

NANOCRYSTALLIZATION EFFECTS ON THE SPECIFIC HEAT OF Fe-Co-Nb-B

AMORPHOUS ALLOY

J.S. Blázquez^a, M. Millán^a, C.F. Conde^a, V. Franco^a, A. Conde^a*,

S. Lozano-Pérez^b

^a *Dpto. Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla, P.O. Box 1065, 41080, Sevilla, Spain*

^b *Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK.*

Abstract

Specific heat at constant pressure, C_p , was measured on amorphous, nanocrystalline and fully crystalline samples of $\text{Fe}_{60}\text{Co}_{18}\text{Nb}_6\text{B}_{16}$ alloy. Magnetic and calorimetric measurements agree, describing a continuously decreasing Curie temperature of the amorphous phase. A clear enhancement of C_p over the Dulong-Pettit limit has been observed (from 14 to 25 %). Part of the enhancement is due to magnetic (mainly amorphous phase) and electronic contributions, although an excess volume can be inferred from the high value of the slope of C_p versus temperature.

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Nanocrystalline materials are characterized by an important fraction of atoms located at the

* Prof. A. Conde: Tel: (34) 95 455 28 85, Fax: (34) 95 461 20 97,
e-mail: conde@us.es

interfaces, which can yield important differences in their properties with respect to those of conventional systems. These atoms can be considered as if they were in a dilated lattice leading to the definition of an excess volume [1], V_x , which affects several mechanical and thermal properties, e.g. enhancement of specific heat at constant pressure, C_p . This enhancement has been observed for nanocrystalline, quasicrystalline and amorphous structures [1,2,3]. In this paper, measurements of C_p for amorphous, nanocrystalline and fully crystalline $Fe_{60}Co_{18}Nb_6B_{16}$ alloy are reported.

Melt-spun amorphous ribbons were devitrified up to different crystalline volume fraction, X_C , by heating at 20 K/min in a Perkin-Elmer DSC7, differential scanning calorimeter (DSC). The devitrification of this alloy (see inset of Fig. 1) occurs through two exothermic processes, the former ascribed to the nanocrystallization of α -FeCo phase and the latter to the completion of devitrification (mainly α -Fe and $Fe_{23}B_6$ type phases). X_C was calculated from the area below the DSC peak between the onset and the maximum temperature achieved during the corresponding heating treatment, taking into account that the end of the nanocrystallization corresponds to $X_C=0.54$ [4]. DSC was also used to measure the specific heat at constant pressure, C_p , following the procedure described elsewhere [5]. The selected temperature range was low enough to prevent any thermal evolution of the samples. High resolution electron microscopy (HREM) was performed in a Jeol JEM3000F operated at 297 kV. Specific saturation magnetization, σ_s , was measured in a vibrating sample magnetometer (VSM), extrapolating to zero field the magnetization curves obtained under a maximum

Two different temperature ranges were chosen for C_p measurements: a first one from 523 to 723 K and a second one from 523 to 573 K. Figure 1(above) shows the C_p values obtained in a continuous scan for three studied samples: relaxed amorphous, nanocrystalline and fully crystalline samples. For amorphous samples, C_p curves show a clear and broad maximum at 662 K ascribed to the Curie transition of the amorphous phase. The broadening of this peak is related to experimental factors [6] (e.g. temperature gradients in the samples). As nanocrystallization progresses this maximum becomes weaker, being undetected for crystalline volume fractions above ~ 0.45 . Excellent agreement is found with T_C obtained from the derivative of the $\sigma_s(T)$ plots (figure 2).

Reducing the temperature range in the second set of measurements, errors due to baseline drift are minimized. Figure 1(below) shows the C_p at 550 K as a function of X_C . The monotonous decrease was confirmed from a different set of measurements in which the reference furnace of the DSC is filled with the sample heated at an immediately lower temperature instead of an empty pan. A clear enhancement of 25 % in the C_p value with respect to the Dulong-Pettit limit ($DP \sim 485 \text{ JK}^{-1}\text{kg}^{-1}$) is observed. This enhancement, ΔC_p decreases as the nanocrystallization progresses saturating at ~ 14 % for nanocrystalline samples with $X_C > 0.45$.

The value of specific heat at constant volume in the harmonic approximation, C_{VH} , at 550 K is close to DP limit, using the Debye temperature values found for similar alloys (~ 350 K)

[7]. For conventional materials, the constant volume specific heat, C_V , results from addition of different contributions [6]: anharmonic vibrations (C_{VA}), conducting electrons (C_{VE}), equilibrium vacancies in the lattice (C_{VV}), and magnetic contribution (C_{VM}). Moreover, $C_P = C_V + C_D$, where C_D is the dilatation correction. In the following discussion, C_{VV} and C_{VA} will be neglected (temperature is far from the melting point [8]). C_D and C_{VE} linearly increase with temperature. The experimental slope of the C_P curves far from the Curie transition ($m_{CP} = m_{C_{VE}} + m_{C_D} \sim 0.25 \text{ J kg}^{-1} \text{ K}^{-2} = 0.013 \text{ J mol}^{-1} \text{ K}^{-2}$) is almost independent of X_C . Considering $m_{C_{VE}} \sim 0.005 \text{ J mol}^{-1} \text{ K}^{-2}$ (pure Fe [9]), the expression $C_D = (C_{VH} \cdot \gamma)^2 / B \cdot V$ [1,6] yields a bulk modulus $B \sim 50 \text{ GPa}$, where $\gamma \sim 2$ [10] is the Grüneisen parameter and V the molar volume. This value of B would imply an excess volume ~ 0.2 [1], ascribed to the nanocrystalline structure. HREM (Fig. 3) was used to locally measure interatomic distances. Results indicate an increase in the lattice parameter near the surface of the nanocrystals compared to the core region (<8%), although the derived error for ΔV is too large, preventing a quantitative estimation.

C_{VM} contributes to the ΔC_P mainly due to the amorphous phase magnetic transition and C_{VM} of α -FeCo can be neglected as its $T_C \sim 1200 \text{ K}$. Therefore, ΔC_P may decrease as nanocrystallization progresses, as observed. Finally, fully crystalline sample exhibits a similar C_P value than nanocrystalline ones. This could be due to the Curie transition of Fe_{23}B_6 -type phase, slightly above the studied temperature range [11].

Specific heat enhancement over Dulong-Pettit limit has been observed on $\text{Fe}_{60}\text{Co}_{18}\text{Nb}_6\text{B}_{16}$

amorphous and nanocrystalline alloys. Part of the enhancement is due to magnetic (mainly amorphous phase) and electronic contributions. An excess volume of ~ 0.2 could be estimated. Magnetic and calorimetric measurements agree, describing a continuously decreasing Curie temperature of the amorphous phase.

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Figure captions

Figure 1. Above: C_p curves at 20 K/min for samples pre-heated at the indicated temperatures.

Inset: DSC scan at 20 K/min of as-cast alloy indicating the heating temperatures used.

Below: C_p values at 550 K. The Dulong- Pettit limit is $485 \text{ J kg}^{-1}\text{K}^{-1}$.

Figure 2. σ_s curves for the different studies samples. Inset: T_C of the amorphous phase as a function of X_C from VSM and C_p measurements.

Figure 3. HREM image of a nanocrystal at [100] zone axis for the sample heated up to 813 K.

Figure 1

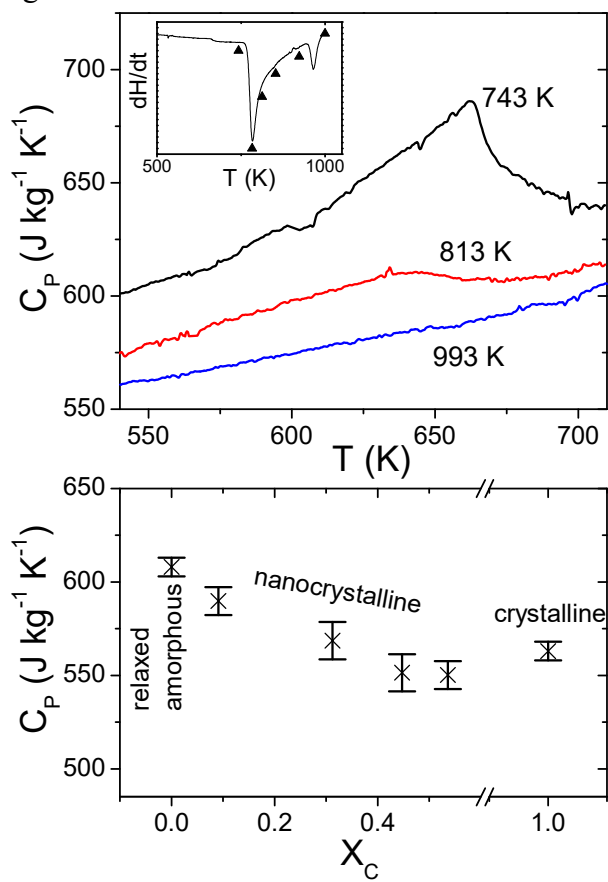
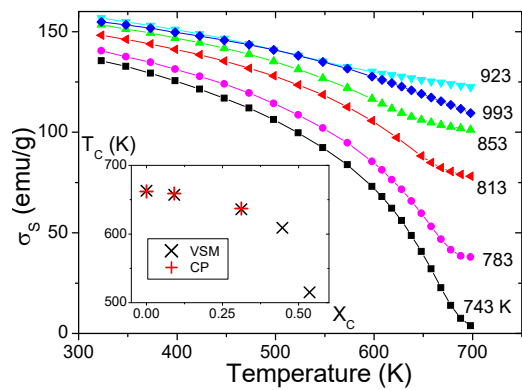
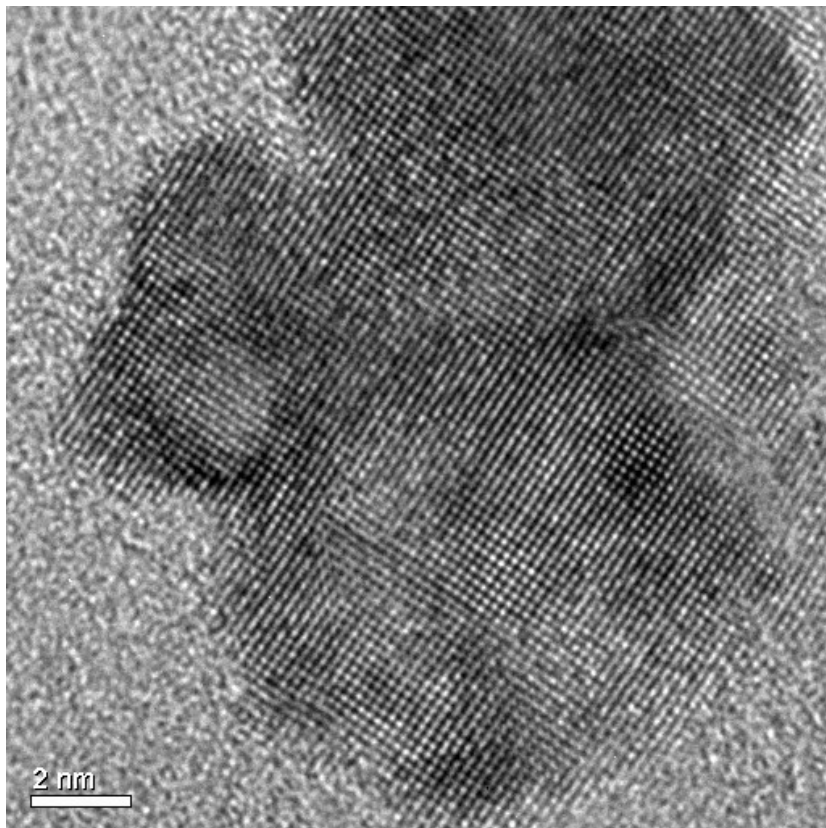


Figure 2





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