

Structural and Magnetic properties of nanocrystalline $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_y$ alloys

L. Bessais¹, R. Fersi² and N. Mliki²

¹CMTR, ICMPE, UMR7182, CNRS–UPEC, 2-8 rue Henri Dunant F-94320 Thiais, France

²LMOP, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Tunis, Tunisia

Keywords: Nanomaterials, Rares earth, Magnetic properties, X-ray diffraction, Transmission Electron Microscopy.

Abstract

We study the influence of the insertion of a light element, such as carbon or hydrogen, on the structural and magnetic properties of the Pr_2Co_7 compounds. The characterizations were performed by powder X-ray diffraction, transmission electron microscopy and thermomagnetic measurements. The X-ray diffraction of these alloys has shown that the $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_y$ phases adopt a hexagonal type Ce_2Ni_7 type structure. The Rietveld analysis points out a lattice expansion after carbon insertion. Moreover, we have shown that the insertion of carbon or hydrogen is an effective way to increase the Curie temperature without changing the nature of the ferromagnetic transition. This could be due to the strengthening of exchange interactions. Important modifications of the anisotropy and coercivity of the compounds are observed to depend on the nature of the inserted element.

Introduction

The study of magnetic properties of rare-earth (R) – 3d transition metals (M) intermetallic compounds has been a subject of great interest from both scientific and applications point of view. This interest is explained by the very rich and exceptional properties of these alloys, which arise from the presence in the same compounds of the outer well delocalized 3d electrons and well localized and anisotropic 4f electronic shell. This combination of R and M elements can give rise to materials exhibiting high Curie temperature, given by the strong exchange interaction between 3d electrons of M metals, and a strong anisotropy provided by the rare earth 4f electrons [1]. The insertion of a light element, such as N, H, and C in these intermetallic compounds is of great interest both in terms of fundamental scale and technology [2, 3]. Indeed, by introducing a light element in the crystallographic cell, an improvement of intrinsic magnetic properties was observed. The insertion of carbon or hydrogen leads to an increase of lattice parameters of intermetallic compounds. Therefore, the interatomic distances increase and modify the exchange interactions between atoms that have an impact on increasing the Curie temperature under the magneto-volumic effect. In this paper, we study the effect of the insertion on light elements (carbon or hydrogen) on the intrinsic and extrinsic properties of nanocrystalline Pr_2Co_7 alloys [4].

Experiment

The carbides $\text{Pr}_2\text{Co}_7\text{C}_x$ and the hydrides $\text{Pr}_2\text{Co}_7\text{H}_x$ were prepared by melting in an argon atmosphere of high purity. The powder mixtures were milled for 5 h in a high energies ball-mill, which was rotated in two dimensions perpendicular to the horizontal plane. The rotation speed of the mill was closed to 600 tr/min. After milling, the samples, wrapped in tantalum foil, were annealed for 30 min in sealed silica tube under 10^{-6} Torr at different temperatures from 873 K to 1323 K followed by quenching in water. The carbonation and hydrogenation process carried out respectively by a solid-solid and solid-gas reaction [5].

The X-ray diffraction (XRD) patterns were registered on a Bruker diffractometer with CuK α radiation. The counting rate was 22 s per scanning step and the step size was 0.04 °. An internal Si standard was used to measure the unit cell parameter with an accuracy of $\pm 1 \times 10^{-4}$ Å. The pattern refinement was performed using FULLPROF computing code based on the Rietveld technique, in the assumption of Thompson-Cox-Hastings line profile [6, 7]. The goodness-of-fit indicators, R_B and χ^2 , are calculated as usual and described earlier [8]. In order to explore the microstructure of $\text{Pr}_2\text{Co}_7\text{C}_x$ alloys, transmission electron microscopy (TEM) studies were used. The observations were made using a JEOL 2010 FEG microscope operating at 200 kV. A slow scan Camera on a Gatan Imaging Filter was employed for image recording. The composition of the grains was analyzed using the EDX system attached to the microscope. Specimens for TEM were thinned using a Focused Ion Beam (FIB) type FEI Helios 600 Nanolab dual beam.

The Curie temperature T_C were measured on a differential sample magnetometer MANICS in a field of 1000 Oe. T_C was determined from the $M(H)$ curve by extrapolating the linear part of the $M(T)$ curve and finding the temperature value of the intersection with the extended baseline [9, 10]. The magnetization versus applied field hysteresis curves $M(H)$ were measured at $T = 293$ K with a Physical Properties Measurement System (PPMS9) Quantum Design and a maximum field of 90 kOe. The MS values are obtained by extrapolation to zero field of the isothermal magnetization curves. In order to determine the easy magnetization direction (EMD), the XRD investigations were performed on powder samples oriented under an external magnetic field. Field-oriented samples were prepared at room temperature by solidifying the mixture of epoxy resin and the powder specimen in a magnetic field of about 1 T. The same procedure is also used to prepare field-aligned samples for the magnetic anisotropy measurements.

Results and discussion

Structural studies

The X-ray diffraction of these alloys has shown that the $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ phases essentially adopt a hexagonal structure type Ce_2Ni_7 ($P6_3/mmc$ space group). The figure 1 show the diffraction of X-ray refinement of the nanocrystalline $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{0.25}$ compounds. The insertion of carbon and the hydrogen leads to an increase of the lattice parameters, c being more affected than a . The observed expansion of $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ unit cell is about $\Delta V/V = 10$ and 7.16 % respectively for $x = 1$ and 3.75. However, the variation of the c/a ratio with C or H content suggests that the

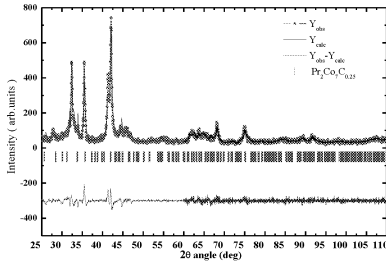


Figure 1: Rietveld analysis for XRD pattern of $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$.

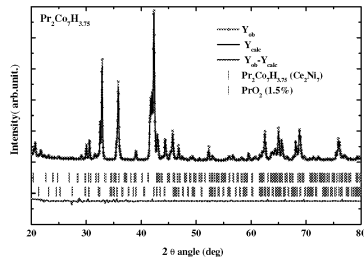


Figure 2: Rietveld analysis for XRD pattern of $\text{Pr}_2\text{Co}_7\text{H}_{0.25}$.

unit cell expansion is anisotropic and more pronounced along the c -axis.

The crystallographic data obtained by Rietveld refinement of the diffraction of X-rays were used to calculate the interatomic distances between nearest neighbors. In nanocrystalline $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ compounds, we notice a slight change in atomic positions of atoms located on sites $12k$ and $4f$. Indeed, the distance $\text{Co}(12k)$ - $\text{Co}(12k)$, $\text{Co}(12k)$ - $\text{Co}(4f)$ and $\text{Co}(4f)$ - $\text{Co}(4f)$ taper while other interatomic distances slightly increase or remain unchanged. The octahedral site $4f$ is formed by two tetrahedra common base $\text{Co}(12k)$ - $\text{Pr}(4f)$ - $\text{Co}(12k)$ - $\text{Pr}(4f)$. Following the insertion of carbon or hydrogen, there is a relative increase in $\text{Pr}(4f)$ - $\text{Co}(12k)$ distances forming the basis of two tetrahedra joined together with a significant increase in those for $\text{Co}(12k)$ - $\text{Co}(12k)$ distances.

Microstructural studies of $\text{Pr}_2\text{Co}_7\text{C}_x$ compounds

The magnetic properties of materials depend on their microstructure. In this context, we undertook a study of the morphology of the samples $\text{Pr}_2\text{Co}_7\text{C}_x$ by conventional transmission electron microscopy TEM and high resolution HRTEM. Based on the result of magnetic measurements, the microstructure of $\text{Pr}_2\text{Co}_7\text{C}$ alloys are chosen in order to study them in details by TEM. For comparison, the parent sample is also included. Figure 2 shows a micrograph bright field Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}$ compounds. The visible aspect is a granular appearance. The corresponding selected area electron diffraction (SAED) patterns are shown in the insert; it exhibits a bright diffraction ring, which is a typical characteristic of nanocrystalline phase. A distribution of fine grains confused with each other. Indeed, the rings are continuous and diffused for $\text{Pr}_2\text{Co}_7\text{C}$ sample, which allows us to say that the grains are much smaller in this sample (<10 - 20 nm).

We systematically analyzed the samples by energy dispersive spectroscopy (EDX) in order to determine the percentages of the elements detected and check that they are well aligned with the stoichiometry of the samples provided by the X-ray. The result shows that the powder is composed of 23% at praseodymium, of 87 % at cobalt; the Carbon can not be detected in these amounts there using this technique. It is also observed the EDX spectrum (Figure 3) the presence of peaks of oxygen (<1 %). The presence of oxygen is due to the oxidation of Pr during the elaboration of $\text{Pr}_2\text{Co}_7\text{C}$ powder. It

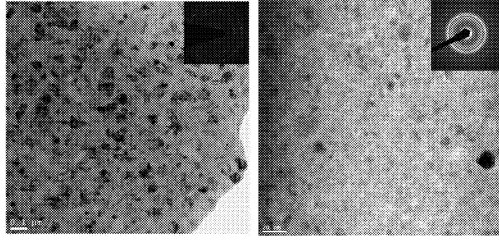


Figure 3: Bright field micrograph, (in insert the selected area electron diffraction) of: Pr_2Co_7 (left), $\text{Pr}_2\text{Co}_7\text{C}$ (right) compounds.

should be noted that we have scored overall in good agreement with these compositions with a 2:7 stoichiometry.

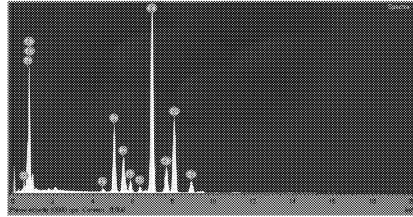


Figure 4: The EDX analysis of $\text{Pr}_2\text{Co}_7\text{C}$ powder.

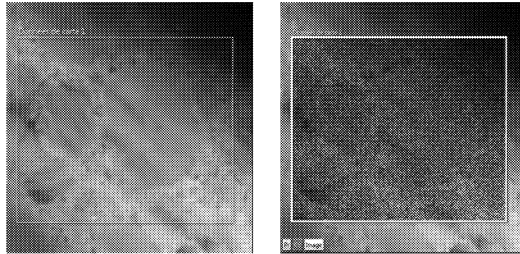


Figure 5: Analysis by X cartography of $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ powder.

Analysis by X cartography thick on a surface of grains of the $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ powder (Figure 4) illustrates the dissolution of the carbon atoms in the Pr-Co matrix. This result confirms the formation of a solid solution Pr-Co-C observed by X-ray diffraction.

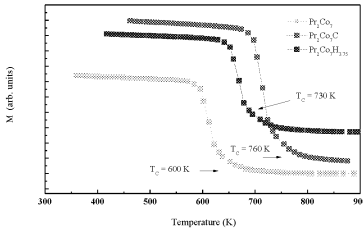


Figure 6: The temperature dependence of the magnetization of Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ compounds.

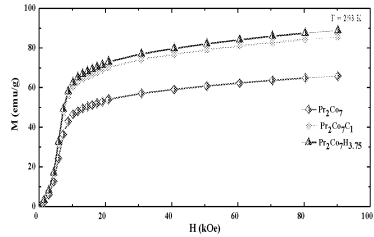


Figure 7: Field dependence of the magnetic moment of Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ compounds.

Intrinsic magnetic properties

The insertion of carbon or hydrogen in nanocrystalline Pr_2Co_7 compounds induced a monotonic increase of the Curie temperature depending on x . It is observed that the Curie temperature increases almost linearly with the concentration of carbon or hydrogen. An improvement of 23.3% and 15% respectively, compared to the starting compounds. This increase is not significant and can not come from stronger exchange interactions type $4f - 3d$ which are an order of magnitude lower than $3d - 3d$ [11], while the $4f - 4f$ are often negligible [12]. It results, in large part, a strengthening of the exchange interaction $3d - 3d$. The insertion of an element such as hydrogen causes the increase of the interatomic distances of the cobalt atoms, and hence the exchange interactions $3d - 3d$. The figure 2 shows the thermal variation of the magnetization of the nanocrystalline Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ compounds.

The magnetization curves of nanocrystalline $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ compounds were measured by an extraction sample magnetometer at room temperature in a magnetic field ranging from 0 to 90 kOe. An insertion of carbon and hydrogen respectively in the $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ compounds induces a significant increase of the spontaneous magnetization compared to $x = 0$, but it does not change the type of their behavior which remains ferromagnetic. The saturation magnetization M_S , are determined from magnetization isotherms, according to the approach to saturation law, $M(H) = MS + a/H^2$ [13]. The values of MS and those converted to the magnetic moment per formula unit. The saturation moment increases from 8.32 to 11.5 and 11.7 $\mu_B/\text{f.u.}$, respectively for $x_C = 1$ and $x_{\text{H}_2} = 3.75$.

Extrinsic magnetic properties

To study the effect of the insert on the coercivity, we measured the coercive field of each of our samples. The figure 8 shows an example, the shape of the hysteresis loops measured at room temperature for nanocrystalline: Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ samples. The allure of these loops shows that these compounds are isotropic and con-

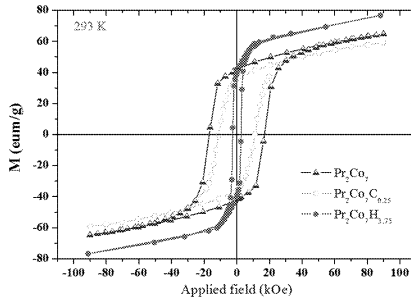


Figure 8: Field dependence of the magnetic moment of Pr_2Co_7 , $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ compounds.

firmly the presence of a single ferromagnetic phase in all samples. The highest coercivities, measured at room temperature for the $\text{Pr}_2\text{Co}_7\text{C}_{0.25}$ and $\text{Pr}_2\text{Co}_7\text{H}_{3.75}$ compounds are respectively: $H_C = 11.5$ kOe and $H_C = 2$ kOe. In addition, the corresponding remanent magnetization are respectively $M_R = 37$ emu/g and $M_R = 45$ emu/g, giving a M_S/M_R ratio of about $0.59 > 0.5$, suggests strong exchange interactions between the adjacent crystallites. This is in good agreement with the small average crystalline size [14]. The decrease in coercivity could be mainly due to the decrease of magnetocrystalline anisotropy after the insertion of carbon or hydrogen. The coercive field depends mainly on the energy of magnetocrystalline anisotropy. Insertion implies a reduction in the contribution of axial 3d subnet and therefore a decrease in coercivity as a function of insertion rate.

Conclusion

We have shown in this study that it is possible to obtain nanocrystalline $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ compounds by high energy mechanical milling. These compounds were prepared in two steps:

- A high energy milling, followed by annealing.
- A carbonation and hydrogenation process realized respectively by a solid-solid and solid-gas reaction.

We have realized the study of the insertion of carbon and hydrogen on the structural and magnetic properties of Pr_2Co_7 compounds. The X-ray diffraction of these compounds shows that $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ phases adopt essentially a hexagonal structure (Ce_2Ni_7 -type). The structural changes induced by the insertion of lightweight elements are causing significant changes fundamental magnetic properties. However, the insertion of carbon and hydrogen in the Pr_2Co_7 unit cell leads to a significant improvement in T_C respectively 23.3% and 15%. This results in the strengthening of exchange interactions which become more positive on increasing the Co-Co distance. When the

study of magnetic properties of extrinsic and $\text{Pr}_2\text{Co}_7\text{C}_x$ and $\text{Pr}_2\text{Co}_7\text{H}_x$ compounds, we noticed a drop in the coercivity in the rate of carbon and hydrogen inserted. This is due to a change in the anisotropy which is no longer axial after insertion.

References

- [1] K. H. J. Buschow, *Ferromagnetic Materials* 7, 297 (1980).
- [2] L. Bessais, C. Djega-Mariadassou, D. K Tung, W. Hing and N. X Phuc, *J. Alloys. Compd.* 455, 35 (2008).
- [3] S. Khazzan, N. Mliki, L. Bessais and C. Djega-Mariadassou, *J. Magn. Magn. Mater.* 322, 224 (2010).
- [4] R. Fersi, N. Mliki, L. Bessais, R. Guetari, V. Russier, and M. Cabie, *J. Alloys Compd.* 14, 522 (2012).
- [5] Sievert, A., *Zeitschrift fur Physikalische Chemie*, 60, 129 (1907).
- [6] H. Rietveld, *J. Appl. Crystallogr.* 2, 65 (1969).
- [7] J. R. Carvajal, *Physica B.* 192, 55 (1993).
- [8] K. Khazzan, N. Mliki and L. Bessais, *J. App. Physics* 105, 103904 (2009).
- [9] L. Bessais, C. Djega-Mariadassou and P. Beaunier *J. App. Physics* 99, 093906 (2006).
- [10] L. Bessais and C. Djega-Mariadassou, *Phys. Rev. B* 63, 054412 (2001).
- [11] K. H. J. Buschow and F. R. Boer, *Physics of Magnetism and Magnetic Materials*, Kluwer Academic Publishing (2003).
- [12] D. Givord and R. Lemaire, *IEEE Trans. Magn.* 10, 109 (1974).
- [13] L. Néel, *Rep. Prog. Phy.* 9, 193 (1948).
- [14] R. Fischer and H. Kronmuller, *Phys. Rev. B* 54, 7284 (1996).