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Magnetization studies of binary and ternary Co-rich phases of the Co–Si–B system

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ABSTRACT

CoB, Co_2B, CoSi, Co_2Si and Co_5Si_2B phases can be formed during heat-treatment of amorphous Co–Si–B soft magnetic materials. Thus, it is important to determine their magnetic behavior as a function of applied field and temperature. In this study, polycrystalline single-phase samples of the above phases were produced via arc melting and heat-treatment under argon. The single-phase nature of the samples was confirmed via X-ray diffraction experiments. AC and DC magnetization measurements showed that Co_2Si and Co_5Si_2B phases are paramagnetic. Minor amounts of either Co_2Si or $CoSi_2$ in the CoSi-phase sample suggested a paramagnetic behavior of the CoSi-phase, however, it should be diamagnetic as shown in the literature. The diamagnetic behavior of the CoB phase was also confirmed. The paramagnetic behavior of Co_5Si_2B is for the first time reported. The magnetization results of the phase Co_2B have a ferromagnetic signature already verified on previous NMR studies. A detailed set of magnetization measurements of this phase showed a change of the easy magnetization axis starting at 70 K, with a temperature interval of about 13 K at a very small field of 1 mT. As the strength of the field is increased the temperature interval is enlarged. The strength of field at which the magnetization saturates increases almost linearly as the temperature is increased above 70 K. The room temperature total magnetostriction of the Co_2B phase was determined to be 8 ppm at a field of 1 T.

1. Introduction

Co–Si–B alloys have been studied for the development of soft magnetic materials [1–3]. The ideal microstructure is constituted by an amorphous matrix embedded with nanocrystals formed during controlled heat-treatments. Since the stable crystals to be formed correspond to the Co-rich phases of the Co–Si–B system, it is important to determine their magnetic behavior as a function of applied field and temperature.

Some magnetic properties of the CoSi, Co_2Si, CoB and Co_2B phases have been found in the literature [4–11]. The Co_2Si phase is reported to be paramagnetic [3], while CoB and CoSi are diamagnetic [9–11]. Only the Co_2B phase is ferromagnetic, with a Curie temperature (T_C) in the 425–433 K [5,6,8] temperature interval and a room temperature saturation magnetization of about 47 A m^2/kg [4], or 378 kA/m (0.48 T) using the mass density of 8050 kg/m^3 [5]. Most of these properties were determined by NMR studies.

The magnetocrystalline anisotropy constant K_1 of Co_2B was found to be negative between 77 and ~433 K [12], presents a minimum at 263 K and is zero for temperatures greater than 433 K (T_C). At 77 K, K_1 is very small and the values extrapolated to low temperatures reach zero at about 68 K. Therefore, K_1 vs. T behavior suggests an easy magnetization axis change from a direction within the a–b plane ($T > 68$ K) to a direction along the c-axis for $T < 68$ K [7,8] in the tetragonal structure of $CuAl_2$ type.

Up to now, it has not been reported any magnetic property data of the ternary Co_5Si_2B phase. The ternary rare-earth metal silicoborides compounds $RE_5Si_2B_8$ (RE = Y, Gd, Tb and Dy) are paramagnetic at room temperature [13]. Other silicoborides such as Fe_5SiB_2 and Mn_5SiB_2 are ferromagnetic [14,15] with Curie temperatures close to 785 and 410 K, respectively.

In the present work, the magnetic properties of CoSi, Co_2Si, CoB, Co_2B and Co_5Si_2B phase were evaluated by means of magnetization measurements as a function of the applied field and temperature.

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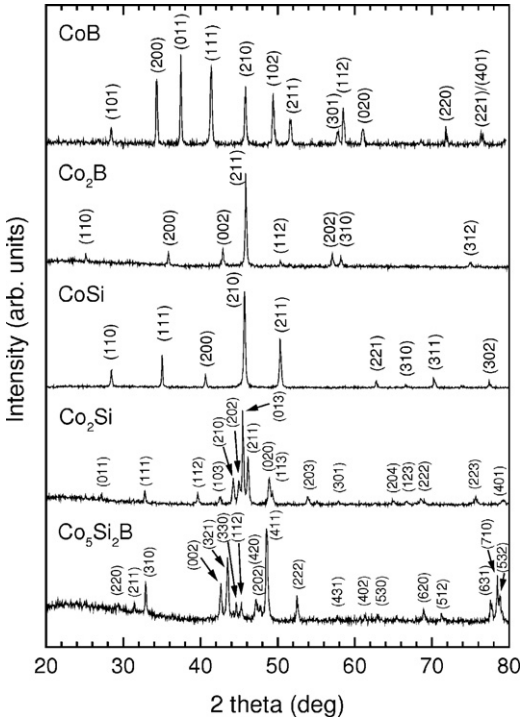

Fig. 1. X-ray diffraction patterns of the samples CoB, Co_2B, CoSi, Co_2Si and Co_5Si_2B single phases.

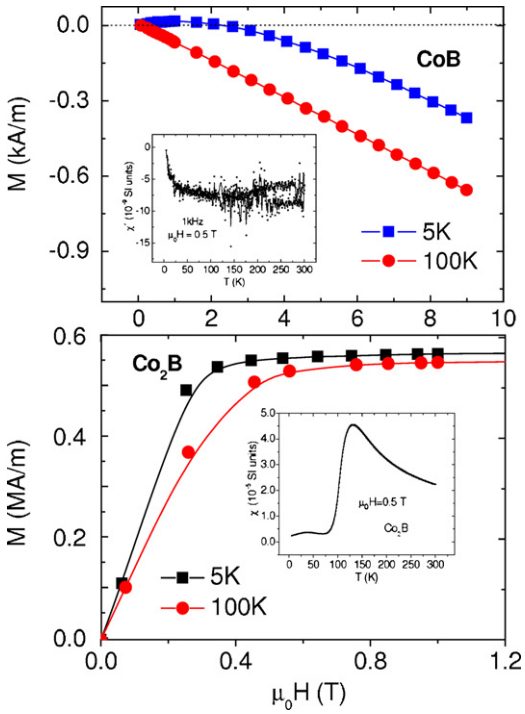

Fig. 2. DC magnetization results vs. applied field and AC susceptibility vs. temperature (inset) of the phases: (a) CoB and (b) Co_2B.

2. Experimental methods

In order to produce the phases of interest, Co–Si, Co–B and Co–Si–B alloys were prepared by arc melting with non-consumable tungsten electrode under titanium-gettered argon (min. 99.995%) from Co (min. 99.93%), Si (min. 99.999%) and B (min. 99.5%) in a water-cooled copper crucible Three melting steps were carried out for each alloy in an effort to produce chemically homogeneous samples. After arc melting all the polycrystalline ingots were encapsulated in quartz tubes under argon, heat-treated at 1000 °C for 50 h then air-cooled. The heat-treated samples were characterized through powder X-ray diffraction in a Shimadzu XRD 6000 diffractometer, with Cu Kα radiation and graphite monochromator. The measurements conditions were: angular interval 2θ from 20° to 80°, angular step of 0.05° and 5 s counting time.

The magnetic behavior characterization of the heat-treated samples was performed by AC susceptibility as a function of temperature (4–300 K) and DC magnetization measurements as a function of the applied field, using a PPMS system from Quantum Design. The DC magnetization measurements were carried out at fixed temperatures for applied fields up to 1.5 T. The samples masses' were in the range of 57–87 mg. The measurements of the longitudinal and transverse magnetostriction of Co_2B (magnetic field parallel and perpendicular to the sample dilatation or contraction direction, respectively) were carried at 290 K using a capacitance dilatometer.

3. Results and discussions

Fig. 1 presents the X-ray diffraction patterns from the different Co–B, Co–Si and Co–Si–B alloys after heat-treatment. In each sample only peaks from the phase of interest were identified, i.e., CoB, Co_2B, CoSi, Co_2Si and Co_5Si_2B.

The DC magnetization vs. applied field (M vs. H) curves at 5 and 100 K and the AC initial susceptibility vs. temperature (χ vs. T curves, insets) of the CoB and Co_2B phases are presented in Fig. 2. It reveals a diamagnetic behavior (negative magnetic moment) of CoB and a ferromagnetic behavior of Co_2B (high value of M) as already observed in other studies [4,6,9]. The change in slope of the Co_2B magnetization curves before saturation for higher temperatures will be discussed later in.

In Fig. 3 the DC magnetization vs. applied field (M vs. H) curves at 4 and 100 K and the AC initial susceptibility vs. temperature (χ vs. T curves, insets) for the CoSi and Co_2Si phases are shown.

The positive results of the magnetic moments and therefore of the susceptibilities and magnetizations, points to a paramagnetic behavior of both phases. The result for Co_2Si agrees with the literature [4], however, the CoSi-phase was determined from NMR studies to be diamagnetic [10,12]. The Co–Si phase diagram [16] shows that the CoSi-phase has a small solubility range (~1.5 at.%), being surrounded by the CoSi + Co_2Si and CoSi + $CoSi_2$ two-phase

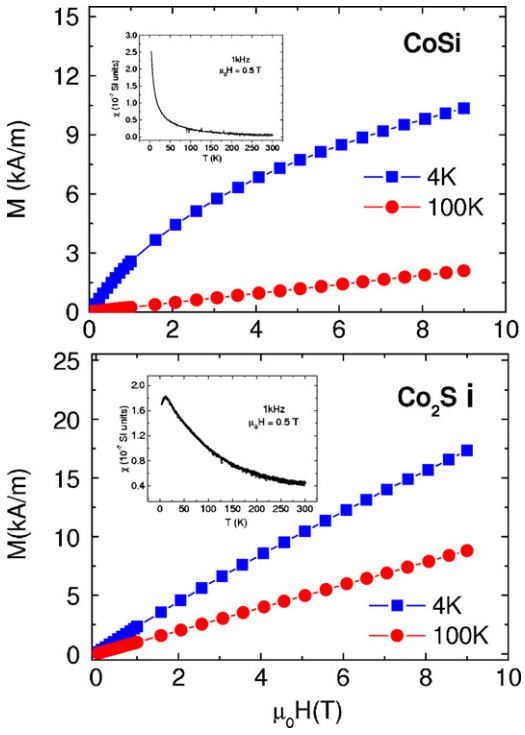

Fig. 3. DC magnetization results vs. applied field and AC susceptibility vs. temperature (inset) of the phases: (a) CoSi and (b) Co_2Si.

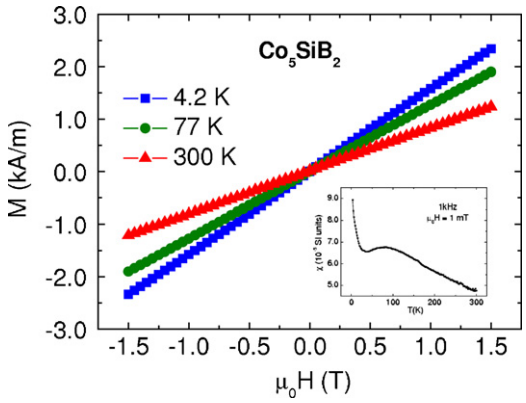

Fig. 4. DC magnetization results vs. applied field and AC susceptibility vs. temperature (inset) of the ternary phase Co_5Si_2B.

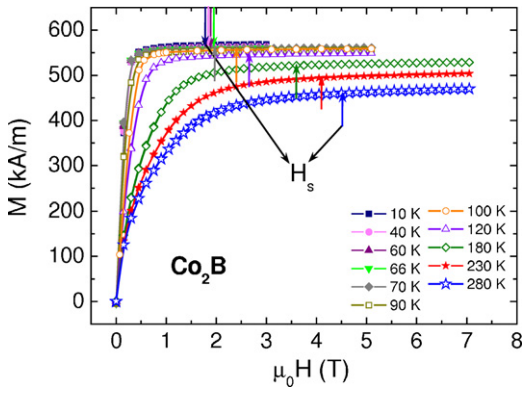

Fig. 5. DC magnetization vs. applied field of the ferromagnetic Co_2B phase for fixed temperatures in the range of 10–280 K.

fields in the Co-rich and Si-rich sides, respectively. From the literature, the $CoSi_2$ phase has a paramagnetic behavior [17]. Therefore, as the diamagnetic signal is usually markedly small, it is likely that a small amount of either Co_2Si or $CoSi_2$ phases were present in the CoSi sample, resulting in the observed paramagnetic-like behavior of CoSi. The Co_5Si_2B ternary phase results are shown in Fig. 4. The magnetization increases linearly with the applied field for the temperatures of 4.2, 77 and 300 K and the susceptibility is positive and small for an applied field of 1 mT and frequency of 1 kHz. Thus, the Co_5Si_2B phase is paramagnetic as Co_2Si and CoB. It is interesting to remind that other borosilicides of transition metals such as Fe and Mn [14,15] are ferromagnetic.

In Fig. 5, the DC magnetization vs. applied field (M vs. H) of Co_2B is plotted for fixed temperatures between 10 and 280 K. At 280 K, a magnetization of 462 kA/m (0.58 T) was determined, consistent with the 378 kA/m obtained at 300 K, since the Curie temperature

Table 1
Parameters calculated using Heisenberg–Ising critical exponent model for saturation magnetization (M_s) for $M_s = M_0\,(1 - T/T_C)^{\beta}$.

β	M_0 (kA/m)	T_C (K)
0.33 (fixed)	72.7	553
0.34 (fixed)	69.3	564
0.35 (fixed)	72.8	575
0.36 (fixed)	72.8	586
0.37 (fixed)	72.8	597
0.2191	72.1	433 (fixed)
0.1623	71.5	373

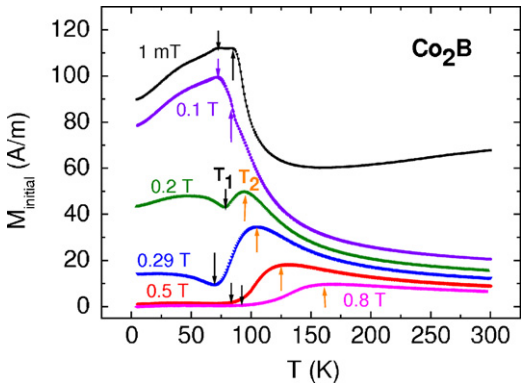

Fig. 7. AC initial magnetization vs. temperature of the Co_2B ferromagnetic phase at a fixed frequency of 1 kHz and applied fields ranging from 1 mT to 0.8 T.

is near 433 K [4]. The magnetization behaviors for temperatures below 70 K are almost identical. However, above 70 K the saturation magnetization (M_s) values start to decrease. Moreover, the field at which the magnetization saturates (H_s) rises as the temperature is increased. The M_s and H_s values were taken from the beginning of the high field linear behavior of the Arrot plot (not shown) M^2 vs. H/M. The curves of H_s vs. T and M_s vs. T are presented in Fig. 6a and b. It is remarkable the change of H_s vs. T behavior (Fig. 6a) near $T \sim 65$ K. Below 65 K the H_s values are approximately constant, while for $T > 65$ K H_s increases almost linearly with T. A correspondent behavior is not observed in the M_s vs. T curve (Fig. 6b) as expected, since M_s intrinsically depends on the density of magnetic moments in the crystalline structure. The features observed in Figs. 5 and 6a are associated with the turn of the Co_2B phase easy magnetization axis near $T \sim 68$ K. The change occurs in the tetragonal structure ($CuAl_2$ type) from a direction along the c-axis for $T < 68$ K to a direction within the a–b plane for $T > 68$ K [7,8]. From Fig. 6b, the Curie temperature could be inferred by using the Heisenberg–Ising critical exponent model (HICE) for real ferromagnets [18]. In this model, the saturation magnetization M_s is written as a function of temperature as $M_s = M_0(1 - T/T_c)^{\beta}$, where M_0 is the magnetization at 0 K and $0.33 < \beta < 0.37$. The T_C data for β values in this range are given in Table 1. In this table it is also

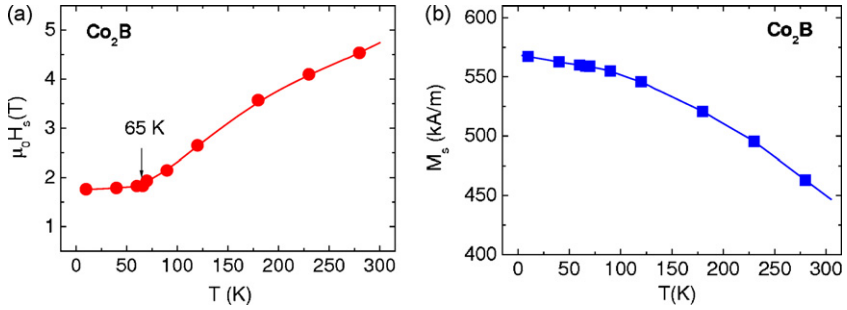

Fig. 6. Saturation magnetization (M_s) and field (H_s) vs. temperature of the ferromagnetic Co_2B phase.

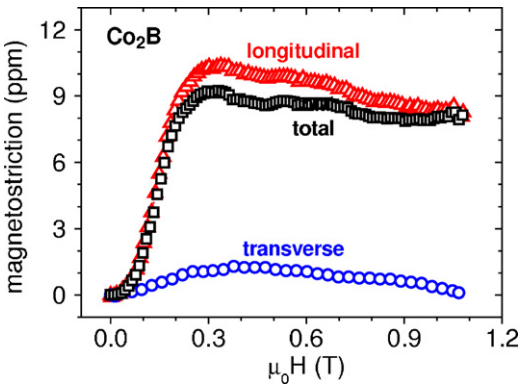

Fig. 8. Co_2B phase magnetostriction as a function of applied field at 290 K.

shown M_0 and β values for a fixed $T_C = 433$ K [9] value and the best fitting (last line of the table) by leaving free the three parameters M_0, T_C and β. The T_C values calculated from the HICE model for $0.33 < \beta < 0.37$ are far from that reported in the literature, 433 K. If the three parameters M_0, T_C and β are left free to adjust, the T_C value is too low compared to the NMR T_C result [9] and β is not consistent with the HICE model. Remarkably, the $\beta = 0.2191$ value obtained for $T_C = 433$ K (NMR result) is very close to the one obtained (0.220) using the HICE model for the silicoboride Mn_5SiB_2 phase, using also a T_C value from NMR [15].

In order to determine the temperature at which the easy magnetization axis change from the *c*-direction to a direction within the *a*–*b* plane of Co_2B, initial magnetization (AC susceptibility) measurements were carried out for fixed magnetic fields varying from 1 mT to 0.8 T at a constant frequency of 1 kHz. The $M_{initial}$ vs. T curves are shown in Fig. 7. For the smallest field of 1 mT, $M_{initial}$ increases from 4 to 70 K, remains constant in the 70–83 K temperature range and then falls rapidly from 83 to 130 K. If the magnetic field is increased a hundredfold, the constant region from the 1 mT curve disappears and a maximum at 70 K is observed, followed by the same rapid decrease observed for 1 mT field. However, some feature can be observed at $T \sim 86$ K, indicated by the arrow pointing up in the figure.

Further increase of the field above 0.1 T reveals a change in behavior. The $M_{initial}$ curves are roughly constant below the temperatures T_1 indicated by downward arrows in Fig. 7, then increases reaching a maximum at T_2 (upward arrows) and for $T > T_2$ gradually decreases. The temperature interval between the down and upward arrows in Fig. 7 becomes wider as the field increases.

We suggest that the temperature interval indicated by the up and down arrows are related to the gradual change of easy magnetization axis from the direction along the *c*-axis to within the *a*–*b* plane direction as the temperature is increased, instead of occurring exactly at the temperature of 68 K as reported in Ref. [7]. For higher fields the magnetic moments are more tightly bound in the field direction, increasing the necessary thermal energy to turn the magnetic moments to the new easy magnetization axis. The detailed behavior of the initial magnetization in the temperature interval that the gradual transition of easy magnetization axis occurs as a function of the field involves more careful measurements and further analyses.

The magnetostriction of the Co_2B phase was measured at 290 K and the results are shown in Fig. 8. The total magnetostriction was found to be only 8 ppm at 1 T, the maximum value being 9.2 ppm at 0.29 T. At zero field, the magnetic moments are aligned in the easy magnetization direction of each grain (within *c*-axis plane for this temperature). As the field is increased, the domain walls move and at 0.29 T they are all aligned in that easy magnetization directions that is closest to field direction, leading to a maximum magnetostriction. Further increase of the field strength beyond 0.29 T promotes the rotation of the magnetic moments to the field direction, away from the easy magnetization direction and the magnetostriction falls to 8 ppm at 1 T. The magnetostriction at temperatures below 70 K, where the *c*-axis is the easy magnetization direction, is the subject of a future investigation.

4. Conclusions

The magnetization study of binary and ternary Co-rich phases of the Co–Si–B system has shown for the first time the paramagnetic behavior of the Co_5Si_2B phase, unlike other transition metal silicoborides such as Fe_5SiB_2 and Mn_5SiB_2 [13,14] that are ferromagnetic.

The magnetic behavior of the Co_2Si, Co_2B and CoB phases where confirmed to be para-, ferro- and diamagnetic respectively [10–12], as was previously found.

The ferromagnetic behavior of Co_2B was explored by magnetization measurements and showed that the change of easy magnetization axis starts at 70 K, very close to the value of 68 K reported previously [14]. The change occurs in a temperature interval of about 13 K for very small field. As the strength of the field is increased this temperature interval width broadens. The initial susceptibility decreases as the field strength is increased for all the temperature interval of the present study.

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