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Structure and properties of Cu_2MnAl synthesized by mechanical alloying

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Abstract. The ferromagnetic Cu_2MnAl Heusler alloy has been prepared via a combination of mechanical alloying and heat treatment. The metastable Cu_2MnAl phase can be formed directly when Cu, Mn and Al powders are mechanically alloyed. The resulting single-phase nanocrystalline material is highly disordered. When heat treated at 473 K, the Heusler phase can be ordered. The saturation magnetization is then approximately half the value achieved in highly ordered alloys, prepared via conventional melting and casting techniques. When heat treated at 973 K, the magnetic properties of the resulting material are similar to those of previous reports. The Cu_2MnAl phase can be disordered by mechanical milling, resulting in a decrease in saturation magnetization and increase in coercivity. The Heusler phase has been found to be unstable when mechanically milled over extended periods.

1. Introduction

The Heusler alloys are a series of ternary compounds, generally having the formula X_2YZ, where X is a transition metal, Z is a group III or IV metal and Y is Mn. Many of the Heusler alloys are soft ferromagnets, the best known being Cu_2MnAl [1–4].

Heusler Alloys exhibit the ordered $L2_1$ crystal structure. When Mn atoms occupy specific lattice positions within the ordered structure, the Mn–Mn nearest-neighbour distances are sufficiently large that indirect coupling of moments gives rise to a ferromagnetic material. Long-range order in these materials is hence a necessary requirement for ferromagnetism. Thus any factor affecting chemical order will also directly influence magnetic behaviour [1].

When Cu_2MnAl is prepared via conventional melting and casting techniques, the as-cast alloy is homogenized at a temperature close to its melting point and then rapidly cooled in order to retain the high-temperature β phase. The alloy is then heat treated for extended periods at 373–473 K in order to ensure maximum ordering. When heat treated in the region 623–973 K, the β phase reverts to the equilibrium phases [5–7]. The equilibrium phases over the temperature range of 623–723 K are Cu_9Al_4, Cu_3Mn_2Al and β-Mn, over the range 723–823 K, β-Cu_2MnAl, Cu_9Al_4 and β-Mn form and for 823–973 K the phases are β-Cu_2MnAl and β-Mn [8]. At temperatures between 973 and 1023 K, the β-Cu_2MnAl phase having a $B2$ ordered structure is the only phase present and at higher temperatures a disordered BCC structure is formed [9].

Previous measurements of the lattice parameter of Cu_2MnAl range from 5.949 Å [3] to 5.963 Å [10]. It is accepted that the Curie temperature of the alloy is approximately 600 K

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and that the coercivity is very low [1]. Results of previous investigations on the room-temperature saturation magnetization range from ~75 emu g^{-1} [11, 12] to ~ 90 emu g^{-1} [3, 13].

The majority of investigations to date on Cu_2MnAl have been conducted using cast alloys. The present work utilizes the mechanical alloying processing technique. It has been found that the magnetic properties of mechanically alloyed materials can vary from those prepared via conventional techniques. Both metastable and amorphous phases can be produced and the resulting nanocrystalline microstructures can give rise to very high coercivities [14–16]. With the exception of Taylor and Tsuei [10], who prepared amorphous thin-film Heusler alloys, the type of disorder studied in Cu_2MnAl has been restricted to slight Mn–Al disorder found in as cast alloys. In the present study, mechanical alloying has resulted in the production of a highly disordered Heusler phase. Mechanical milling has then been used to introduce varying degrees of structural disorder to the heat-treated alloy.

2. Experimental procedure

The starting materials used in this study were high-purity Cu, Mn and Al powders. Mechanical alloying was performed in a hardened steel vial, under an argon atmosphere using a Spex 8000 mixer/mill with a ball/powder ratio of 10:1. X-ray diffraction measurements of as-milled and heat-treated powders were carried out at room temperature under argon using a Siemens D5000 powder diffractometer, with Cu Kα radiation. An Si standard was mixed with the powders for accurate lattice parameter determination. Samples were heat treated under vacuum in Vycor tubing and water quenched. Differential scanning calorimetry measurements were made under argon, using a Perkin–Elmer DSC 4 at a heating rate of 20 K min^{-1}. Crystallite sizes have been assessed by examination of particles using a Philips 430 transmission electron microscope. Magnetic measurements were made at 298 K using an Oxford Instruments vibrating sample magnetometer with applied fields up to 50 kOe. Samples were compacted at approximately 0.8 GPa pressure and sealed under argon prior to testing.

3. Results

Chemical analysis of the as-milled powders showed that when Cu, Mn and Al powders were mechanically alloyed in the ratio 2:1:1, the resulting alloy was deficient in Mn and Al, having the approximate composition $Cu_{2.00}Mn_{0.95}Al_{0.97}$. The small loss of Mn and Al was attributed to the formation of a thin coating of these metals on the balls and vial during milling. The addition of excess Mn and Al resulted in an alloy having the composition $Cu_{2.00}Mn_{1.02}Al_{1.00}$, and the results presented here refer to powder of this composition. Iron contamination from the vial and balls was limited to approximately 0.3 wt%.

X-ray diffraction patterns of samples milled for 1, 4 and 48 h are shown in figure 1. After milling for 1 h, only diffraction peaks associated with elemental Cu, Mn and Al were present. With further milling to 4 h, Mn peaks could be detected, along with Cu_2MnAl peaks. After 4 h, the diffraction pattern indicated that the only phase present was β-Cu_2MnAl. The peaks were very diffuse, indicating a small crystallite size and the presence of internal strains. A TEM dark-field image of a typical particle, milled for 4 h is shown in figure 2. The refinement of crystallite size with milling time is shown in figure 3.

The magnetic properties of the mechanically alloyed material were found to be highly sensitive to heat treatment. The effect of heat treatment temperature on the magnetization in

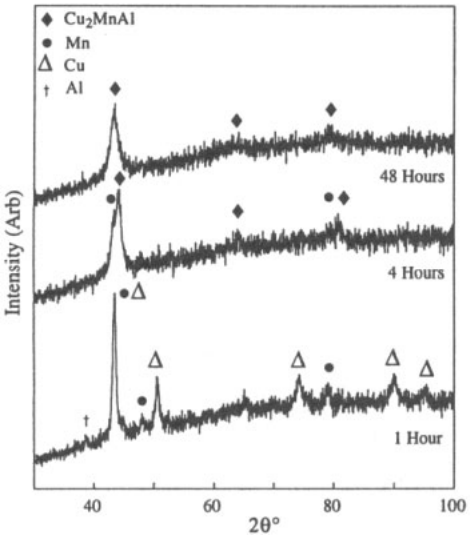

Figure 1. X-ray diffraction patterns of as-milled powders; milling time indicated.

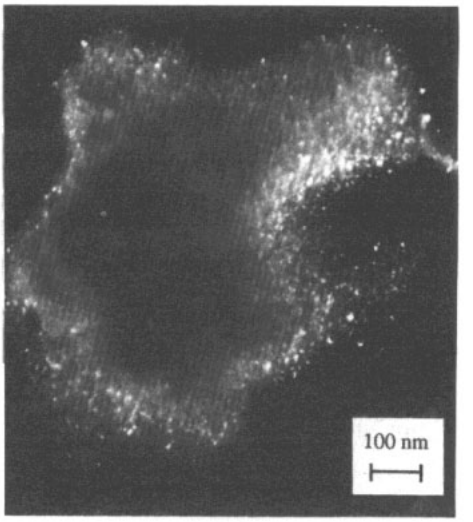

Figure 2. A TEM dark-field image of a particle milled for 48 h.

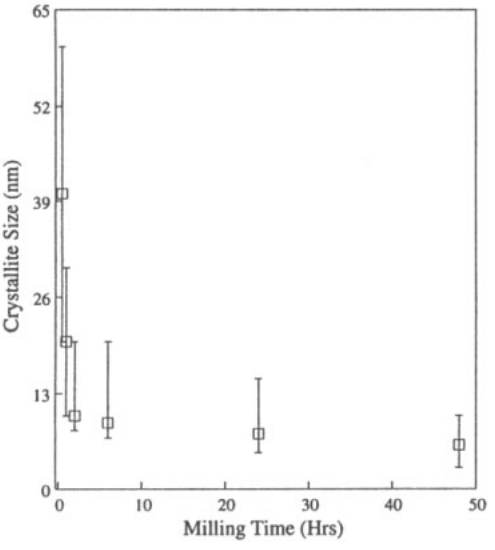

Figure 3. Crystallite size refinement with milling time.

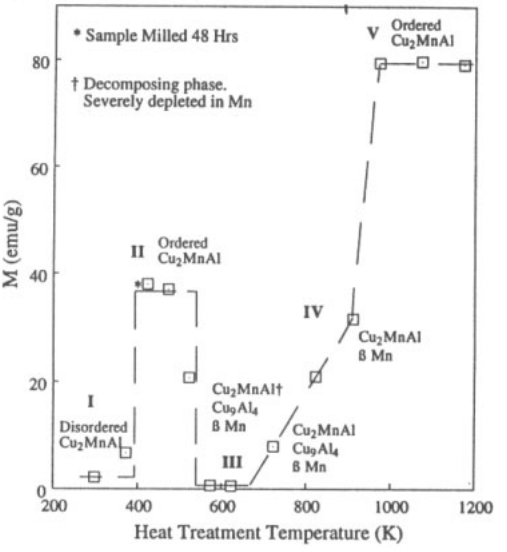

Figure 4. The magnetization (50 kOe field) of a sample ball milled 24 h against heat treatment temperature.

a field of 50 kOe is shown in figure 4. The phases present at each stage, as determined by x-ray diffraction, are also shown. Region I corresponds to the as-milled disordered material, which exhibited a magnetization of only 2.2 emu g^{-1} and a coercivity of approximately 50 Oe.

Heat treatment in regions II and V resulted in the ordered ferromagnetic Cu_2MnAl

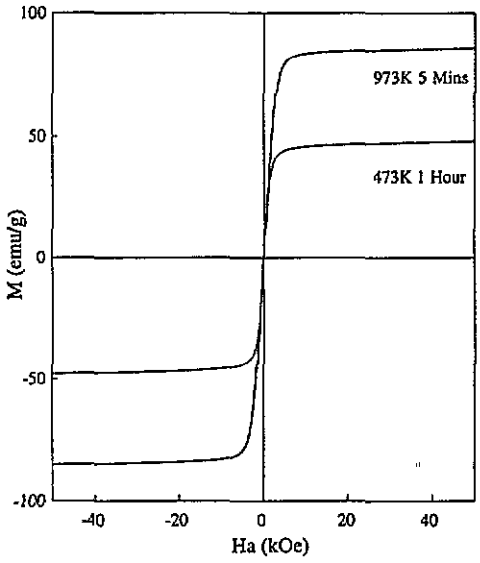

Figure 5. Magnetic hystersis loops of samples ball milled for 48 h after heat treatment.

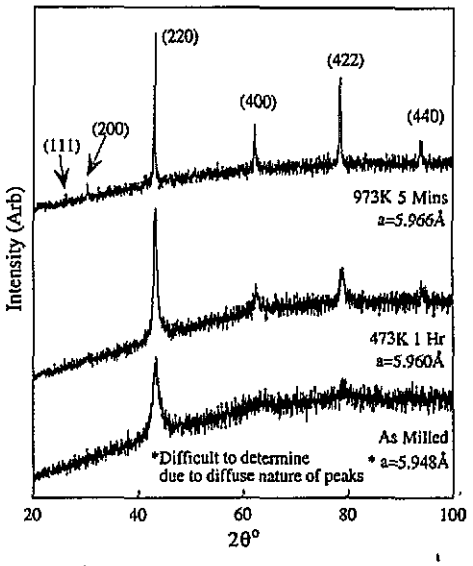

Figure 6. X-ray diffraction patterns of as-milled and heat treated samples ball milled for 48 h.

phase. Magnetic hysteresis loops of samples milled for 48 h and heat treated at 473 K and 973 K are shown in figure 5. After heat treatment at 473 K for 1 h, a maximum saturation magnetization of 47.9 emu g^{-1} was obtained. This corresponds to a spontaneous magnetization of $1.79\mu_B$ per Mn atom. The coercivity was typically 40 Oe, with very low values of remanence. After heat treatment for 5 min at 973 K, followed by a further ordering treatment at 473 K for 165 h, the saturation magnetization increased to 85.5 emu g^{-1}, or $3.20\mu_B$/Mn atom. The coercivity was approximately 35 Oe, also with very low remanence. X-ray diffraction patterns of the samples in the as-milled state and after heat treatment at these temperatures are shown in figure 6. The lattice parameters of each are also given. TEM studies indicated that the average grain sizes of the materials heat treated at 473 K and 973 K were ~20 nm and 120 nm, respectively.

When heat treated within region III, the Cu_2MnAl Heusler phase decomposed, giving rise to the abrupt drop in magnetization seen in figure 4. The Cu_3Mn_2Al equilibrium phase could not be detected on the x-ray diffraction curves of any of the samples heat treated within this region. The saturation magnetization of the sample heat treated for 24 h at 473 K was less than after 1 h heat treatment at this temperature. Very small Cu_9Al_4 peaks could be detected along with Cu_2MnAl peaks on the x-ray diffraction curve of this sample. This suggests that the Heusler phase decomposes at this temperature also. In region IV, part of the Cu_2MnAl phase remained in equilibrium with the other phases, providing a ferromagnetic contribution. The fraction of the Cu_2MnAl phase present and hence the magnetization increased as the heat treatment temperature increased. These trends were also observed in samples milled for periods up to 48 h.

The saturation magnetization of samples heat treated at 473 K for 24 h after varying durations of milling was used to judge the progress of mechanical alloying. In figure 7, measurements of M_s as a function of milling time are shown. The reaction was essentially complete after milling for 48 h. As discussed above, the heat treatment at 473 K resulted in ordering of the Heusler phase formed during milling, causing it to become ferromagnetic.

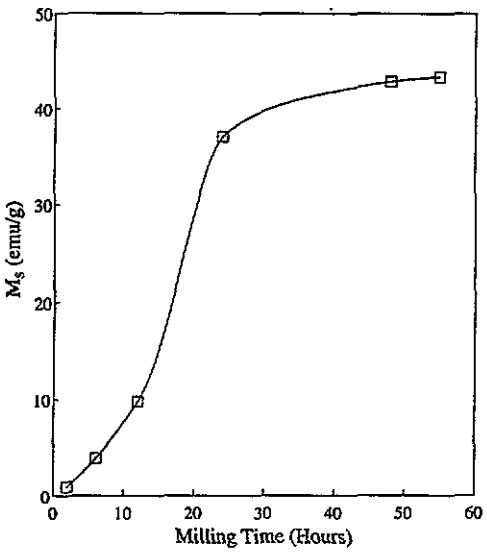

Figure 7. Saturation magnetization after 24 h heat treatment at 473 K against milling time.

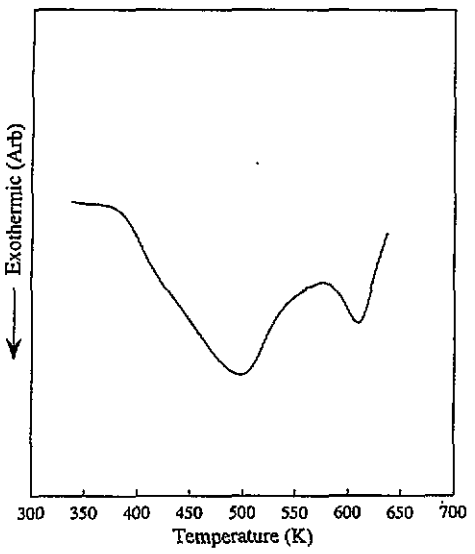

Figure 8. The DSC heating curve of a sample ball milled for 48 h.

The Cu, Mn and Al that remained unreacted or partially reacted after milling underwent a solid state reaction, to form α-Mn and Cu_9Al_4.

A DSC heating curve of a sample milled for 48 h is shown in figure 8. Two broad exothermic peaks can be seen. The initiation temperatures of the first and second peaks were respectively 383 K and 582 K. The enthalpy changes associated with these peaks were $\sim$2.2 kJ mol^{-1} and 1.3 kJ mol^{-1}, respectively.

It is very difficult to assess the state of order of a ternary alloy using x-ray diffraction alone. The superlattice peak intensities of the present material obtained using Cu Kα radiation were very weak and difficult to measure accurately. Calculation of the superlattice/fundamental intensity ratios $I(111)/I(220)$ and $I(200)/I(220)$ for a perfectly ordered $L2_1$ structure, using the structure factors given by Webster [1] and the atomic scattering factors and intensity relationships given by Cullity [17], gave 0.04 and 0.07 respectively. After heat treatment at 473 K, superlattice lines could not be detected above the background in the x-ray diffraction patterns. After heat treatment at 973 K, superlattice/fundamental ratios were respectively 0.03 and 0.05. After further heat treatment at 473 K for 165 h, these values increased to 0.04 and 0.05. There was a corresponding increase in saturation magnetization from 80.4 emu g^{-1} to 85.5 emu g^{-1} as a result of this ordering treatment. An increase in lattice parameter was also observed, from 5.966 Å to 5.970 Å.

A sample heat treated at 973 K was subsequently remilled. X-ray diffraction patterns after remilling for 4 min and 24 h are shown in figure 9. Comparison of the diffraction curves shows that the intensity of superlattice peaks decreased with remilling, indicating the introduction of disorder. The diffraction peaks also became broadened, suggesting the introduction of internal strains and refinement of crystallite size. As shown in figure 10, the lattice parameter of the Heusler phase varied with remilling time. Also shown in figure 10 is the decrease in the $I(111)/I(220)$ intensity ratio with remilling time. The effect of remilling time on the saturation magnetization and coercivity is shown in figure 11.

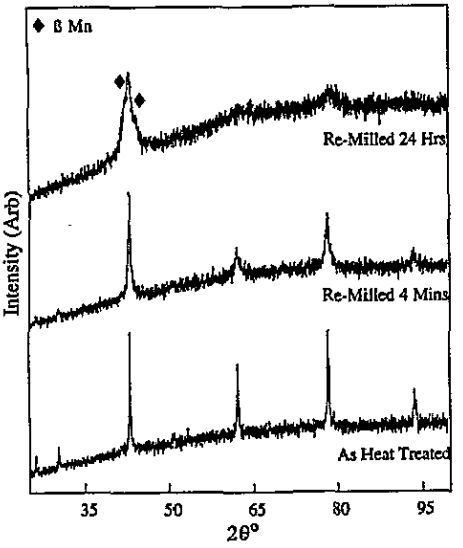

Figure 9. X-ray diffraction patterns of samples heat treated at 973 K and remilled.

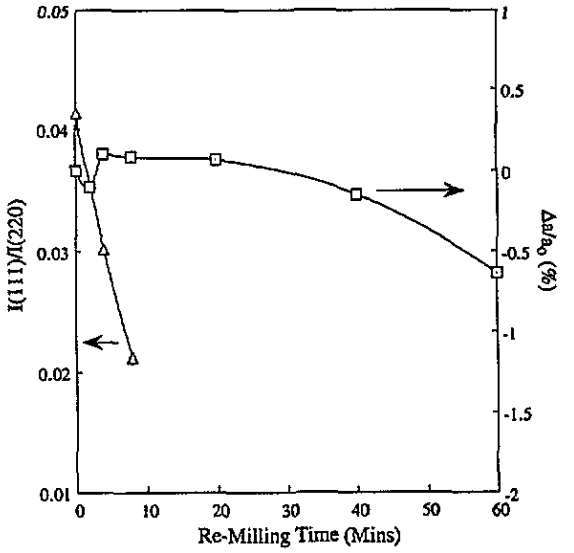

Figure 10. The variation in lattice parameter and $I(111)/I(220)$ intensity ratio with remilling time.

Remilling decreased M_s while increasing H_c, with no effect on the remanence being oberved. A sample remilled for 40 min was heat treated at 473 K for 96 h, this had the effect of reordering the Heusler phase. As a result of heat treatment, M_s increased to within 7.3 emu g^{-1} of the as-heat-treated material. The lattice parameter was restored to within 0.001 Å of the starting value. As shown in figure 9, β-Mn peaks were detected on either side of the (220) Cu_2MnAl peak in the sample remilled for 24 h, indicating that decomposition of the Heusler phase occurred. This sample was then heat treated for 96 h at 473 K, which had the effect of reordering the remaining β-Cu_2MnAl phase. The lattice parameter returned approximately to that of the starting value and the M_s increased, but was 54 emu g^{-1} below

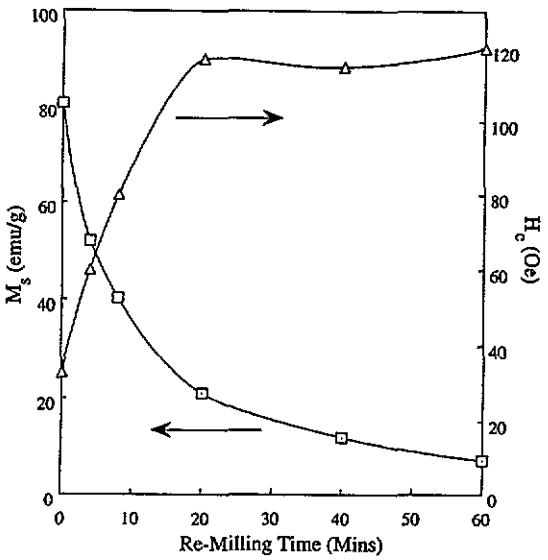

Figure 11. The variation in saturation magnetization and coercivity with remilling time.

the initial value, due to the decomposition that occurred during milling. The presence of the β-Mn was clearly evident on the x-ray diffraction curve of the re-heat-treated sample.

4. Discussion

The Cu_2MnAl phase produced by the mechanical alloying of elemental Cu, Mn and Al was clearly in a highly disordered state. The disordered BCC Cu_2MnAl phase is metastable at room temperature; however, above 1023 K this phase is stable. In the absence of long-range order, the as-milled structure is not expected to be ferromagnetic [1]. The magnetic hysteresis measurements made on this material indicate the presence of non-interacting paramagnetic and ferromagnetic phases. The spontaneous magnetization is in agreement with the value expected from the presence of the 0.3 wt% Fe picked up during milling. This suggests that the disordered Cu_2MnAl is paramagnetic. The amorphous thin-film Cu_2MnAl alloy prepared by Taylor and Tsuei [10] also behaved paramagnetically.

When heat treated at 973 K, the saturation magnetization of the mechanically alloyed material was comparable to that of alloys reported by other investigators. Conventionally prepared Cu_2MnAl usually possesses some degree of Mn–Al disorder, which affects only the intensity of odd superlattice lines [1, 18]. The increase in (111) superlattice line intensity when the sample initially heat treated at 973 K was re-heat treated at 473 K suggests that some Mn-Al disorder was removed from the material. The resulting increase in saturation magnetization is also in agreement with previous studies [13].

The saturation magnetization of the sample heat treated at 473 K was considerably lower than that of a conventionally prepared Cu_2MnAl alloy. It is possible that this is a consequence of the small grain size (~20 nm). After heat treatment at this temperature, the present material possesses a high grain boundary volume fraction. Grain boundaries are regions of high disorder and, since chemical order affects magnetic behaviour in this alloy, this result is not suprising. The saturation magnetization of Taylor's thin-film Cu_2MnAl alloy, after annealing at 473 K, was 255 Gauss when measured at room temperature [10].

This is approximately 50% of the value attained by Heusler in a bulk alloy, prepared in the conventional manner [11]. Taylor's alloy was reported to have a small grain size and the difference was attributed to disorder at the grain boundaries.

Comparison of the M_s of the present alloy after heat treatment at 473 K, to that of the sample heat treated for 5 minutes at 973 K followed by 165 h at 473 K suggests that approximately 44% of the mass of the alloy is disordered. Assuming that the reduction in M_s is due to the disordered grain boundaries, and assuming equal density within the grains and grain boundaries and modelling the grains as cubes of side length 20 nm, the calculated effective grain boundary width is approximately 4 nm. In a study of ordered stoichiometric $L1_2$ compounds, Yan and coworkers [19] found that the disordered material surrounding grain boundaries was confined to a ribbon of approximate width $1.5a_0$ in a strongly ordered Ni_3Al compound and $2a_0$ in a weakly ordered Cu_3Au compound. If this trend were true for the $L2_1$ Heusler alloy, then this would lead to an effective grain boundary width of approximately 0.9–1.2 nm. Therefore, it is suggested that the present material is likely to possess some degree of disorder within the grains as a result of residual internal strain from the milling process, since 473 K is a relatively low heat treatment temperature.

The magnetization achieved after heat treatment within region III of figure 4 was very low. The magnetic hysteresis measurements were similar to that of the as-milled material, except the spontaneous magnetization was considerably lower. The low values of M_s in samples heat treated in region III are interpreted as resulting from the Fe atoms taking positions within the structure of one or more of the phases present. The remaining β-Cu_2MnAl, while depleted in Mn, may have made a small ferromagnetic contribution.

The β phase in conventionally cast Cu_2MnAl alloys is stable when heat treated at temperatures up to 623 K [5–7]. The results presented in figure 4 indicate that the β phase of the mechanically alloyed material decomposes at temperatures below 623 K, with slow decomposition occurring as low as 473 K. However, after an initial heat treatment at 973 K, the material was stable when aged at 473 K for 165 h. A clear reason for this behaviour cannot be given. It is possible that even after milling for very long periods, the as-milled powder is not completely homogeneous. During heat treatment at 473 K, the Cu_9Al_4 phase could form in inhomogeneous particles, as was found when samples milled for short periods were heat treated at this temperature. Hence, nucleation of this phase from the β phase would not be necessary and decomposition would proceed as the Cu_9Al_4 phase grew at the expense of the β phase. Kozubski and Soltys [20] reported that when the β phase of a cast alloy was partially decomposed by heat treatment at 733 K, subsequent annealing at 473 K caused the decomposition to continue.

The two exothermic peaks seen on the DSC curve of figure 8 are similar to those observed by Zhou [21] during the heating of a CoV sample that had been disordered by mechanical milling. Zhou showed that superlattice lines were present in the x-ray diffraction pattern of the material removed from the DSC at a temperature between the two peaks. When measurements were made on material removed from the DSC at a temperature above that of the second peak, Zhou found that the diffraction peaks were not as broad as seen in the previous results. It was then concluded that the first peak had been due to the ordering of the alloy and that the second was due to grain growth. These results are not conclusive in the present alloy, since superlattice peaks cannot be detected after the material is ordered by low temperature heat treatment and the Heusler phase decomposes in the temperature range of interest. However, it can be seen from figure 4 that the initiation of the first peak at 383 K corresponds to the temperature at which the onset of ferromagnetism is observed in heat-treated samples. This indicates that the first peak is due to the ordering of the alloy; strain recovery processes are likely to be in operation during this period also. The second peak

may result from additional recovery processes and grain growth similar to that proposed by Zhou [21]. It is also possible that the second peak is associated with the decomposition of the Heusler phase, which, as seen in figure 4, occurred in this temperature range. However, no peak was observed at this temperature on DSC measurements of samples initially heat treated at 973 K, although x-ray diffraction measurements showed the occurrence of decomposition at this temperature.

It is well known that mechanical milling can be used to disorder ordered structures [22, 23]. The type of disorder introduced corresponds to that found after quenching from high temperatures, or by bombardment with heavy particles [24]. Changes in lattice parameter have been observed in compounds disordered in this manner. Increases in lattice parameter have been noted in milled compounds having the A15 structure [25–27]. X-ray and neutron diffraction techniques have concluded that antisite disorder can be induced in these compounds [28, 29]. It has been concluded that the increase in lattice parameter results from the size mismatch associated with the tendency of atoms of one type to occupy positions on the incorrect sublattice. Antisite disorder has also been found to cause a decrease in lattice parameter in the Ni_3Si ordered $L1_2$ compound [21]. Other decreases in lattice parameter have been observed by Di *et al* when CoGa and CoAl ordered $B2$ compounds were milled [30, 31]. In this case, the decrease was attributed to the introduction of triple-defect disorder. Vacancies are created when an atom leaves its own sublattice to join another [32–34], which results in a decrease in lattice parameter.

Apart from a small fluctuation during the first few minutes of milling, the lattice parameter of Cu_2MnAl was observed to decrease with increasing milling time. Since the superlattice intensity ratios and saturation magnetization also decreased, it is evident that the lattice parameter of Cu_2MnAl is dependent upon its state of order. The type of disorder expected is a function of the complexity of the starting structure [21]. The $L2_1$ structure of the Heusler alloys is very complex and the type of disorder introduced by milling is not known. The restoration of the lattice parameter observed when a remilled sample was reordered by heat treatment at 473 K suggests that the observed variations were not due to contamination or changes in composition of the samples.

A dependence of the lattice parameter upon the state of order is further suggested by comparison of the heat treated samples shown in figure 6. Disorder, reflected by lower values of M_s is accompanied by a smaller value of a_0. In each case where heat treatment at 473 K has been used to increase the ordering of the alloys, either after initial heat treatment at 973 K or after remilling, there has been a corresponding increase in a_0.

Figure 11 indicates that the saturation magnetization rapidly decreased with remilling time. As previously discussed, this represents an increase in structural disorder. Di *et al* [25, 30, 31] used magnetic saturation in a similar way to assess the state of order of mechanically milled CoGa and CoAl alloys . In these alloys, the saturation magnetization increased as disorder was introduced by milling. The coercivities of the Cu_2MnAl samples remilled for 20 min or longer are the highest known reports of coercivity in a stoichiometric Heusler alloy. The observed increases are thought to be due to the increase in dislocation density associated with remilling. Lapworth and Jakubovics showed that magnetic domain walls may be pinned by antiphase domain boundaries (APBs) in Cu–Mn–Al alloys [9]. These could either be thermal APBs or dislocation APBs, which were introduced by compression of the alloys. It was found that the coercivity of the alloys depended upon the antiphase domain size and the strength of the pinning effect. It is not known whether dislocation APBs are formed in this alloy as a result of mechanical milling. If so, the very high dislocation density expected could give rise to a very small antiphase domain size and high coercivities would be expected. It has been suggested by several authors that a possible mechanism

for mechanically induced disorder is the movement of dislocations, creating more and more APBs, finally resulting in homogeneous disorder [26, 35, 36].

It is not understood why the Cu_2MnAl phase should decompose when remilled for an extended period. Disproportionation is known to occur in other systems as a result of mechanical milling. The increase in free energy associated with the introduction of defects caused by milling can give rise to these non-equilibrium structures. Examples of this are the $Nd_2Fe_{14}B$ [37] and Sm_2Fe_{17} [38] compounds, both of which separate to α-Fe and an amorphous phase when milled. La–Ni compounds have been found to separate to elemental La and Ni upon milling [39]. However, these systems differ from the present results in that the products of milling are independent of the starting materials. The same result is achieved whether the compounds or some combination of the constituent elements are milled. Here, the Cu_2MnAl phase is stable when the elemental powders are milled, but not when the compound is remilled after heat treatment.

5. Conclusions

A disordered paramagnetic Cu_2MnAl phase is formed by the mechanical alloying of Cu, Mn and Al powders. This phase can be ordered when heat treated at 473 K and is then ferromagnetic. The saturation magnetization is lower than that expected for a fully ordered Cu_2MnAl Heusler due to the nanocrystalline grain size and chemical disorder existing within the grains. The material reverts to the equilibrium phases when heat treated in the temperature range 523 K $< T <$ 973 K. After heat treatment at 973 K, the resulting material is single-phase ferromagnetic Cu_2MnAl and the saturation magnetization is comparable to previous reports of conventionally prepared alloys. When the heat-treated material is disordered by remilling, the coercivity increases, while the saturation magnetization and lattice parameter decrease. Extended remilling resulted in decomposition of the Heusler phase.

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