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Atomic disorder, phase transformation, and phase restoration in Co_3Sn_2

L. M. Di, G. F. Zhou, and H. Bakker
Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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The behavior of the intermetallic compound Co_3Sn_2 upon ball milling was studied by x-ray diffraction, high-field-magnetization measurements, and subsequently by differential scanning calorimetry. It turns out that starting from the stoichiometric-ordered compound, mechanical attrition of Co_3Sn_2 generates atomic disorder in the early stage of milling. The nonequilibrium phase transformation from the low-temperature phase with orthorhombic structure to the high-temperature phase with a hexagonal structure was observed in the intermediate stage of milling. It was accompanied by the creation of increasing atomic disorder. After long milling periods, the phase transformation was completed and the atomic disordering became saturated. All the physical parameters measured in the present work remained constant during this period. The above outcome was confirmed by comparison with the high-temperature phase thermally induced by quenching. The good agreement of the results obtained by different techniques proves that the ball milling generates well-defined metastable states in Co_3Sn_2.

I. INTRODUCTION

Mechanical milling of an intermetallic compound can transform its crystalline structure to the amorphous state as was observed for a number of metallic alloys.[1-3] In some systems, phase transformations of compounds to solid solutions which exist in the phase diagram only at high temperatures have also been found upon mechanical impact.[4-6] In the present paper we report the observation of a mechanically induced phase transformation from a low-temperature crystalline phase to a high-temperature phase with a complex crystalline structure. The compound studied is Co_3Sn_2.

The intermetallic compound Co_3Sn_2 crystallizes in an orthorhombic structure at room temperature with a homogeneity region of about 2 at. % near the stoichiometric composition.[7,8] At a temperature of 550 °C, the low-temperature phase transforms to another phase with a hexagonal crystalline structure. The present investigation shows that such a phase transformation could also be induced by mechanical milling. The evidence of the phase transformation during the ball milling was obtained from x-ray-diffraction patterns and by differential scanning calorimetry (DSC) analyses of the metastable high-temperature phase. Additionally the high-field magnetization was also measured on samples after various milling periods. The high-temperature phase obtained by ball milling was confirmed by comparison with a sample that was quenched from high temperature.

II. EXPERIMENTAL PROCEDURE

The stoichiometric intermetallic compound Co_3Sn_2 was obtained by arc melting of weighted amounts of pure cobalt and tin in a purified argon atmosphere. The arc melting was performed several times to ensure homogeneity. The arc-melted button was crushed into powder and subsequently annealed at 500 °C for 50 h. The x-ray diffraction pattern of the arc-melted sample shows the low-temperature phase with an orthorhombic structure. The ball milling was carried out in a hardened-steel cylindrical vial (inner diameter 6.5 cm) with a tungsten carbide bottom. Inside the vial, a hardened-steel ball with a diameter of 6 cm was kept in motion by a vibrating frame (Pulverisette 0, Fritsch), upon which the vial was mounted. To prevent oxidation, the milling was done in a glove box in a purified argon atmosphere (with a level of oxygen and water of less than 5 ppm). All experiments with different milling times started with an amount of 0.5 g of the as-prepared sample. The milling periods ranged from 20 min to 48 h. X-ray-diffraction patterns were taken at room temperature by means of a Philips vertical powder diffractometer with Cu $K\alpha$ radiation. High-field magnetization measurements at 4.2 K were performed in the Amsterdam High Field Installation[9] in which fields can be generated up to 42 T, constant with 10^{-4} during 0.1 s. The pulse shape can be electronically regulated. For magnetization measurements on metallic specimens, usually stepwise pulses are applied in which the field is constant during the steps for about 40 ms, a time long enough to let eddy current in metallic specimens decay. In the present investigation, fields up to 14 T were used, regulated in seven steps of 2 T. The sensitivity of this magnetometer is about 10^{-5} Am^2. Differential scanning calorimetry (DSC) analyses were carried out in a Perkin-Elmer DSC-7 in argon gas flux at a speed of 30 cc/min to protect the sample against oxidation. The temperature and the reaction heat were calibrated by pure indium and zinc standards.

The compound Co_3Sn_2 for the quenching experiment was obtained in the same way as described above. The self-designed Powder Quenching Device (LOPOQ)[10] was used to quench the Co_3Sn_2 powder from various temperatures ranging from 600 to 900 °C.

III. RESULTS AND INTERPRETATION

Figures 1 and 2 show the x-ray-diffraction patterns for the Co_2Sn_2 compound after various milling periods. All the x-ray-diffraction peaks of the starting material (0 min milling time) can be identified as belonging to the low-temperature phase (LTP) with an orthorhombic structure. For the ball milling periods up to 6 h, the material remains in the orthorhombic structure of the low-temperature phase as can be seen from Figs. 1 and 2. For the samples milled for periods from 12 to 48 h, the x-ray-diffraction patterns show the structure change to another phase which can be identified as the high-temperature phase (HTP) with a hexagonal structure. The orthorhombic structure of the LTP can be distinguished from the hexagonal structure of the HTP by some extra reflections which appear in the x-ray-diffraction patterns of the sample in the low-temperature phase. For comparison, the x-ray diffractogram was taken for the same compound which was quenched from 800 °C (1073 K). This diffractogram is also shown in Fig. 2. It is clear from Fig. 2 that the quenched sample has the same structure as the samples after ball milling for more than 12 h. The broad diffraction peak at about 44° of 2θ for the milled samples, instead of the two peaks for the hexagonal structure as observed in the x-ray diffractogram of the quenched sample, is probably due to the small crystallite size caused by the heavy mechanical impact.

For a better understanding of the milling process, the high-field magnetization was measured on samples after various milling times and on samples quenched from various temperatures. The measurements of the field dependence of the magnetization at 4.2 K for samples after different milling periods are shown in Fig. 3. The magnetization measured at 14 T as a function of milling time is given in Fig. 4. For comparison the magnetization was also measured for the samples quenched from different temperatures, e.g., 873, 973, 1073, and 1173 K. All the quenched samples exhibit the same magnetization behavior and have an almost constant magnetization value at 14 T. Therefore, in Figs. 3 and 4, only the results for the sample quenched from 1073 K are presented by crosses. Figure 3 shows a considerable increase of the magnetization with increasing milling time. For the sam-

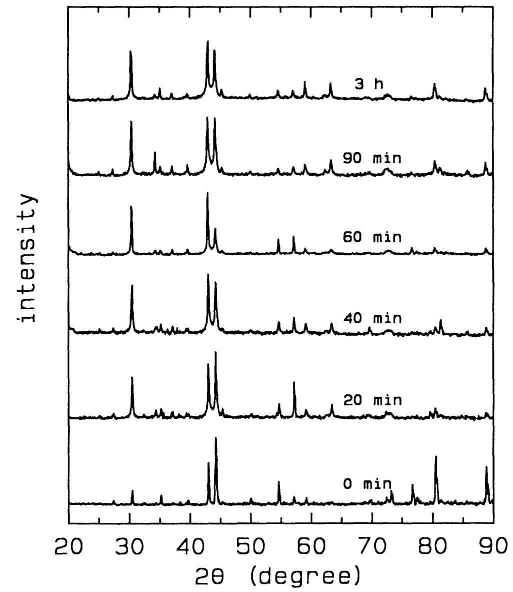

FIG. 1. X-ray-diffraction patterns of Co_3Sn_2 after various milling periods up to 3 h.

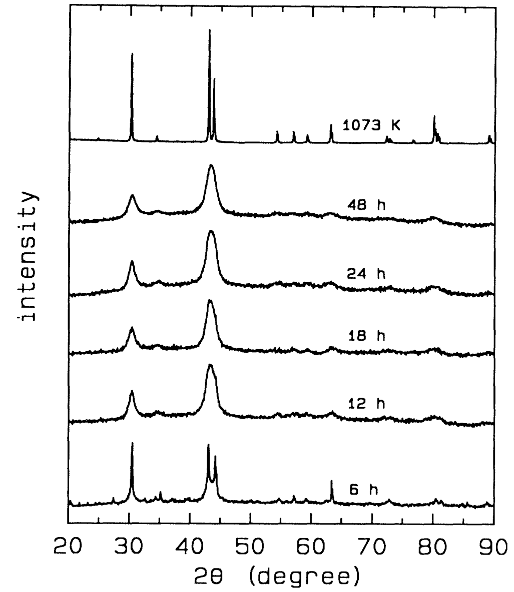

FIG. 2. X-ray-diffraction patterns of Co_3Sn_2 after milling periods longer than 3 h. The top curve represents Co_3Sn_2 quenched from 1073 K.

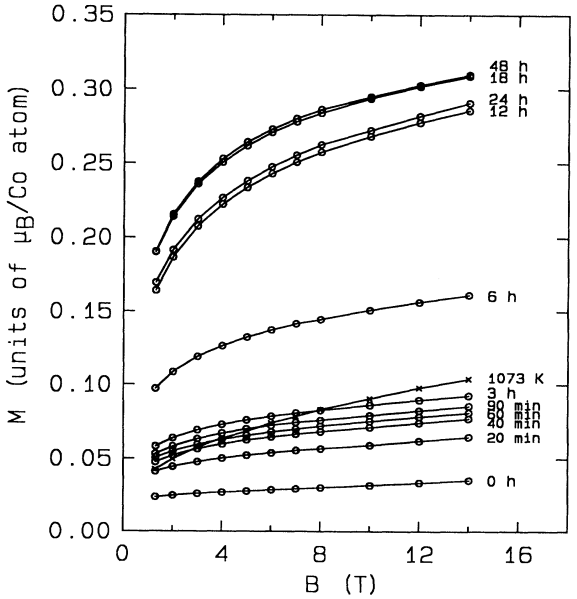

FIG. 3. Magnetization measured at 4.2 K as a function of applied magnetic field for Co_3Sn_2 after various milling periods. The crosses represent the magnetization for Co_3Sn_2 quenched from 1073 K.

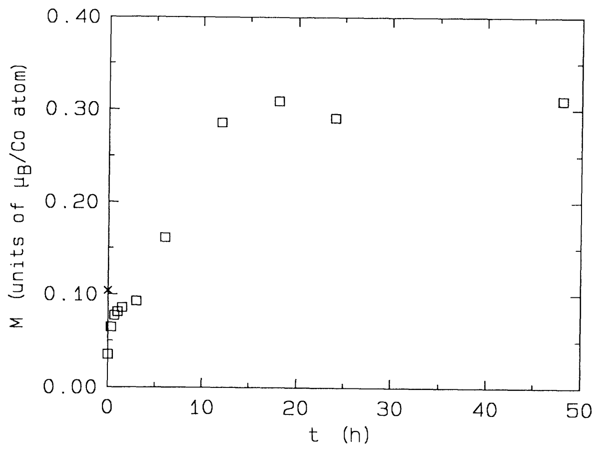

FIG. 4. Magnetization of Co_3Sn_2 measured at 14 T and 4.2 K as a function of milling time. The cross at zero milling time represents the magnetization of Co_3Sn_2 quenched from 1073 K.

ples milled up to 3 h, the magnetization of the compound increases continuously with the milling time as indicated in Fig. 4. After about 6 h of milling, there is a large change in magnetization. After more than 12 h of milling, the increase of the magnetization is even more drastic and after that the magnetization tends to become constant. From Fig. 4 it can be seen that the magnetization measured at 14 T for the HTP obtained by quenching from 1073 K is much lower than that of the HTP obtained after a long time of milling. It is of the same order as that of the LTP obtained by ball milling for short periods. However, the shape of the magnetization curve of this sample is closer to the shape of the magnetization curves of the samples after long periods of milling than of the samples up to 3 h of milling (see Fig. 3).

Obviously the high-temperature phase obtained either by quenching or by ball milling is a metastable phase at ambient temperature. At higher temperature where the atoms become mobile, the material should transform to the equilibrium low-temperature phase. Then an exothermic heat effect should be observed. In the present paper, we shall call this process "phase restoration." In order to get more insight in the ball milling process, the kinetics of the phase restoration was studied by the DSC technique.

DSC scans for the samples after various periods of milling are shown in Figs. 5 and 6. The samples were heated in the DSC from room temperature to 873 K at a heating rate of 10 K/min. The starting material shows an endothermic peak at a temperature of 853 K, which corresponds to the equilibrium phase transition to the high-temperature phase. The transition temperature of 853 K is higher than the transition temperature of 823 K (550 °C) from the phase diagram.[7] The heat of the phase transition is estimated to be 1.08 kJ/mol (g at.). For the samples milled for less than 6 h, this original endothermic peak diminishes somewhat and meanwhile, a new small endothermic peak (called the second endothermic peak) appears at a temperature of about 835 K. The second endothermic peak develops quickly upon further milling and becomes dominant for periods between 12 and 48 h. Only a trace of the original transition peak can be observed after a long time of milling. The transition temperature of the second endothermic peak does not depend on milling time and remains near 835 K. The total heat consumed in the endothermic reaction (the sum of the two endothermic peaks) decreases slightly with milling time in the early stage of milling as can be seen from Fig. 7, and is significantly reduced to an almost constant value of about 0.57 kJ/mol for milling periods from 12 to 48 h.

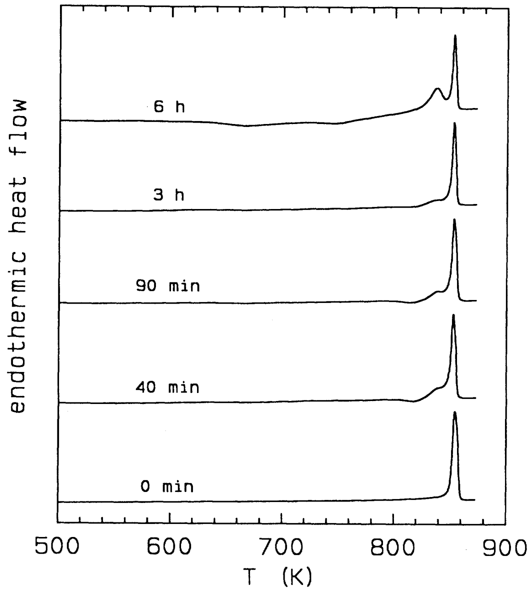

FIG. 5. DSC scans with a heating rate of 10 K/min for samples after various milling periods up to 6 h.

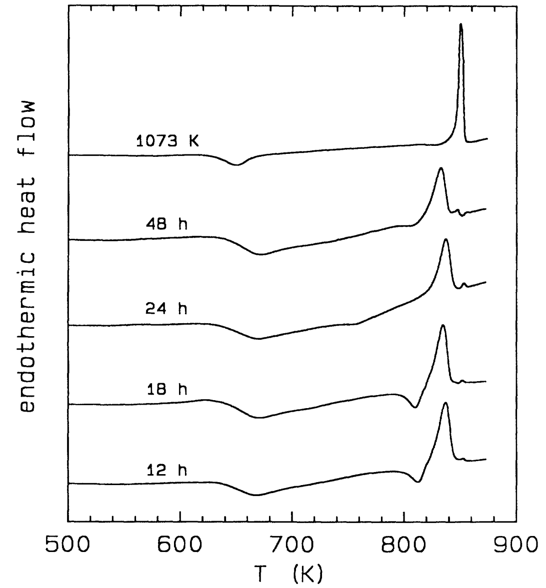

FIG. 6. DSC scans with a heating rate of 10 K/min for samples after milling periods longer than 6 h. the top curve represents Co_3Sn_2 quenched from 1073 K.

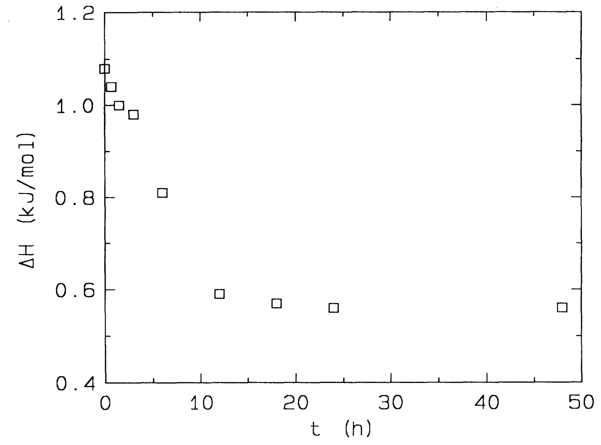

FIG. 7. The total heat involved in the endothermic reaction (the sum of the two endothermic peaks) as a function of milling time.

Apart from the endothermic peaks, the DSC scan of the sample milled from 6 h reveals two exothermic peaks at temperatures of 665 and 750 K, respectively. The heat effect of the first exothermic peak is about 0.17 kJ/mol. The first exothermic peak develops steadily after a long milling time. Both the temperature and the heat effect of the first exothermic peak hardly change with milling time and were estimated to be 669±2 K and −0.49±0.03 kJ/mol, respectively, for milling periods between 12 and 48 h. The second exothermic peak, which appeared after 6 h of milling, behaves rather unsystematically. Sometimes it is even absent. For example, for a sample milled for 18 h, the exothermic peak nearby the second endothermic transition does not exist when the sample is heated at a speed of either 20 or 40 K/min. Therefore only the first exothermic peak was considered as the phase restoration reaction for samples after long milling periods.

The sample quenched from 1073 K shows a similar DSC scan as the samples milled for long periods (top curve of Fig. 6). Here, only one single exothermic peak at a temperature of about 649 K and one endothermic peak at a temperature of about 853 K was observed. The temperature of the exothermic peak is somewhat lower than that of the first exothermic peak of the samples after long periods of milling. The heat evolved in the exothermic peak is 0.40 kJ/mol, which is also smaller than for the milled material. In contrast the temperature of the endothermic transition is higher than that for samples after long milling periods and the transition heat (1.08 kJ/mol) is larger. Moreover, for the quenched sample the transition temperature and the transition heat are the same as the original transition peak for the starting material.

X-ray-diffraction patterns were taken for the samples milled for 24 and 12 h, respectively and heated to different temperatures in DSC at a rate of 10 K/min and subsequently rapidly cooled to the room temperature at a rate of 200 K/min. The results for the sample milled for 24 h are shown in Fig. 8. The three temperatures chosen are 630 K, which is the starting temperature of the first exothermic peak, 725 K, the end temperature of the first exothermic peak, and 801 K, the temperature before the equilibrium phase transition starts. It can be seen from Fig. 8 that at 630 K, the sample is still in the high-temperature phase with the hexagonal structure. The separate double peaks around 44° of 2θ indicate that the growth of crystals had already started below 630 K. X-ray-diffraction patterns for the sample cooled from 725 K show the orthorhombic structure which belongs to the low-temperature phase. The sample cooled from 810 K gives the same x-ray pattern as the sample cooled from 725 K, which indicates that there is no structural change in this temperature range. The sample milled for 12 h gives the same results.

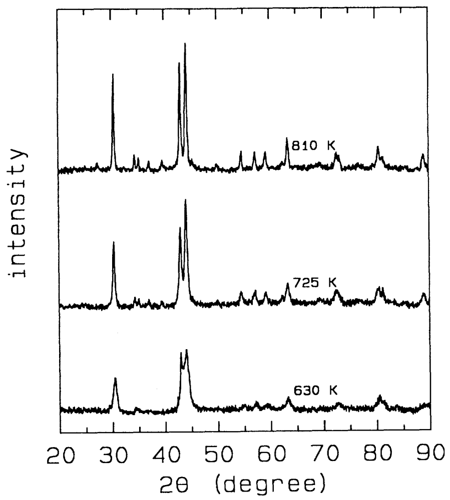

FIG. 8. X-ray-diffraction patterns for Co_3Sn_2 milled for 24 h after heating to different temperatures in DSC.

Finally, in order to have an idea about the stability of the high-temperature phase obtained after ball milling, various heating rates 5, 10, 20, and 40 K/min, were applied to measure the heating rate dependence of the peak temperature (the first exothermic peak) for the samples milled for 18 and 48 h, respectively. A Kissinger[11] plot is displayed in Fig. 9 for the sample milled for 18 h. From

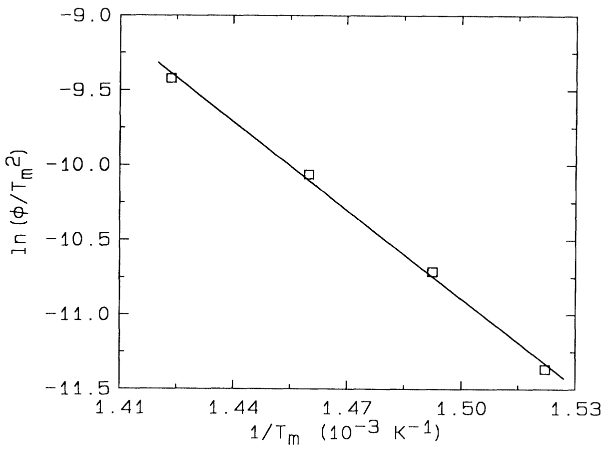

FIG. 9. Kissinger plot of the first exothermic peak (phase restoration reaction) for Co_3Sn_2 milled for 48 h in DSC. The heating rates ranged from 5 to 40 K/min.

the slope of the straight line the activation energy of the restoration reaction can be derived as 165 kJ/mol. The sample milled for 48 h gives a value of the same order.

IV. DISCUSSION

The change of the magnetic properties of the intermetallic compound Co_3Sn_2 upon mechanical milling is consistent with the x-ray-diffraction patterns. That is, up to 3 h of milling, the compound remains in the structure of the low-temperature phase and has only a continuous change in the magnetization. After milling for more than 12 h, the material has changed to the high-temperature phase with hexagonal structure and has a much higher value of the magnetization which is no longer dependent on the milling time.

The x-ray results presented in Fig. 8 prove that the phase restoration occurs in the temperature range from 630 to 725 K accompanied by an exothermic heat effect. That is, the first exothermic peak in Fig. 6 is responsible for the phase restoration of the high-temperature phase obtained by long-time ball milling. The single exothermic peak at 649 K in the DSC scan of the quenched sample gives the same conclusion. The lower restoration temperature of the quenched sample means that the high-temperature phase obtained by quenching is less stable than the high-temperature phase obtained by mechanical milling. After the phase restoration, the samples restore to the LTP and then exhibit a transition to the HTP at higher temperature. The latter transition for the quenched sample has characteristics very similar to the same transition in the original as-prepared sample. The behavior of this transition in the samples milled for long times is somewhat different. This can be understood when we take into account that the quenched sample has fewer defects than the milled samples.

The combination of the results of the x-ray diffractograms, magnetization measurements, and the DSC scans for the intermetallic compound Co_3Sn_2 after various milling times gives a clear picture of the ball milling process.

The process of the ball milling of Co_3Sn_2 can be divided into three stages.

The first stage is the stage with a milling time up to 3 h. In this period, x-ray-diffraction patterns show that the material remains in the low-temperature phase (Fig. 1), whereas the magnetization continuously increases with milling time (Fig. 4). The increase of the magnetization is interpreted in terms of atomic disorder. The low-temperature phase of Co_3Sn_2 crystallizes in the Ni_3Sn_2-type orthorhombic structure and belongs to the space group *Pnma*.[8] The Co atoms occupy two different sublattice sites. One of those sublattices (position A) is fully occupied by Co atoms, whereas the other sublattice (position B) is only half occupied by Co atoms and half by vacancies. It was observed in similar compounds[12] that the atoms at position B, the half occupied sublattice, have a larger magnetic moment than the atoms at position A, the fully occupied sublattice. This is due to different interatomic distance and different coordination. During the heavy mechanical impact, probably some of the Co atoms in position A are transferred to the empty sites of position B, which increases the magnetization of the material. In our previous investigations on an $A15$-structure superconducting compound[13] and a $B2$-structure magnetic compound,[14] we were able to prove that atomic disorder was generated by the mechanical milling. The type of disorder turned out to be characteristic of the material. Therefore, it would not be surprising if ball milling would also generate atomic disorder in the compound Co_3Sn_2. The DSC scans for the samples milled during these periods show the appearance of a second endothermic peak at a temperature lower than the original LTP-HTP transition peak and a decrease of the heat effect. This indicates that disordered LTP Co_3Sn_2 has an equilibrium phase transition to the HTP at a somewhat lower temperature than the perfectly ordered compound.

The second stage of ball milling takes place during periods of more than 3 h and less that 12 h. In these periods, the material undergoes a mechanically induced nonequilibrium phase transformation to the HTP. Although x-ray diffraction of the sample milled for 6 h still contains the reflections of the LTP, the DSC scan reveals the appearance of the high-temperature phase, which indicates that the material in this stage is a mixture of the LTP and the HTP. The fact that the heat effect for the sample with 6 h of milling is only 35% of the heat effect after long milling time leads to the same conclusion.

It is clear from the magnetization measurement for quenched HTP that the high-temperature Co_3Sn_2 has a higher magnetic moment than the low-temperature Co_3Sn_2 (Fig. 4). Therefore we observed a big change in magnetization upon milling of Co_3Sn_2 during periods from 3 to 12 h. The much larger magnitude of the magnetization increase in milled HTP than quenched HTP can be explained by the phase transformation accompanied by atomic disorder. The high-temperature Co_3Sn_2 crystallizes in the AsNi-type hexagonal structure and belongs to the space group $P6_3/mmc$.[8] From Ref. 15 it appears that the phase transition from the Co_3Sn_2-type orthorhombic structure to the hexagonal structure is a diffusionless transition and occurs by only slight atomic displacement. Therefore, the disorder of the LTP generated in the early stage of milling remains in the compound during the phase transformation to the HTP. Meanwhile, more atomic disorder is generated during this period as can be seen from the growth of the second endothermic peak in the DSC scan for the sample after 6 h of milling and even large growth of the peak after 12 h milling. The disordered HTP has a higher magnetization than the ordered HTP, because of the same reasons as described above for the LTP. The effect of both phase transformation and atomic disorder induced by ball milling gives a greater increase of the magnetization than that of the phase transformation induced purely by quenching.

Our further experiments on ball milling of a related compound, namely Ni_3Sn_2 with the same LTP and HTP structures as Co_3Sn_2 shows a similar behavior. The structure changes and magnetic properties are discussed in more detail in that paper.[16]

So far we have interpreted the second stage of ball milling in terms of phase transformation accompanied by atomic disorder. However, it is not clear whether all of the disorder in the HTP was induced by milling in the LTP first and remained in the material after the phase transformation. Probably some more disorder could also be generated upon further milling after the phase transformation.

The third stage of the ball milling is the saturation stage, i.e., ball milling after 12 h. In this stage, all the parameters turned out to be constant and the properties do not depend on the milling time anymore. The phase transformation to the HTP is completed and the atomic disorder is saturated.

Another interesting outcome of the present investigation is that the disordered LTP is less stable than the ordered LTP which was reflected by the lower transition temperature and the smaller transition heat. In contrast, the metastable disordered HTP (obtained by ball milling) is more stable than the metastable ordered HTP (obtained by quenching).

V. CONCLUSIONS

Ball milling of the intermetallic compound Co_3Sn_2 induces a nonequilibrium phase transformation from the ordered LTP with an orthorhombic structure to the disordered HTP with a hexagonal structure. The ball milling process of Co_3Sn_2 can be divided into three steps.

The first step is atomic disordering of low-temperature Co_3Sn_2 for milling times less or equal to 3 h. The atomic disordering gives an increase of the magnetization and a decrease of the equilibrium LTP-HTP transition temperature and transition heat in DSC. the disordered LTP is less stable than the ordered LTP.

The second step is nonequilibrium mechanically induced phase transformation to the high-temperature phase together with an increasing amount of disordering. This occurs during milling periods from 3 to 12 h. The change of the properties of the compound Co_3Sn_2 in this period is remarkable. X-ray-diffraction patterns show the structure change from orthorhombic to hexagonal. The magnetization measurements give a large increase of the magnetization. The DSC studies indicate that the amount of both the high-temperature phase and the atomic disordering increase with the milling time.

The last step is the saturation stage where all the parameters measured in the present investigation tend to be constant. The final state of the ball milling of the ordered stoichiometric compound Co_3Sn_2 is the disordered high-temperature phase. The disordered high-temperature phase obtained by ball milling has a magnetization value of about $0.30\mu_B$/Co atom and a phase restoration to LTP at the temperature of 669 K with a heat effect of -0.49 kJ/mol. The activation energy is estimated to be 165 kJ/mol.

The agreement of all results obtained by different types of measurements used in the present investigation is excellent. It establishes that by the ball milling of Co_3Sn_2 well-defined nonequilibrium states can be generated in the material.

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