-Ta alloy 92.82±11.96 kJ/mole with frequency factor of $5.3*10^{-10}$ m^2/s.The nitrogenation times to obtain fully nitrided alloy were around 6 hours for the powder with average grain size of 10 μm (for the given processing parameters) which is less than predicted by calculations assuming spherical powder particles with uniform grain size distribution. The discrepancy between the idealised powder used for theoretical calculations and real powder was attributed to the condition of the milled powder.

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Dr. Boris Saje,
Magneti Ljubljana d.d.,
Stegne 37, 1000 Ljubljana, Slovenia
Jo'ef Stefan Institute,
Jamova 39, 1001 Ljubljana, Slovenia
159 87 64/159 26 69/boris.saje @ijs.si

Dr. Spomenka Kobe-Beseničar,
Jo'ef Stefan Institute,
Jamova 39, 1001 Ljubljana, Slovenia
177 32 51/126 3 126/spomenka.kobe @ijs.si

Prof. dr. Drago Kolar,
Jo'ef Stefan Institute,
Jamova 39, 1001 Ljubljana, Slovenia
177 32 92/126 3 126/drago.kolar @ijs.si

Dr. Bernd Reinsch
Max Planck Institute for Metals Research, PML,
Heisenbergstr.5, D-70569 Stuttgart, Germany
fvflw_rb @sh_x4.bosch.de

Prof. Dr. I.R. Harris
School of Metallurgy and Materials,
University of Birmingham,
Birmingham B15 2TT, United Kingdom
I.R.Harris @bham.ac.uk

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