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NEW GENERATION OF PERMANENT MAGNET MATERIALS BASED ON Sm-Fe NITRIDES

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Abstract: The microstructure and magnetic properties of the $Sm_2Fe_{17-x}Ta_x$ ($0< x <2$) cast and annealed alloys were investigated by means of the microstructural, X-ray diffraction and thermomagnetic analysis. A process for obtaining the Sm_2Fe_{17} phase free of iron in the as-cast state is described. The method consists of adding 5 at % of Ta in the melt. By this addition of Ta to the basic alloy two phase structure of the as-cast ingots consisting of the Sm_2Fe_{17} phase and Pauli paramagnetic $TaFe_2$ hexagonal Laves phase can be obtained. Less than 0.5 wt.% of free iron in the cast ingot with 5 at.% of Ta addition was determined with isothermal magnetic analysis.
X-ray diffraction showed an increase of the lattice spacing dependent upon the tantalum concentration in the alloy which indicated some possible solid solubility of Ta in the Sm_2Fe_{17} phase. Quantitative electron probe microanalysis confirmed the solid solubility of tantalum in the Sm_2Fe_{17} phase up to 2.3 at %. This resulted in an increase of the Curie temperature of the Sm_2Fe_{17} phase which was determined by means of thermomagnetic analysis.

Nova generacija trajno magnetnih materialov na osnovi Sm-Fe nitrida

Ključne besede: magneti trajni, magneti zemelj redkih, Sm-Fe-N magneti, mikrostrukture materialov, analiza termomagnetna, analiza mikroelektronska, X-žarki analiza, zlitine kovin

Povzetek: Z elektronsko mikroanalizo mikrostrukture in termomagnetno analizo so bile preiskane zlitine s sestavo $Sm_2Fe_{17-x}Ta_x$ ($0< x < 2$). Opisan je postopek priprave Sm_2Fe_{17} faze, ki se uporablja za pripravo trdomagnetne spojine $Sm_2Fe_{17}N_y$, v litem stanju z nizko vsebnostjo prostega mehkomagnetnega železa. Fazna modifikacija je bila dosežena z dodatkom 5 at% Ta, ki v nominalni sestavi Sm_2Fe_{17} zamenjuje železo. Tako dobljena zlitina je v litem stanju dvofazna in vsebuje Sm_2Fe_{17} fazo in Pauli paramagnetno $TaFe_2$ heksagonalno Lavesovo fazo. Vsebnost preostalega prostega železa v liti strukturi se giblje okoli 0.5 ut.%, kar je bilo ugotovljeno z izotermalno magnetno analizo. S termomagnetno, x-žarkovno in mikroelektronsko analizo vzorcev je bilo tudi ugotovljeno da obstaja območje trdne topnosti Ta v Sm_2Fe_{17} fazi (do 2.3 at.%) zaradi česar se Curiejeva temperature te faze zviša.

I. INTRODUCTION

The R_2Fe_{17} compounds with most of the rare earths (R) have been found to absorb large quantities of nitrogen when treated at about 500°C in gaseous NH_3 or N_2(1). The structures of the interstitial nitrides are related to those of the hexagonal Th_2Ni_{17} (for compounds with heavy rare earth) or rhombohedral Th_2Zn_{17} (for compounds with light rare earth) parent compounds (Fig. 1).

The $R_2Fe_{17}N_y$ with y = 2.8 have Curie temperatures that are in the range from 678 to 758 K, compared to those for y = 0 which are in the range from 214 to 477 K. This increase in Curie temperature in the nitrides is due to more than doubling of the Fe-Fe exchange interactions, associated with an increase in cell volume of about 7% (2). The R-Fe exchange interaction is slightly reduced in the nitrides. All compounds exhibit easy c-plane anisotropy at room temperature, except for R = Sm, which is easy c-axis. The negative sign of the Fe sublattice anisotropy constant K1 is unchanged after nitrogenation.

These materials possess a unique combination of high Curie temperature, strong uniaxial anisotropy and large iron moment. The comparison of intrinsic magnetic properties between $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_y$ is the following; $Nd_2Fe_{14}B$: Tc= 588 K, Ms = 1.60 T, Ha = 7.5 T, BH max (teor.) = 509 kJ/m^3; $Sm_2Fe_{17}N_x$: Tc = 749 K, Ms = 1.55 T, Ha = 14 T, BH max (teor.) = 472 kJ/m^3. This is the reason that permanent magnets based on the $Sm_2Fe_{17}N_y$ ternary interstitial phase with rhombohedral Th_2Zn_{17} - type structure are considered to be competitive with the well-known Nd-Fe-B based magnets, especially because of the higher Curie temperature which is the main disadvantage in Nd-Fe-B based magnets.

Unfortunately the Sm_2Fe_{17} binary phase which is used for production of the $Sm_2Fe_{17}N_y$ interstitial ternary compound via the gas-phase interstitial modification process (2), is formed through a peritectic reaction between primary crystallised iron and Sm-rich liquid (3). This process always leads to considerable amounts of free iron (up to vol. 25 %.) and some Sm-rich phases in the as-cast state. Free iron especially, unless removed by a

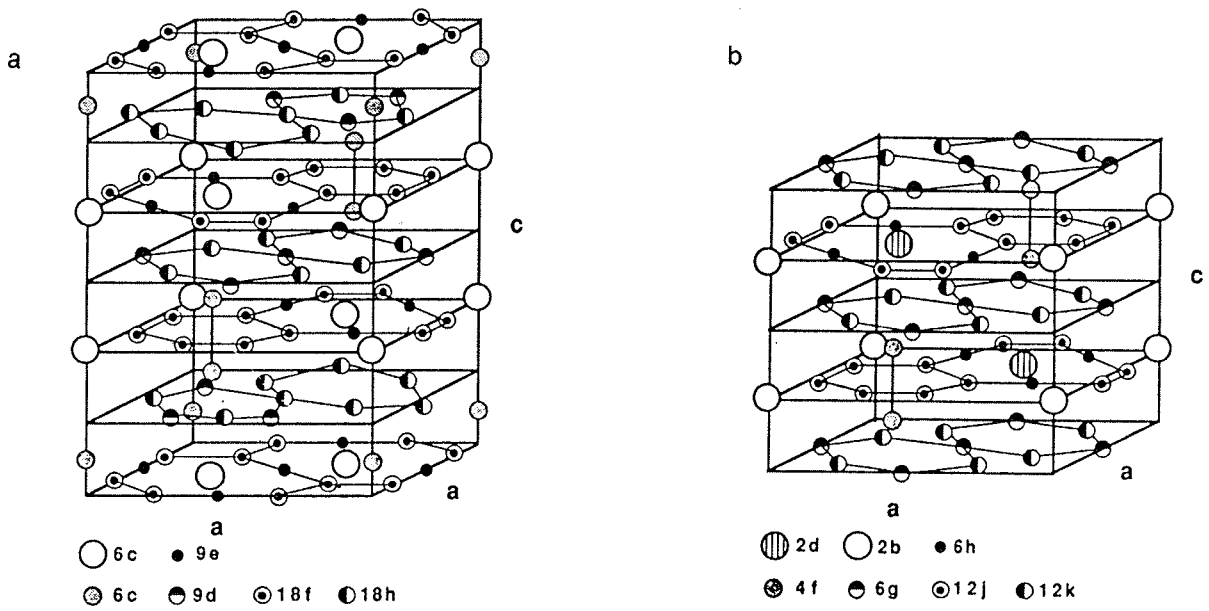

Fig. 1: Th_2Zn_{17} (A) and Th2Ni17 (B) crystall structures showing the octahedral interstitial 9e or 6h sites that may be occupied by N

subsequent isothermal homogenization treatment, reduces the coercivity of the subsequent Sm_2Fe_{17} nitride when used for permanent magnets.

Known methods for creating an alloy without soft magnetic phases are either high temperature-long term annealing of samarium-rich cast alloy or addition up to 5 at.% of Nb (4) which modifies crystallization and leads to two phase structure consisting of Sm_2Fe_{17} phase and $NbFe_2$ paramagnetic intermediate Laves phase.

From other transition elements it was shown that also Zr, Mo, Hf, V, Ti and Ta form intermediate Laves phases of AB_2 - type (5). $HfFe_2$ and $ZrFe_2$ are ferromagnetic (6) and thus inappropriate due to their magnetic interaction with demagnetising field, WFe_2 and $MoFe_2$ do not melt congruent but are formed through peritectoid reaction thus making formation kinetics unsuitable (7). Ti forms $TiFe_2$, antiferromagnetic Laves phase with Neel temperature of 272 K (8) but work in Sm-Fe-Ti system showed that Sm_2Fe_{17} and $TiFe_2$ are not in the equilibrium at melting temperature (9).

Tantalum forms Pauli paramagnetic $TaFe_2$ intermediate hexagonal Laves phase with iron (6). While it is possible in Sm-Fe-Nb to obtain two-phase as cast structure,similarity of Nb-Fe and Ta-Fe binary phase diagrams and while Nb and Ta form isomorphic system (5), we choose Ta as a promising candidate for addition element which would lead to a two phase structure in the as cast state consisting of Sm_2Fe_{17} and $TaFe_2$ without presence of soft magnetic free iron. This modification would lead to an precursor alloy suitable for producing $Sm_2Fe_{17}N_y$ ternary interstitial phase without isothermal annealing treatment of the cast ingots prior to nitrogenation.

We also expected some enhancement of the Curie temperature due to possible existence of solid solubility of Ta in the Sm_2Fe_{17} phase as it was reported for Sm-Fe-Ti (9) and Sm-Fe-Nb (10) systems.

II. EXPERIMENTAL WORK

As-cast alloys were prepared by arc-melting of 2 g samples in a Ti purified Ar atmosphere using elemental Sm (99.9 %, Johnson Matthey), Fe (99.9 %, Ventron) and Ta (99.9 %, Plansee). Excess Sm was added to a nominal composition of $Sm_2Fe_{17-x}Ta_x$ ($0< x <2$) to counterbalance Sm evaporation losses during melting. The samples were remelted four times to improve homogeneity.

Cast ingots were sealed in the evacuated quartz tubes with some addition of elemental Sm to counterbalance Sm vapour pressure at annealing temperature. Sealed samples were annealed at 1200°C for 5 hours and subsequently water-quenched.

Microstructural analysis was performed on a JEOL 840A SEM/EPMA electron probe microanalyser. Phase contents were calculated using digitised SEM micrographs and image analysis software.

XRD measurements of the powders were conducted on Phillips 1710 diffractometer using CuK a radiation.

Thermomagnetic analysis of the bulk samples (up to 100 mg) was carried out in vacuum in the temperature range from 300 to 1000 K at an applied field of 2 kOe , and isothermal magnetic analysis was performed at 550 K in an applied field from 0 to 15 kOe by means of sensitive

magnetometer- susceptometer (Manics) based on a Faraday principle.

III. RESULTS AND DISCUSSION

The microstructural analysis showed phase composition changes dependent upon increasing of Ta content of the investigated alloys. From Fig. 2, which shows microstructure of tantalum free alloy, we can observe the normal appearance of as cast state of nominally stoichiometric Sm_2Fe_{17} alloy. Dendrites of primary crystallised iron are surrounded by peritectically formed Sm_2Fe_{17} phase with some Sm-rich phase which was identified as $SmFe_2$. This is consistent with previous findings (3) that formation of $SmFe_3$ (which would be expected from the phase diagram) was suppressed due to its sluggish formation kinetics.

After annealing the nominally stoichiometric Sm_2Fe_{17} as-cast samples the microstructural image analysis

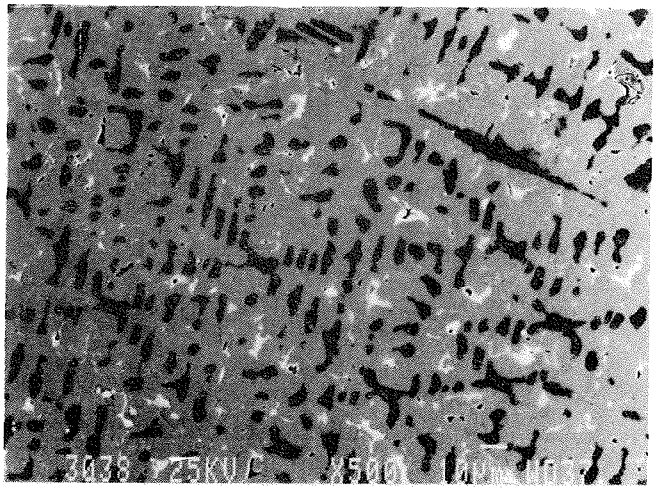

Fig. 2: SEM micrograph (SE/BSE Comp. Image) of the Sm_2Fe_{17} as cast alloy showing dendrites of primary Fe (dark), Sm_2Fe_{17} (grey), and $SmFe_2$ (white) phases.

revealed that the microstructure is still multiphase consisting of approximately 97 vol. % of Sm_2Fe_{17} phase, 2 vol % of Sm-rich phase and 1 vol. % of iron.

Microstructural analysis (supported by thermo magnetic analysis) also showed, that proportion of free iron dendrites as well as Sm-rich phases diminishes progressively with increase of Ta content (Fig. 3), and appearance of some $TaFe_2$ phase was identified which indicates some non- equilibrium solidification due to fast cooling.

The microstructure significantly changed for an alloy with 5 at % of tantalum which replaces iron in the nominal composition of $Sm_2Fe_{17-x}Ta_x$ as it is shown in Fig. 4. Image analysis of the digitised SEM micrograph showed that microstructure consists of approximately 85 vol % of Sm_2Fe_{17} phase and 15 vol % of $TaFe_2$ phase. It should be noted that due to the relatively large amount and

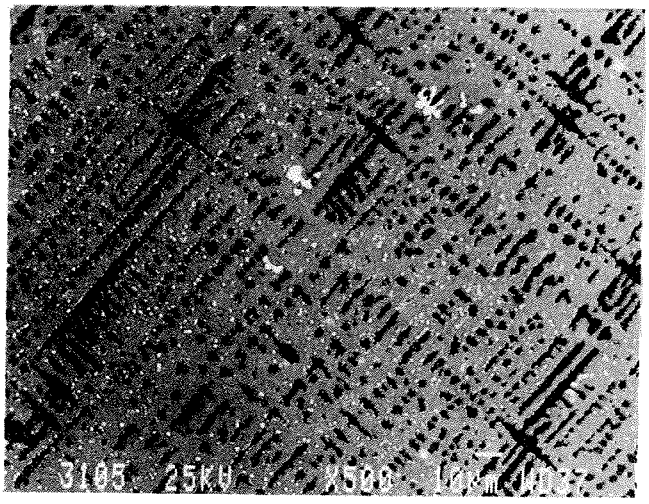

Fig. 3: SEM micrograph (SE/BSE Comp. Image) of the cast Sm-Fe-Ta alloy with 2 at.% of Ta showing Sm_2Fe_{17} (grey), Fe (dark), $SmFe_2$ (light grey) and $TaFe_2$ (white) phases

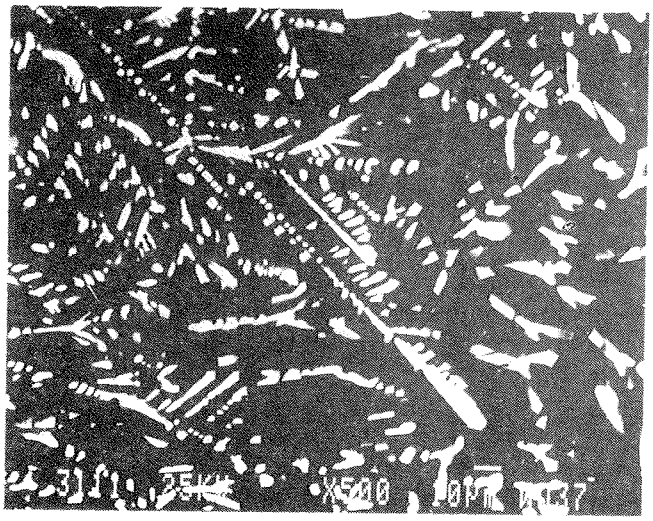

Fig. 4: SEM micrograph (SE/BSE Comp. Image) of the cast Sm-Fe-Ta alloy with 5 at. % of Ta showing Sm_2Fe_{17} (grey) and $TaFe_2$ (white) phases

dendritic appearance of the $TaFe_2$ phase optimal amount of Ta addition for preparation of Sm_2Fe_{17} precursor alloy for nitrogenation is somewhat lower than 5 at.% of Ta.

For qualitative confirmation of the present phases in as cast alloy we additionally used thermomagnetic analysis of the samples for Curie temperature determination of the existent phases.

The magnetic difference between the tantalum free alloy and 5 at% Ta material is evident from Fig. 5. The analysis of Ta free alloy showed three characteristic steps on M = f(T) curve, corresponding to the Curie temperature of Sm_2Fe_{17}, $SmFe_2$ and Fe respectively. Thermomagnetic curve of the 5 % Ta material shows only one large step, consistent with Curie temperature of Sm_2Fe_{17} phase. As expected, thermomagnetic scan of $TaFe_2$ phase showed the paramagnetic nature of the phase. It has to be noted from Fig. 5 (curve B) that after the Curie temperature of the Sm_2Fe_{17} phase a paramagnetic state of the alloy

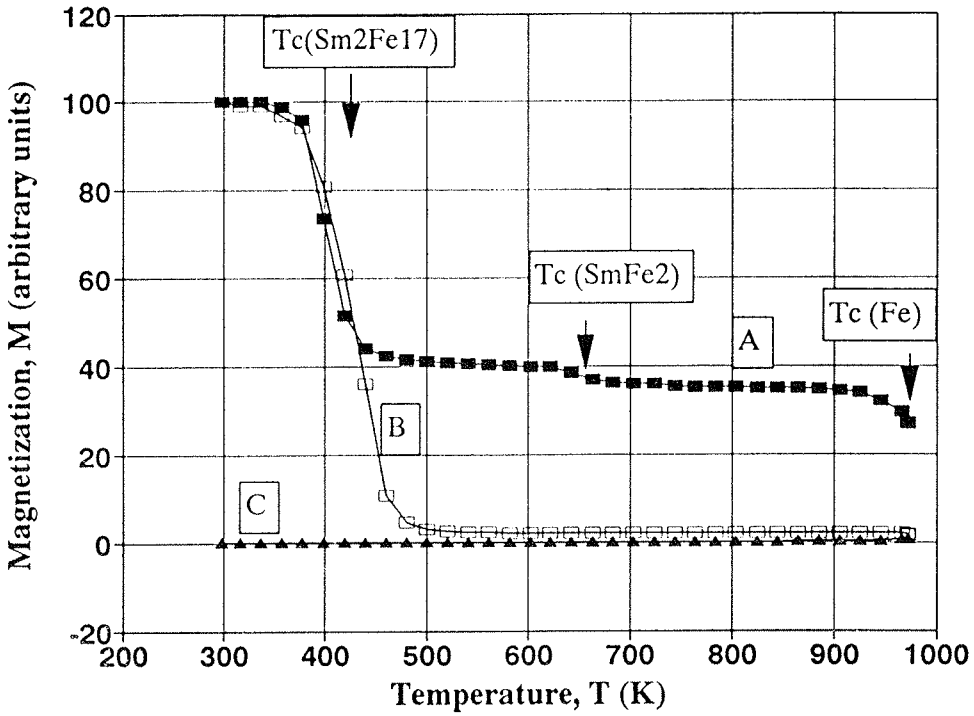

Fig. 5: Normalized thermomagnetic curves for A) as cast Ta free Sm_2Fe_{17} alloy, B) as cast Sm-Fe-Ta alloy with 5 at.% of Ta and C) $TaFe_2$ as cast alloy.

with 5 at. % was not attained. Therefore for quantitative determination of free iron dendrites or iron precipitates, which still might be present in the cast ingot, due to suspected inhomogeneous distribution induced by non-equilibrium solidification, isothermal magnetic analysis (ITMA) was used. The principle is originally based on the method of Honda (11) and Owen (12) for determination of ferromagnetic impurities in paramagnetic samples and applied in Rare-Earth -Transition Metals systems in work of Liu et all.(13).

Fig. 6 shows a typical M = f(H) curve of the as cast ingot with 5 at.% of Ta measured at 550 K. The measuring temperature is above the Curie temperature of Sm_2Fe_{17} phase therefore making its contribution to measured magnetisation paramagnetic. To estimate the amount of remaining free iron we separated the ferromagnetic and paramagnetic contribution from the measured M = f(H) curve. The ferromagnetic contribution (curve C on Fig.5) shows that the saturation magnetisation of residual ferromagnetic component in the alloy is 1.04 emu/g. Assuming this is free iron then this value divided by the value of saturation magnetisation of pure iron at measuring temperature gives 0.5 wt.% of remaining free iron in the alloy.

Quantitative electron probe microanalysis of the annealed samples revealed the existence of solid solubility of tantalum in Sm_2Fe_{17} phase as is shown in Table 1.

phase	element	concentration of the element (at %)		
		0 at % Ta	5 at % Ta	8 at % Ta
Sm_2Fe_{17}	Sm	10.85	10.55	10.83
	Fe	89.15	87.14	87.88
	Ta	-	2.31	1.29
Sm-rich	Sm	38.13	-	-
	Fe	61.87	-	-
$TaFe_2$	Fe	-	71.64	70.39
	Ta	-	28.36	29.61
Fe	Fe	100	-	99.35
	Ta	-	-	0.65

Table 1: Quantitative electron probe microanalysis of the phase composition of the phases present in the samples of the Sm-Fe-Ta alloys with different tantalum concentration

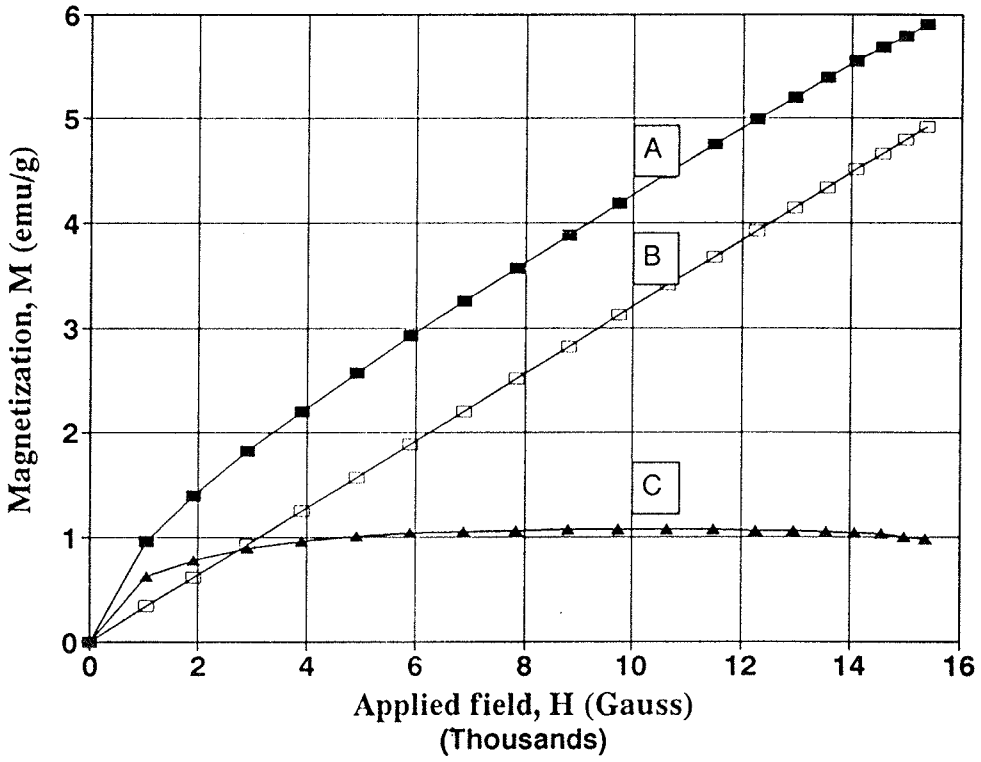

Fig. 6: *Magnetization as a function of applied field of as cast Sm-Fe-Ta alloy with 5 at.% of Ta measured at 550 K. Shown curves represents A) measured magnetization of the sample, B) paramagnetic contribution, C) free iron contribution.*

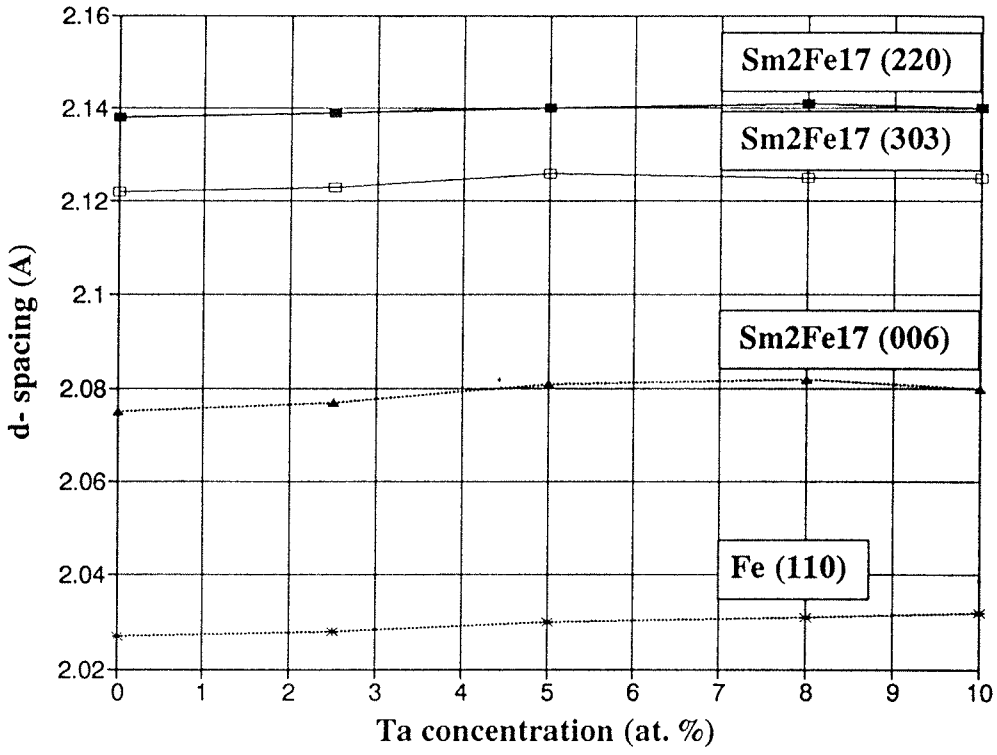

Fig. 7: *Enhancement of the d-spacings for characteristic reflections as a function of Ta concentration for Sm_2Fe_{17} phase and iron.*

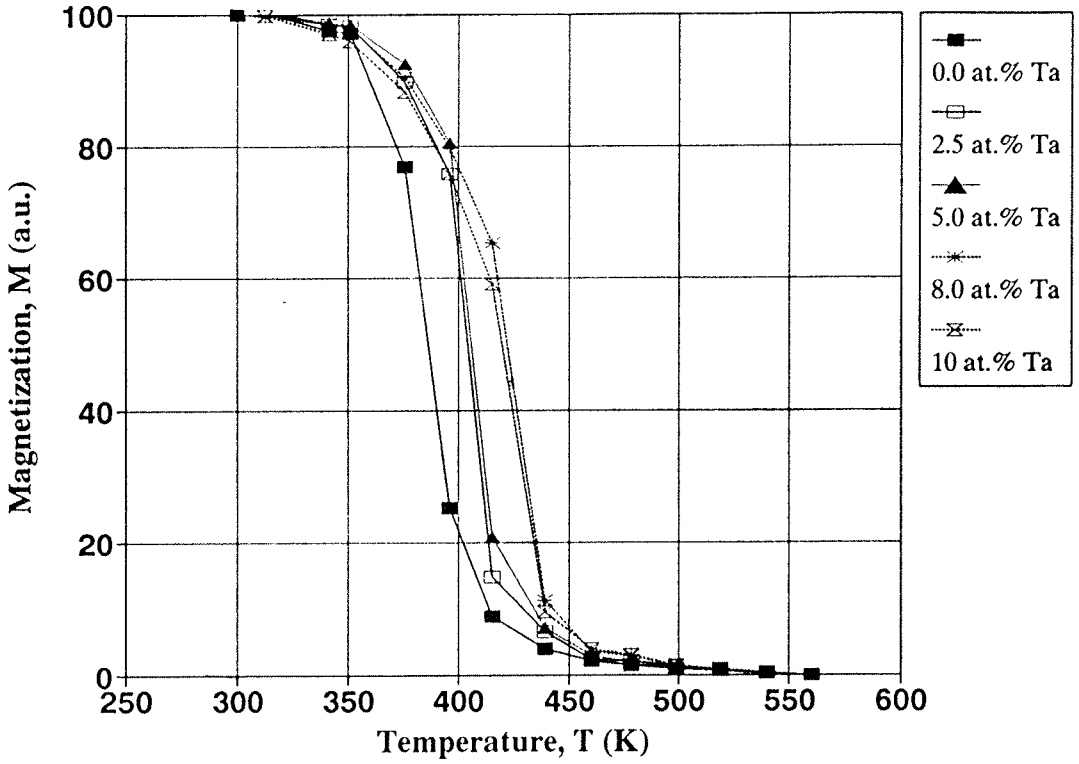

Fig. 8: Thermomagnetic curves normalized with respect to Sm_2Fe_{17} phase for Sm-Fe-Ta annealed alloys with different Ta content.

Quantification of the elemental analysis showed that Sm-rich phase in the sample is not purely stoichiometric $SmFe_2$ phase.

It has to be noted from Table 1 that $TaFe_2$ phase should be attributed to nearly stoichiometric Ta_3Fe_7 phase. Deviation from the stoichiometry of $TaFe_2$ originates from the homogeneity range of about 28 - 36 at % Ta which is consistent with the Fe-Ta phase diagram (7). It should also be noted from Table 1, that Fe is not pure iron, but solid solution of Ta in Fe which is also in good agreement with Fe-Ta phase diagram (7).

To confirm the solid solubility determined by quantitative electron probe microanalysis X-ray diffraction was used for measuring the changes of lattice spacings as a function of Ta concentration. The shift of the strongest diffraction lines ((220), (303) and (006) for Sm_2Fe_{17} phase and (110) for Fe) was measured to study the lattice expansion due to Ta solid solubility in the phases.

It is evident from Fig. 7 that the largest expansion appeared at 5 at % of Ta for the Sm_2Fe_{17} phase. However, it has to be noted, that maximum shift of d spacings is not uniform for all three reflections which may indicate some anisotropic deformation of the Sm_2Fe_{17} unit cell due to possible preferential substitution of the Ta into Fe sites.

Also it should be noted from Fig. 7 that there is some solid solubility of Ta in the Fe as well, which resulted in the shift of the d spacing corresponding to the (110) reflection.

Since the volume expansion of the unit cell in the Rare Earth Transition Metal systems usually results in the change of the Curie temperature thermomagnetic analysis was applied to study the effect of Ta concentration on the Curie temperature.

The thermomagnetic scans of the samples with tantalum concentration from 0 to 10 at %, normalised with respect to the Sm_2Fe_{17} phase (Fig. 8) showed increase of the Curie temperature of the Sm_2Fe_{17} phase by about 40 K. This enhancement is most likely attributable to changes of the Fe-Fe molecular field coefficient.

IV. CONCLUSIONS

We have described a process by which Sm_2Fe_{17} phase nearly free of iron dendrites or iron precipitates in as cast

state may be obtained via tantalum addition which replaces free iron in nominal composition. Microstructure of as cast alloy with 5 at.% of Ta consists therefore of Sm_2Fe_{17} and $TaFe_2$ paramagnetic phase. The overall remaining free iron content in the cast ingots was shown to be less than 0.5 wt.%.

It was also shown that in $Sm_2Fe_{17-x}Ta_x$ ($0< x < 2$) exist some solid solubility of tantalum in Sm_2Fe_{17} phase and in free iron. The maximum Ta concentration in the Sm_2Fe_{17} phase determined by means of electron probe microanalysis is 2.31 at % of Ta and for free iron is 0.65 at % of Ta. The solid solubility of Ta in Sm_2Fe_{17} phase gives rise to volume expansion of Sm_2Fe_{17} unit cell which was confirmed with XRD measurements of the d-spacing shift as a function of Ta concentration. This resulted in increase of the Curie temperature of the Sm_2Fe_{17} phase which was determined to be about 40 K by means of thermomagnetic analysis.

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