

On the synthesis of the new intermetallic phase $\text{Nd}_3(\text{Fe,W})_{29}$

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Abstract

A novel intermetallic compound, $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$, that shows the monoclinic $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type crystal structure (space group $A2/m$) has been obtained from powders homogeneously mixed and processed by arc melting. A notable reduction in the annealing time at 1100°C was obtained by using this procedure. From the Rietveld refinement of the powder X-ray diffractogram, the phase constitution and crystal structure were determined. The analysis shows that a 3:29 type compound is the majority phase (90 wt.%). It coexists with α -(Fe,W) (8 wt.%) and a 1:12 type phase (2 wt.%) as minority components. SEM and EDAX analyses were performed in order to characterize the microstructure. It was concluded that the 3:29 phase is the main component, in agreement with the results obtained by XRD and TMA. The $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ compound exhibits a Curie temperature of 124°C and a room temperature saturation magnetization of 96 emu/g (at $H_{\text{max}} = 16$ kOe).

Keywords: Rare earth compounds; Transition metal compounds; Magnetization; Crystal structure; X-ray diffraction.

Since the discovery of the $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type (3:29) ternary phase, much attention has been devoted to study its obtained was relatively low. However, we performed a existence in different ternary systems and its magnetic and preliminary structural and magnetic characterization. We structural properties. $\text{RE}_3\text{Fe}_{29-x}\text{M}_x$



compounds are stabilized by small concentrations of a third element, M, and they can exist only at high temperatures. These compounds have been synthesized for RE=Y, Ce, Pr, Nd, Sm, Gd, Tb and Dy, with M=Ti, V, Cr, Mn, Mo and W [1-13]. The structure is monoclinic with the space group $A2/m$ [14]. It is intermediate between the rhombohedral Th_2Zn_{17} -type (2:17) and tetragonal $ThMn_{12}$ -type (1:12) phases, and may be viewed as alternate stacking blocks consisting of these phases in the ratio of 1:1 [15]. In fact, the three structures derive from that of the hexagonal compound $CaCu_5$ in which Ca atoms are periodically replaced by pairs of transition metal atoms (referred in literature as dumbbells). The unit cell of $Nd_3(Fe,Ti)_{29}$ has two Nd sites and 11 Fe(Ti) sites.

In a recent paper, we first reported the formation of the $Nd_3(Fe, Ti)_{29}$ -type phase in bulk $Nd_3Fe_{27.5}W_{1.5}$ ingots [16]. The specimen was produced by arc melting the pure metallic components followed by annealing at 1100°C for 3 weeks (504 h). The amount of the novel compound obtained was relatively low. However, we performed a preliminary structural and magnetic characterization. We attributed this low amount to the poor incorporation and inhomogeneous distribution of tungsten in the volume of the sample. The metallographic analysis revealed that relatively large unmolten particles of tungsten were present. In our opinion, this is a consequence of the notable difference in the melting point, T_{MP} , of W ($T_{MP}(W)=3387^\circ\text{C}$), with that of the other starting elements ($T_{MP}(Fe) = 1536^\circ\text{C}$ and $T_{MP}(Nd)=1024^\circ\text{C}$, respectively). This letter is a further study on the formation of this compound. Introducing a minor modification in the preparation method commonly employed, we were able to obtain a notable increase in the relative

amount of the 3:29 phase. The results obtained are compared with those previously reported.

Raw materials were used in the form of powders with purity of 99.95% for Fe (BDH Chemical; average particle size, <10 μm), 99.9% for Nd (Aldrich; particle size, <50 μm) and 99.9% for tungsten (Aldrich; particle size, <50 μm). They were adequately mixed in a mortar and then pressed into tablets at 3.5 ton / cm^2 . Small buttons with nominal composition $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ were produced by arc melting under a high purity Ar atmosphere. The as-cast alloys were wrapped in tantalum foil and annealed in argon in closed quartz tubes at 1100°C for 100 h. Annealing was followed by quenching in water. This sample will be referred as sample A. As mentioned before, this will be compared with the sample obtained in Ref. [16], which we have termed as sample B.

X-ray diffraction analysis was performed on finely ground powders with an automated Siemens model D5000 diffractometer. A graphite monochromator was used to select the Cu $K\alpha$ -doublet ($\lambda = 1.542\text{\AA}$). Scanning was carried out in the interval $20^\circ < 2\theta < 80^\circ$ with a step increment of 0.040° . In order to determine the phase composition and lattice parameters, the XRD pattern was refined by the Rietveld method using the DBWS-9411 computer program [17]. The values used for the atomic scattering factors were taken from the *International Tables of Crystallography* (Vol. 4). The microstructure of the sample was studied by means of a JEOL microscope Model JSM-5800LV in back-scattering emission mode. EDAX analysis was done with a Link silicon detector. Prior to examination, the sample was carefully polished by employing alumina and diamond powders.



Magnetic measurements were done in a vibrating sample magnetometer, LDJ Model 9600. Hysteresis loops were recorded with a maximum field of $H_{\max} = 16$ kOe. Thermomagnetic (TMA) analysis curves were determined in a static external magnetic field of 200 Oe with a heating rate $5^{\circ}\text{C}/\text{min}$.

Fig.1 shows the TMA curves for as-cast and annealed $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ alloys. For the as-cast sample (Fig. 1a), the plot shows a broad transition at 83°C that we attribute to the presence of a $\text{Nd}_2\text{Fe}_{17-x}\text{W}_x$ phase, in agreement with the results reported by Girt et al. [18].

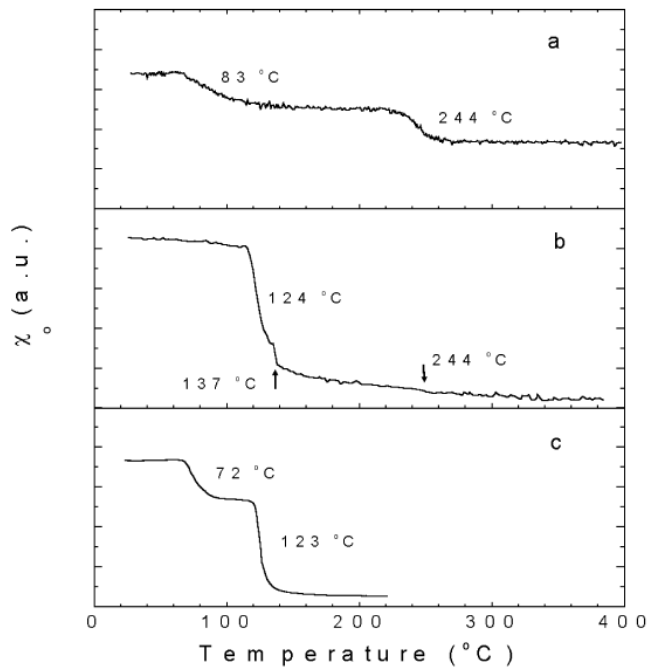


Fig. 1. TMA curves for $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ alloys: (a) in the as-cast state (sample A); (b) after 100 h of annealing at 1100°C (sample A); (c) after 504 h of annealing at 1100°C (sample B, obtained in Ref. [16]).

A second drop of the initial susceptibility occurs at 244°C . The latter is within the expected value for the phase 1:12 [19]. In addition, there is a transition at 753°C that we assign to $\alpha\text{-(Fe,W)}$. For pure $\alpha\text{-Fe}$ T_c equals 770°C [20]. XRD analysis also confirmed

that these are the phases that crystallize from the melt. After annealing for 100 h (Fig. 1b), a major and well-defined transition at $T_C = 124^\circ\text{C}$ appears. However, at 244°C a very slight knee is still observed. Above this temperature the signal does not drop to zero indicating the presence of $\alpha\text{-(Fe,W)}$. Fig. 1c shows the TMA curve exhibited by sample B. In this sample the amount of the 3:29 phase only reached 73 wt.%. It coexisted with $\text{Nd}_2(\text{Fe,W})_{17}$ (25% wt.) and $\alpha\text{-(Fe,W)}$ (2% wt.). The Curie temperature measured for the 3:29 phase in both samples is the same, suggesting that the chemical composition of the phase formed is similar.

The experimental XRD pattern of sample A is plot in Fig. 2 (open dots). The pattern qualitatively resembles that of the 3:29 phase. However, near $2\theta=45^\circ$ the most intense reflection of $\alpha\text{-Fe}$ is observed (marked by an arrow in the figure). As structural model for the 3:29 phase we employed the one reported by Kalogirou et al. (i.e., monoclinic symmetry with space group $A2/m$) [14]. According to the features observed in the TMA curve, $\alpha\text{-(Fe,W)}$ and $\text{Nd}(\text{Fe,W})_{12}$ coexist with $\text{Nd}_3(\text{Fe,W})_{29}$. Therefore these were the additional phases considered in the Rietveld refinement. For 1:12 it was assumed a ThMn_{12} -type crystal structure (space group $I4/mmm$, No. 139). At the bottom of the figure we have plotted the difference between the calculated (solid line) and experimental (open dots) XRD patterns, the vertical bars marking the 3:29 phase. Table 1 compares the results of the quantitative XRD phase analysis for samples A and B. It is emphasized that, in spite of the severe reduction in the annealing time, the amount of 3:29 phase was notably increased, indicating the advance made in the present study due to the preparation procedure followed.

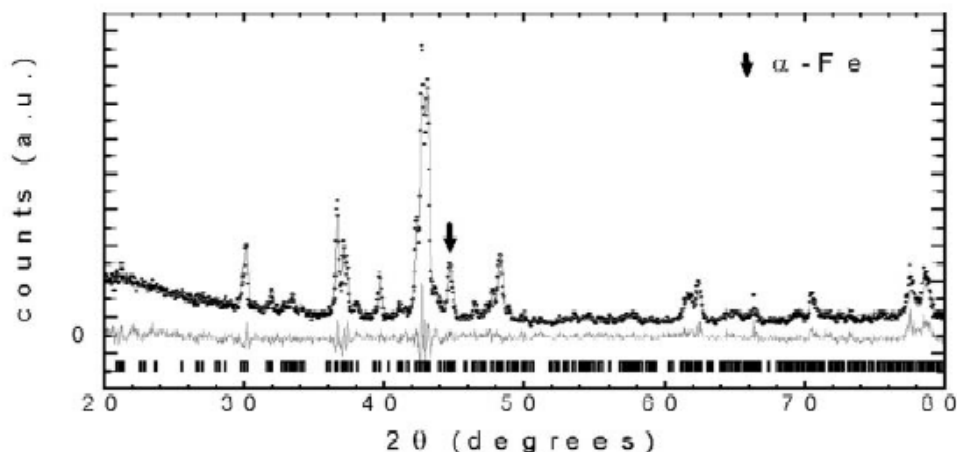


Fig. 2. Experimental (open dots) and calculated (solid line) X-ray powder diffraction patterns of $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ (sample A). At the bottom of the figure are a plot of the residual between both XRD patterns, and the peak marks of the phase 3:29. The arrow indicates the most intense reflection of $\alpha\text{-Fe}$.

The cell parameters, crystallographic density (ρ_x), and agreement factors for the refinement are listed in Table 2. A slight difference in the lattice parameters, and therefore in ρ_x for the 3:29 phase was found in comparison with sample B (see Ref. [16]).

Table 1
Phase composition of $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ alloys annealed at 1100°C for 100 h (sample A) and 504 h (sample B)

Sample	Nominal composition	Annealing conditions (temp. (°C)/time (h))	Phases identified by XRD (wt.%)			
			2:17	3:29	1:12	$\alpha\text{-(Fe,W)}$
A	$\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$	1100/100	–	90	2	8
B	$\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$	1100/504 ^a	25	72	–	2

^a Sample obtained in Ref. [16].

Fig. 3 shows the microstructure of sample A. In the backscattered image we observe a dark gray majority region (matrix), a light gray minor region and small brilliant particles. In addition, some pores (black zones), which are attributed to the preparation

method employed, are also present. The X-ray microanalysis spectra reveal that the dark and light gray zones are quite similar. According to XRD and TMA results the amount of 1:12 is very low, so it is suggested that the different contrast between them results from the formation of grains of the 3:29 intermetallic with different chemical composition.

Table 2

Cell parameters and crystallographic density (ρ_x) of $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ obtained from a Rietveld refinement of powder XRD pattern based on the space group $A2/m$

$a=10.612(6) \text{ \AA}$	$b=8.577(7) \text{ \AA}$	$c=9.742(4) \text{ \AA}$	$\beta=96.745(4) \text{ \AA}$
$V=880.72(8) \text{ \AA}^3$	$\rho_x=7.449 \text{ g/cm}^3$	$Z=2$	

$R_p=9.77\%$; $R_{\text{expect}}=7.50\%$; $R_{\text{wp}}=12.49\%$;
 $S=1.66\%^a$.

2θ range: $20-80^\circ$ with step increment of 0.040° .

Number of reflections: 620.

Number of observations: 1500.

Function profile: pseudo-Voigt.

[2^a $S=R_{\text{wp}}/R_{\text{expect}}$.

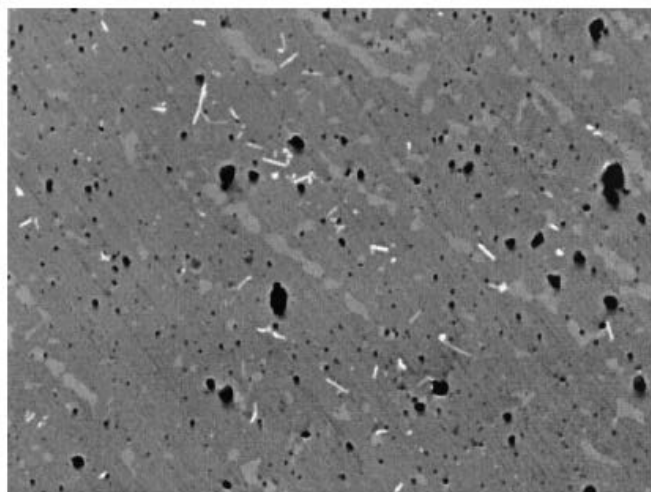


Fig. 3. Back scattered electron micrograph of $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ alloy (magnification, $\times 550$; horizontal width, $240 \mu\text{m}$).

The X-ray microanalysis spectrum of the brilliant regions reveals that they are composed of Fe and W. The Rietveld analysis showed a slight increase in the lattice parameter for the α -Fe formed ($a= 2.879(2) \text{ \AA}$; cell volume= 23.868 \AA^3) in comparison with that of non-substituted α -Fe ($a= 2.8665 \text{ \AA}$; cell volume = 23.5535 \AA^3 [21]. This suggests that these particles are that of α -(Fe,W).

At room temperature the saturation magnetic moment per gram was estimated to be equal to 96 emu/g. In this determination we took into account the amount of the different minority phases present in the specimen.

In summary, the preparation procedure employed suppressed the existence of unmolten W particles in the as-cast and annealed $\text{Nd}_3\text{Fe}_{27.5}\text{W}_{1.5}$ sample. In our opinion, the results obtained are mainly attributed to a better incorporation of tungsten during arc melting into the phases that crystallize from the melt. The method could be effective in the synthesis of other rare earth transition metal alloys containing elements with a high melting point. A noticeable increment in the traditional procedure previously used. The structure was satisfactorily described as monoclinic with the space group $A2/m$ (type $\text{Nd}_3(\text{Fe, Ti})_{29}$). XRD, TMA and microstructural analyses revealed the coexistence of 3:29 and α -(Fe,W) phases.

Acknowledgements

This work was partially supported by 'Concurso Alma Mater 1997' (University of Havana).

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