A comparative study of magnetostrictive strain in Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$-ingot and Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$-melt spun

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Abstract: In this work, the structural and magnetic properties of ingot and melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compounds have been investigated. The structural characterization of the compounds, by X-ray powder diffraction, is evidenced for a monoclinic Nd$_3$(Fe,Ti)$_{29}$-type structure (A2/m space group). A 2-type FOMP have been observed in the magnetic AC susceptibility curves of the ingot and melt-spun compounds. Magnetostriction and linear thermal expansion measurements have been performed by the standard strain gauge method in magnetic fields up to 1.5 T, and temperature range of 77 to 575 K. The calculated values of the ordering temperature, the room temperature saturation magnetization for the melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound are several times smaller than the corresponding values obtained in ingot Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound. The above obtained results have explained the behavior of measured values of spontaneous volume, longitudinal and transverse magnetostriction.

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Keywords: 3:29 Intermetallic compounds; X-ray diffraction; thermal expansion; magnetostriction.

Introduction

Rare-Earth (R) iron intermetallic compounds based on R$_3$ (Fe, M)$_{29}$ (R is a Rare Earth or Y, and M are stabilizing elements, Ti, V, Cr, Mo,...) with Nd$_3$(Fe,Ti)$_{29}$-type structure and their interstitial compounds have attracted considerable interest. This is because some of them, like Sm$_3$(Fe, M)$_{29}$N$_5$, exhibit excellent hard-magnetic properties [1]. The Nd$_3$(Fe,Ti)$_{29}$-type compounds (3:29) crystallize in the A2/m space group and consist of rhombohedral Th$_2$Ni$_{17}$-type (2:17R) and tetragonal ThMn$_{12}$-type (1:12) segments in a ratio of 1:1 [2]. In this type of compounds, the Rare Earth ions occupy two crystallographic sites (2a and 4i), and the Fe atoms occupy eleven sites (one 2c, one 4e, one 4g, four 4i and four 8j) [3].

Partial replacement of Fe by Co in 3:29 influences strongly the local anisotropy, the structure, and magnetic properties of these compounds. Co may substitutes preferentially at Fe$_1$ (2c), Fe$_8$ (8j) and Fe$_{11}$ (4e) for partial replacement of Fe [4]. There, the Fe atoms couple with a negative exchange interaction with the neighboring Fe atoms. The substitution of Co leads to an increase of $T_c$ by reducing the negative contribution of antiferromagnetic coupled sites on the 3d sublattice [4,5]. Ti, Mo and V also occupy Fe$_2$ (4i), Fe$_3$ (4i) and Fe$_6$ (4g) sites where the sites of dumb-bell Fe atoms are found [6]. However, for high Co concentrations, Co atoms are positioned in the dumb-bell sites [7]. For more than 40% Co, when the amount of the stabilizing atom is low, a disordered modification of the hexagonal Th$_2$Ni$_{17}$-type structure is formed. It is commonly believed that 3:29 structure exists only for light rare earth based compounds [8]. For heavy rare earth compounds beyond Tb, a different type of structure may be expected [9]. However, the formation of

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3:29 phase in R₃(Fe₁₋ₓCoₓ)₂₉,M₄ system was found for more than 40% substitution of Fe by Co atom for a large amount of stabilizing atom such as R = Gd, and M = Cr with y = 4–7 [10] and R = Sm, M = Cr [11] with y = 4.5–7.

There are some measurements reported on the magnetic properties of ingot [12-15] and melt-spun Pr₃(Fe, Co, Ti)₂₉ ferromagnetic compounds [16, 17]. Shah et al. [12,13] reported the effects of Co substitution for Fe on the magnetocrystalline anisotropy and site occupancies of Pr₃(Fe₁₋ₓCoₓ)₂₇₅Ti₁₅ (x ≤ 0.3) alloys. The Rare Earth sublattice anisotropy is found to dominate over the Fe sublattice anisotropy at room temperature and the easy magnetization direction (EMD) is found to be along the b-axis of the monoclinic structure for Pr₃Fe₂₄.₇₅Co₂₇₅Ti₁₅ and away from the b-axis for other concentrations. The hard magnetization direction (HMD) except for x = 0, in all other compounds, is almost in the a-c plane [12]. The saturation magnetization increases with Co concentration at both 5 and 300 K. A large increase in Curie temperature has been found [13]. The Curie temperature and saturation magnetization values observed in the melt-spun alloys were lower than those observed in fully crystalline alloys [16].

Some reports are available on the magnetic and magnetoelastic properties of the R₃(Fe, T)₂₉ compounds (R = Y, Ce, Nd, Pr, Tb, and Gd and T = Ti, and Cr) [18-23]. A large spontaneous magnetostriction and Invar-like behavior in the thermal expansion coefficient have been observed in the vicinity of T_C in these series. This offers the possibility of increasing the ordering temperatures by introducing interstitial atoms that suggest promising properties for hard permanent magnets [24,25]. In this work, we have studied the structure, magnetic properties, and the existence of magnetovolume effect in the ingot and melt-spun Pr₃Fe₂₄.₇₅Co₂₇₅Ti₁₅ compounds. The magnetoelastic effects of these compounds between 77 to near T_C are studied by measuring the magnetostriiction and thermal expansion using strain gauge method. To our knowledge, these measurements so far have not been studied.

**Experimental**

Pr₃Fe₂₄.₇₅Co₂₇₅Ti₁₅-ingots were prepared by arc melting of high-purity (at least 99.9%) of the constituent elements. In order to maximize the amount of R₃Fe₂₉,M₄ phase, the ingots were subsequently annealed in sealed quartz tubes under protective argon atmosphere at 1323 K for a period of three days then followed by quenching in water. Pieces of the ingots were then cast into ribbons using the melt-spinning technique, in an argon atmosphere with employing linear wheel speed of 20 m/s. The ribbon samples were annealed for 20 min at 1323 K. The phase purity of the prepared samples was examined by X-ray diffraction analysis that was performed at RT using CuKa radiation. The XRD data were analyzed using a commercial TOPAS package and Fullprof program. The Bragg diffraction patterns were plotted using Fullprof program. The crystallite size was calculated from the XRD peak broadening of the strongest peak (1-13) at 42.5° using Scherer’s formula. Crystalline density of the samples was obtained from TOPAS package. Magnetization curves of the samples were recorded using a pulsed field magnetometer at room temperature applying external magnetic fields up to 5 T. The temperature dependence of the low-field AC magnetic susceptibility _x_(ω) was measured between 100 and 300 K at 333 Hz with an AC magnetic field of 50 Am⁻¹ peak value using Lake-Shore AC susceptometer model 7000. Magnetostriction and linear thermal expansion (LTE) measurements were performed by the standard strain gauge method on disk-shaped samples of 6 mm diameter and 3 mm thickness in magnetic fields up to 1.5 T, and temperature ranging from 77 to 575 K. The spontaneous volume magnetostriction _ω₀_ was calculated as _ω₀_ = 3[(Δl/l)_exp - (Δl/l)_lat], where (Δl/l)_exp = [(l (T) - l (77 K)) / l (77 K)] and (Δl/l)_lat is the lattice contribution that can be obtained from the extrapolation of the paramagnetic regime of the LTE curve, where only the non-magnetic inharmonic phonon contribution is expected. The extrapolation has been performed using the Grüneisen–Debye model, with a Debye temperature of _T_D_ = 450 K [10]. The magnetostriction was measured (with the accuracy of 2×10⁻⁶) parallel (longitudinal magnetostriction, _λₚₚ_) and normal (transverse magnetostriction, _λₚₜ_) to the applied field direction. It should be emphasized that no significant difference was observed between the strains measured in the plane and perpendicular to the plane of the disc of the samples, suggesting the absence of any preferred orientation effects.

**Results and discussion**

The XRD patterns for annealed ingot and melt-spun of Pr₃Fe₂₄.₇₅Co₂₇₅Ti₁₅ are presented in Fig. 1.
The data were analyzed using commercial TOPAS package and Fullprof program. Results of the Rietveld analysis indicate that the main phase of each sample has the Nd$_3$Fe$_{27.5}$Ti$_{1.5}$-type structure with monoclinic symmetry (A2/m space group). In addition, there is some amount of α-Fe (S. G. Im3m) phase. The strongest impurity peak of α-Fe (20 ~ 44.65°) has been marked on X-ray diffraction patterns of Fig. 1. Rietveld analysis gave a phase distribution of 95.5 Pr$_3$ (Fe, Co, Ti)$_{29}$, and 4.5 wt.% α-Fe for the ingot and 74.3 Pr$_3$ (Fe, Co, Ti)$_{29}$ and 25.7 wt.% α-Fe for the melt-spun sample, respectively. Phase composition, unit cell parameters, crystalline size and crystalline density of the monoclinic ingot and melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ are summarized in Table 1. A trace of α-Fe phase is also reported in the other ingot Pr-based compounds [26]. Gjoka et al. [17] in the melt-spun Nd$_3$Fe$_{27.5}$Ti$_{1.5}$ and Pr$_3$Fe$_{27.5}$Ti$_{1.5}$ alloys and K. Sirisha et al. [16] in the melt-spun Pr$_3$ (Fe$_{1-x}$Co$_{0.2}$)$_{27.5}$Ti$_{1.5}$ annealed alloys found the 3:29 phase and strong presence of α-Fe phase. A significant decrease of the cell volume is observed from 886.383 to 843.955 Å$^3$ with respect to the bulk sample, which represents a lattice contraction of about 5%. This difference was observed in other melt-spun alloys that have smaller crystalline size with respect to the bulk sample [16,17].

Fig. 1 X-ray diffraction of (a) ingot and (b) melt spun of Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound. The circles represent the raw data. The solid line represents the calculated profile. Vertical bars indicate the position of Bragg peaks for the 3:29, 1:12, and α-Fe structures, respectively. The lowest curve is the difference between the observed and the calculated patterns. The strongest impurity peaks are marked with (■) for α-Fe phase.
Table 1 The phase composition and unit cell parameters of the monoclinic ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds; space group \( \text{A2/m} \).

<table>
<thead>
<tr>
<th>sample</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( \beta ) (°)</th>
<th>( V ) (Å³)</th>
<th>Crys. Size (nm)</th>
<th>Crys. Density (g/cm³)</th>
<th>( R_{wp} )</th>
<th>( R_{exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>melt-spun</td>
<td>10.250</td>
<td>8.609</td>
<td>9.631</td>
<td>96.774</td>
<td>843.955</td>
<td>21.958</td>
<td>7.645</td>
<td>15.9</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Figure 2, illustrates the magnetic isotherms measured at room temperature. The room temperature saturation magnetization for ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds deduced from the law of approach to saturation are 142.4 and 132.5 emu/g, respectively. It is known that metallic iron presents a saturation magnetization of 220 emu/g at RT. Therefore, the saturation magnetization of 3:29 phase for melt-spun sample decreases from 132.5 to 102.2 emu/g compared to the bulk sample. In the inset of Fig. 2, we display the room temperature hysteresis loops for ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds. The coercivity often increases in alloys that are melt-spun to form nanocrystalline alloys due to smaller crystalline size [16].

Figure 3 shows the real part of the magnetic AC susceptibility versus temperature for ingot and melt-spun compounds. Peaks are observed at 190 K and 210 K, in the magnetic AC susceptibility of ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds, respectively. Markandeyulu et al. [27] reported the presence of a type-2 FOMP (first order magnetization processes) in the temperature range between 5 K and 200 K for \( \text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5} \) \((x = 0-0.4)\). Gholizadeh et al. [28], observed the FOMP of type 2 using the singular point detection (SPD) technique from 5 to 300 K, in \( \text{Tb}_3(\text{Fe}_{28-x}\text{Co}_x)_{V_{1.0}} \) \((x = 0, 3, 6)\) polycrystalline compounds. The observed maximum in AC susceptibility can be attributed to type-2 FOMP transition in ingot and melt-spun compounds.

Fig. 2 The magnetic isotherms measured at room temperature for ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds. Inset: hysteresis loops at 300 K of ingot and melt-spun \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds.
The measured linear thermal expansion (LTE), the LTE coefficient, \( \alpha \), and the spontaneous volume magnetostrictiv, \( \omega_s \) (T), for ingot and melt-spin \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compounds are displayed from 77 to 575 K in Fig. 4. The magnetic ordering temperature \( (T_C) \) can be obtained accurately from the LTE coefficient data showing a well-defined anomaly at \( T_C \). The values of \( T_C \) are found to be 502 K and 331 K for ingot and melt-spin samples, respectively. The results indicate a reduction in the \( T_C \) values for the melt-spin compound compared to ingot. This reduction was also reported by Sirisha et al. [16] in melt-spin \( \text{Pr}_3 \) (Fe, Co, Ti) 29 compounds that has been attributed to the increasing negative contribution of antiferromagnetic coupled sites on 3d sublattice. The average LTE coefficients below magnetic ordering temperatures are almost \( 8 \times 10^{-6} \) and \( 6.5 \times 10^{-6} \) K\(^{-1}\) for ingot and melt-spin, respectively. Fig. 4 (c) shows the spontaneous volume magnetostrictic, \( \omega_s \) (T), for two samples. The large magnetovolume effect observed in ingot compound is expected to originate from the dependence of the exchange interaction on distance and also the effect of volume on the 3d sublattice magnetic moment [20]. It can be seen that as the temperature increases from 77 K to \( T_C \), \( \omega_s \) decreases from \( 8.3 \times 10^{-3} \) and \( 0.5 \times 10^{-3} \) to near zero for ingot and melt-spin \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \), respectively. The non-zero value of \( \omega_s \) beyond \( T_C \) indicates the existence of strong short-range magnetic correlations similar to those found in other \( \text{R}_3\text{Fe(Ti)}_2 \) compounds [18, 19]. However, the magnitude of \( \omega_s \) (77 K) obtained for the ingot is much bigger than the melt-spin value.

It is well known that the major contribution to \( \omega_s \) of intermetallic compounds originates from the spontaneous volume magnetostriction of the iron sublattice arising from the exchange interactions between the magnetic moments of the Fe atoms. The unit cell volume of ingot and melt-spin is 886.383 and 843.955 Å\(^3\), respectively (see Table 1). The values of \( T_C \) and the saturation magnetization observed for the melt-spin are smaller than the ingot. In the ingot sample, the substitution of Co leads to an increase of \( T_C \) and saturation magnetization [5]. However, the latter values are found to be smaller for the melt-spin samples of the same composition having lower unit cell volume and higher impurity \( \alpha \)-Fe phase [16]. It is worth mentioning that the value of unit cell volume of these compounds influence on different values and signs of the Fe-Fe exchange interactions on the 3d sublattice magnetic moments [29]. The Fe atoms couple with a negative exchange interaction at Fe1 (2c), Fe8 (8j) and Fe11 (4e) sites with their neighboring atoms in monoclinic structure where there are two Fe atoms in a distance closer than 2.45 Å [29]. The decrease of the unit cell volume observed in the melt-spin \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) compound decreases net exchange interactions by increasing the negative contribution of antiferromagnetically coupled sites on the 3d sublattice. Therefore, the lower values of \( T_C \), \( M_S \) and \( \omega_s \) determined for the melt-spin \( \text{Pr}_3\text{Fe}_{24.75}\text{Co}_{2.75}\text{Ti}_{1.5} \) with respect to the ingot sample can be attributed to the much lower value of the unit cell volume. In addition, free \( \alpha \)-Fe atoms as well as other impurity phases found may cause a variation of the actual Fe, or Co concentrations in
the alloy composition of the samples. The α-Fe phase can produce short-range ferromagnetic interaction originated from magnetic phase separation in samples [30]. The existence of strong short-range ferromagnetic interaction has been found in the non-zero value of \( \omega_s \) beyond \( T_C \) of samples. The higher value of α-Fe phase in the melt-spun Pr\(_7\)Fe\(_{24.75}\)Co\(_{2.75}\)Ti\(_{1.5}\) with respect to the ingot sample may extremely decrease the long range ferromagnetic interaction and increase the short range ferromagnetic interaction in Fe sites. Therefore, the increase of short range ferromagnetic interaction may explain the lower values of \( T_C \), \( M_S \) and \( \omega_s \) determined for the melt-spun Pr\(_7\)Fe\(_{24.75}\)Co\(_{2.75}\)Ti\(_{1.5}\) sample with respect to the ingot sample.

Fig. 4 Temperature dependence of the measured linear thermal expansion (LTE) and the LTE coefficient, \( \alpha \), for (a) ingot and (b) melt spun of Pr\(_7\)Fe\(_{24.75}\)Co\(_{2.75}\)Ti\(_{1.5}\). (c) Display the spontaneous volume magnetostriction, \( \omega_s \) (T), of samples.
Isothermal curves of the longitudinal magnetostriction ($\lambda_{pa}$) for ingot and melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ at selected temperatures are shown in Fig. 5. $\lambda_{pa}$ of both samples shows parabolic behavior at all temperatures tending to saturate near $T_C$. In addition, saturation trend of $\lambda_{pa}$ is consistent with the fact that the anisotropy field of Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound is determined to be 1.2 T at room temperature [12]. It can be noted that $\lambda_{pa}$ values versus field strength for the ingot is several times larger than the values for the melt-spun. In accordance with the above results, the lower values of $\lambda_{pa}$ observed for the melt-spun relative to the values obtained for the ingot sample is attributed to the higher value of the unit cell volume of the latter sample. In addition, the value of $\lambda_{pa}$ at maximum applied field decreases with temperature. The non-zero values of $\lambda_{pa}$ beyond the ordering temperature for melt-spun sample can be due to the presence of α-Fe in the compound.

In Figure 6; the transverse magnetostriction ($\lambda_{pe}$) of the ingot and melt-spun samples are plotted versus the applied fields at selected temperatures. $\lambda_{pe}$ passes through a minimum at different applied fields and higher temperatures for the ingot and the melt-spun samples. The EMD for the Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound is along the $b$-axis and there is an anisotropy field of 1.2 T at RT in the $a$-$c$ plane of the monoclinic structure [12]. The analysis of the present data may the of follows; low temperatures, where the maximum applied field ($H$) is smaller than anisotropy field ($H_a$) and consequently the magnetisation vector rotates in the $a$-$c$ plane, $\lambda_{pe}$ for the ingot sample shows a decrease. Finally, when $H > H_a$, the magnetization vector rotates toward the applied field and then increases with the applied field and reaches to a small value at $T_C$. In the case of melt-spun sample, $\lambda_{pa}$ behaviour is nearly the same, except that the minimum of the curves occur at lower applied fields. The results and behavior of $\lambda_{pa}$ and $\lambda_{pe}$ versus magnetic field at different temperatures for the ingot and melt-spun samples can be related to their different microstructure, grain size and their crystallographic texture. Future systematic experimental investigations should be carried out to elucidate the anisotropic $\lambda$ behavior in these compounds.

![Isothermal curves of the longitudinal magnetostriction of (a) ingot and (b) melt spun of Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound as a function of applied field at selected temperatures.](image-url)
Conclusion
The type of the results observed for the linear and volume magnetostriction for both studied samples are believed to belong to the main Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ phase. The lattice parameters refined show a reduction in the melt-spun compound with respect to ingot compound. The room temperature saturation magnetization of 3:29 phase for ingot and melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compounds deduced from the law of approach to saturation (LAS) are 132.5 and 77.7 emu/g, respectively. The 2-type FOMP has been observed at 190 K and 210 K, in the magnetic AC susceptibility of ingot and melt-spun compounds, respectively. The magnetic ordering temperatures obtained from the LTE coefficient, are 502 K and 331 K for ingot and melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compounds, respectively, indicating a reduction in the $T_C$ values for the melt-spun compound. The spontaneous volume magnetostriction obtained from the extrapolation of the paramagnetic regime of the LTE curve and the longitudinal and transverse magnetostriction values measured for ingot Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound are several times larger than the melt-spun. The observed magnetic behaviors in melt-spun Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compounds are related to the different values and signs of the Fe-Fe exchange interactions on the 3d sublattice magnetic moments originated from the volume effect. The values of the longitudinal and transverse magnetostriction at the maximum applied field decreases and reaches

**Fig. 6:** Temperature dependence of the transverse magnetostriction of ingot and melt spun of Pr$_3$Fe$_{24.75}$Co$_{2.75}$Ti$_{1.5}$ compound as a function of applied field at selected temperatures.
to a small value at $T_C$. Future systematic experimental investigations should be carried out to elucidate the magnetostrictive behavior in these compounds.

References
[2] O. Kalogirou, V. Psycharis, L. Saettas, and D.N. Niarchos, “Existence range, structural and magnetic properties of Nd$_8$Fe$_{27.5}$Ti$_{1.5}$-$_{0.0}$ and Nd$_8$Fe$_{27.5}$Ti$_{1.5}$-$_{0.1}$N$_2$ (0.0 $\leq y \leq$ 1.5)” J. Magn. Magn. Mater. 146 (1995) 335-345.
[19] A. Gholizadeh, N. Tajabor, F. Pourarian, “A study on magnetoeelastic properties of Tb$_3$(Fe$_{28}$,Co$_x$)$_{V_{1.0}}$ (x=0, 3, 6) compounds” Physica B 407 (2012) 2816-2819.


