Microstructure evolution of mechanical alloyed Ni–24 at % Si

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Nickel and silicon powders, of average composition Ni_3Si, were mechanical alloyed in a high energy ball mill. The severe plastic deformation produced by mechanical milling induced transformations with increasing milling time as follows: mixture of elemental Ni and Si powder → f.c.c. solid solution → nanocrystalline f.c.c. The structural evolution with milling time was followed by X-ray diffraction, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). Complete f.c.c. solid solution occurred at a milling time of 4 h and the saturated ΔH (by DSC) peak in the range of estimated enthalpy even after 24 h milling. The similarity of the mechanism of structural development by mechanical alloying of the $Ni_{76}Si_{24}$ powder mixture, and by mechanical milling of $Ni_{76}Si_{24}$ compound was also investigated in this study.

1. Introduction

The destabilization of crystalline material has been a recent interest of materials research. It has been shown that under certain thermodynamic and kinetic conditions the crystalline state is unstable and may collapse catastrophically into a disordered state [1, 2]. Crystal-to-glass transition has been achieved by means of rapid quenching, by ion and electron irradiation, by hydriding, and by solid state reaction in thin film diffusion couples [1]. More recently, it was shown that grinding a mixture of pure metals (mechanical alloying (MA) [3, 4]), or of metal compounds (mechanical milling (MM) [5, 6]), in a high-energy ball mill can result in amorphization.

The process of amorphization of elemental powders by MA has been explained by Schwarz *et al.* [4] and Hellstern *et al.* [7] as the synthesis of an ultra-fine composite in which a solid-state amorphizing reaction takes place, i.e. a method for producing fine-scale diffusion couples. The driving force for this reaction is the composition-induced destabilization of the crystalline phases in systems with large negative heats of mixing [8]. A kinetic constraint on formation of the equilibrium phase(s) is aided by asymmetry of the component diffusivities. However, in MA the severe plastic deformation creates defects: dislocations, planar defects, point defects, which can alter the reaction both thermodynamically and kinetically. Hellstern *et al.* [9] have demonstrated that high energy ball milling can introduce large values for the stored energy of cold work ($6 \, kJ \, mol^{-1}$ for AlRu and $10 \, kJ \, mol^{-1}$ for Ru); these are much larger than those obtained by conventional deformation processes. By

raising the free energy of the crystalline state relative to the amorphous phase the stored energy of cold work might influence the composition range for amorphization. The effect of defects introduced by the deformation might also have a significant effect on the kinetics of amorphization by providing diffusion short circuits and/or nucleation sites. The latter effects might favour or oppose amorphization. In addition, the defects introduced by the deformation also have the effect of grain refinement. Recently, it has been shown for Ni_3Al and Ni_3Si ($L1_2$ type) [10, 11] that ball milling results in only a crystal refinement of nanocrystalline dimensions, and even a partially amorphized phase. In this paper, the structure evolution of milling of the mixture of elemental Ni and Si powders was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). The results of these experiments are discussed as they relate to the mechanism for phase transformation by mechanical alloying as well as comparing to the phase transition mechanism of the ordered f.c.c. ($L1_2$ type) Ni_3Si intermetallic compound by mechanical milling.

2. Experimental procedure

The initial powders were 325 mesh ($\approx 45 \, \mu m$) 99.99 wt % nickel and 99.99% silicon and were blended in proportions to give a final mixture of ≈ 24 at % Si. Mechanical milling was carried out in a Spex Mixer/Mill, model 8000, using a hardened tool steel vial and 440C martensitic balls (3.2 mm in

diameter). The vial was sealed with a viton O-ring in an argon-filled glove box, the ball to powder weight ratio was 4:1. X-ray measurements were made with a Philips diffractometer, model PW1710 with CuK_{α} ($\lambda = 0.1542$ nm) radiation. Oxygen analysis reveals oxygen contamination levels of less than 0.4 at % O during milling. Thermal analyses were performed by means of a computerized differential scanning calorimeter (DSC), Du Pont 9900 thermal analyser.

Specimens for TEM were prepared by making powder pellet compacts (3 mm in diameter and 140 to 180 μm in thickness) by compressing the powder in a laboratory press under a pressure of 2 GPa. The compacted powder discs were thinned electrochemically in a Fischione Twin-Jet Electropolisher (model 110) in a solution of 10 vol % perchloric acid, 5 vol % hydrofluoric acid, 85 vol % methanol at a potential of 20–30 V. The polishing bath was maintained at a temperature of $-25\,^{\circ}C$. TEM was performed in a Jeol-2000FX microscope operating at 200 kV.

3. Results

MA of pure crystalline nickel and silicon powder was carried out at a composition of $Ni_{76}Si_{24}$. Fig. 1 shows XRD patterns of the powders after selected milling times. The starting powders show only nickel and silicon peaks. With increasing milling time, the peak intensities decrease and the fundamental f.c.c. peaks become broader. After 4 h milling, all of the silicon peaks have disappeared. For a longer milling time (24 h), only a broad peak between $2\theta = 40$ and 50°
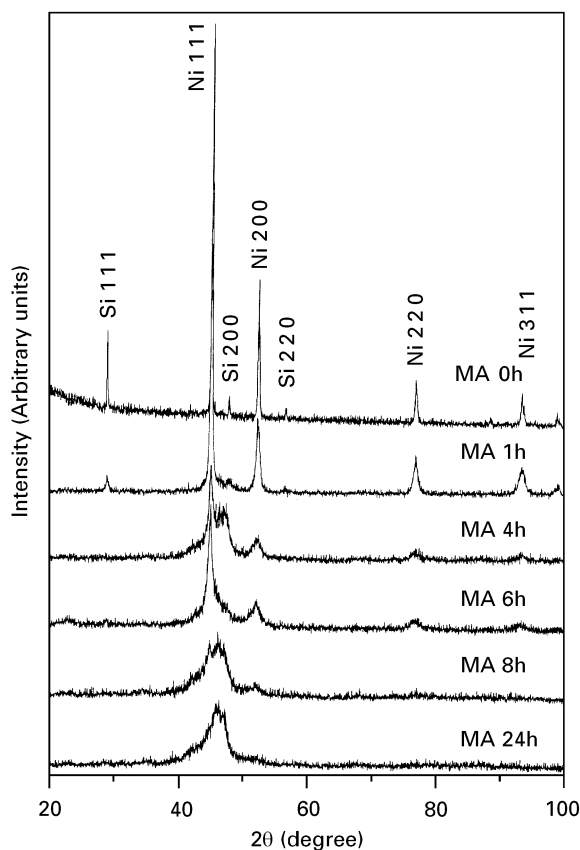
remains, indicating that the formation of a single phase is complete to the limit of resolution of XRD. When the powder milled for 24 h was annealed at $600\,^{\circ}C$ under vacuum of 6.665×10^{-3} Pa torr, the f.c.c. solid solution structure is transformed to an ordered f.c.c. structure, $L1_2$ phase. This is shown in Fig. 2.

If the Scherrer formula [12] is applied to the breadth of the major X-ray diffraction peak, the effective scattering length decreases with milling time and saturates at a value of 15 nm, as shown in Fig. 3. This is similar to the results of milling Ni_3Si compound by
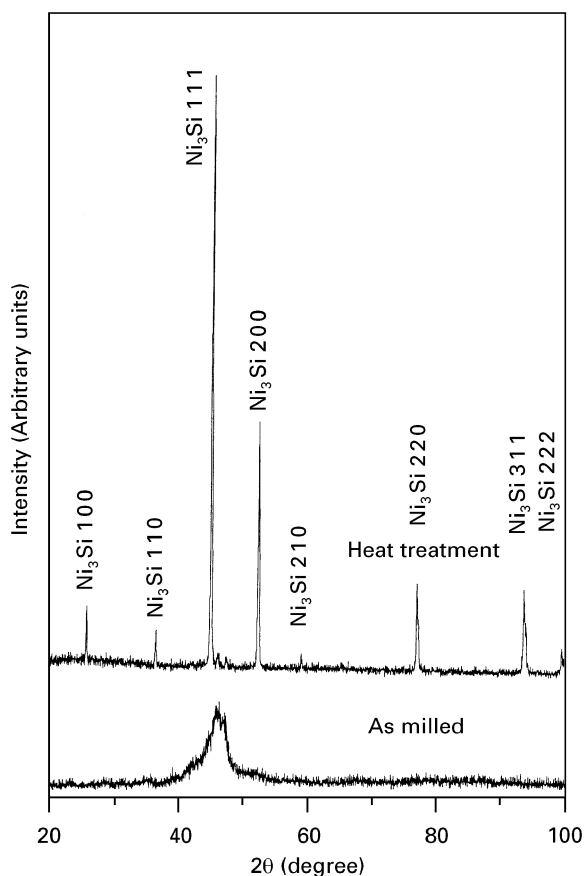
Figure 2 X-ray diffraction patterns of $Ni_{76}Si_{24}$ powder mixture for 24 h milling and annealed at $600\,^{\circ}C$.

Figure 1 X-ray diffraction patterns of some representative $Ni_{76}Si_{24}$ powder mixture before and after mechanical alloying.
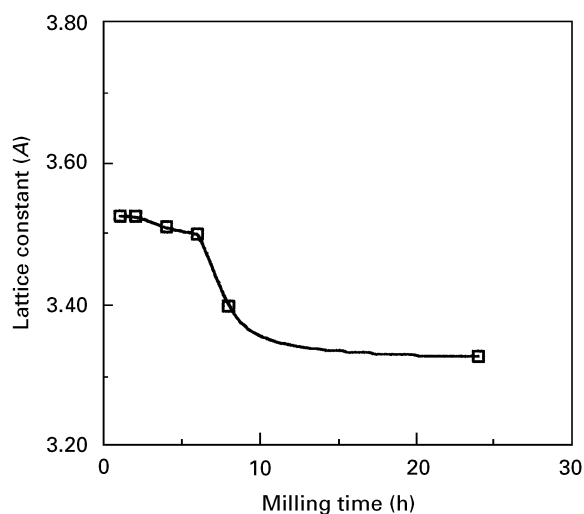
Figure 3 Lattice constant variation as a function of milling time.

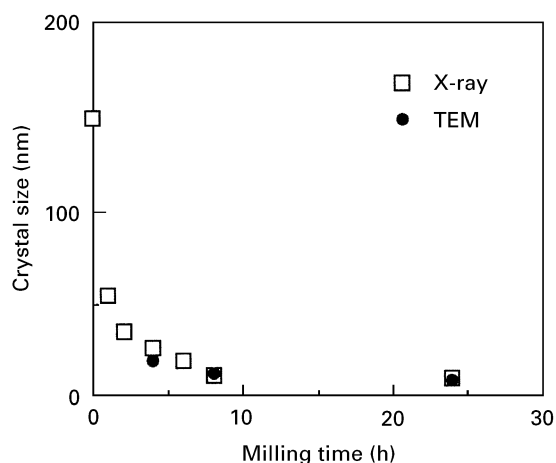*Figure 4* Crystal size as a function of milling time at room temperature for $Ni_{76}Si_{24}$ powder mixture. (□) XRD; (●) TEM.

Jang *et al.* [11]. Meanwhile, the lattice constant, calculated from the f.c.c. fundamental peaks of nickel, exhibits a decreasing trend with increasing milling time and saturates at the lattice constant at about 0.333 nm, as shown in Fig. 4.

The microstructures for the powder after varied milling times were investigated by TEM. After 4 h milling a completely f.c.c. solid solution structure is observed in the selected area diffraction pattern and the TEM observation reveals that an image of fine equiaxed cell or grain structure, as illustrated in Fig. 5. The data for crystallite sizes measured by TEM are plotted in Fig. 3 together with the average coherent scattering distances determined from X-ray line broadening, using the Scherrer equation. Fair agreement for these quantities is observed at 8 h milling time and 24 h milling times, respectively. This is illustrated in Figs 6 and 7. It appears that a metastable equilibrium on the nanocrystalline grain/cell refinement is induced by the severe plastic deformation of ball milling. Meanwhile, no evidence is observed to reveal the amorphization on the Ni–Si powder by ball milling.

The DSC measurements revealed an exothermic peak at about 530 °C which developed on milling $Ni_{76}Si_{24}$ powder mixture, as shown in Fig. 8. The measured enthalpies of the peak obtained from the calibrated integrated areas are plotted against milling time in Fig. 9. The peak enthalpy increases and reaches a saturation value of about 8 kJ mol^{-1} at about 6 h of milling. A change in the slope of the monotonically increasing ΔH versus milling time curve for the 530 °C peak is evident at about 2 h, which is the milling time when the silicon peak of X-ray diffraction disappears.

4. Discussion
Two considerations are always involved for any phase transformation: (1) the thermodynamics of the system – i.e. the differences in free energies of the parent and product phase which is the driving free force and (2) the kinetics – i.e. the mechanisms and constraints on
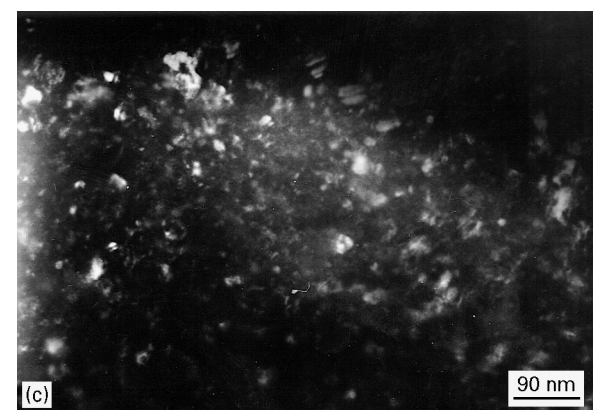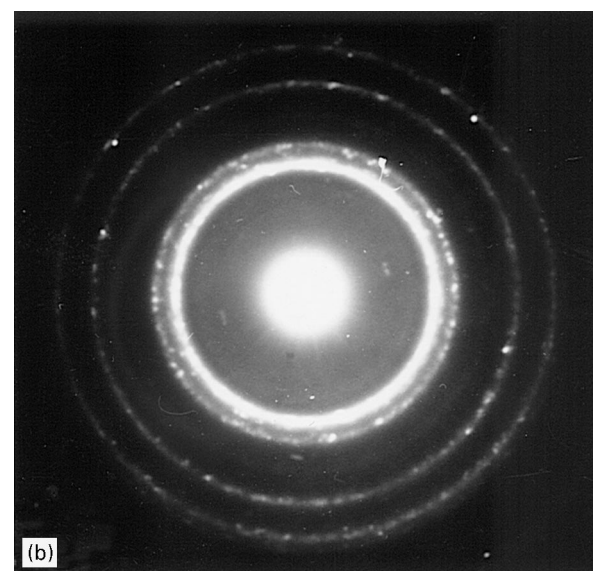

Figure 5 TEM micrograph of $Ni_{76}Si_{24}$ powder mixture milled for 4 h; (a) bright field image, (b) electron diffraction pattern, and (c) dark field image of (1 1 1) reflection.

the nucleation and growth of the product phase. Several phase transitions are evident in the present work on mechanical alloying of $Ni_{76}Si_{24}$ powder mixture that is introduced by the severe plastic deformation of high energy ball milling. This is a mixture of f.c.c. and diamond structure → f.c.c. solid solution → f.c.c. nanocrystalline.

In order to evaluate the thermodynamics of this transformation, a free energy diagram for the Ni–Si system was constructed for a temperature of 300 K.
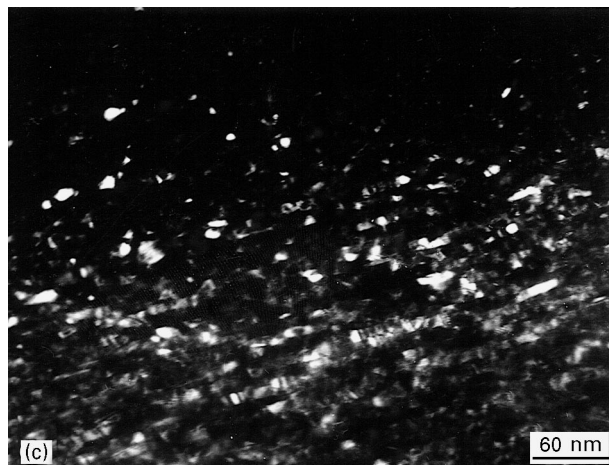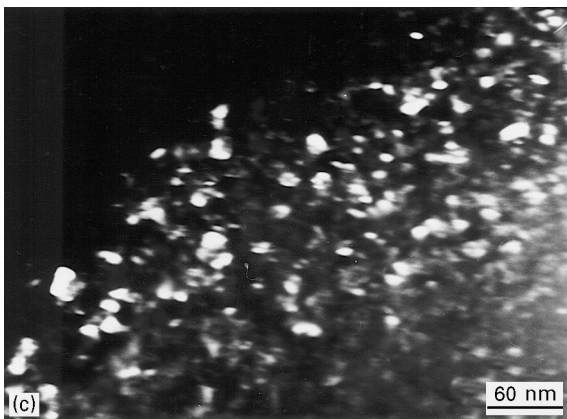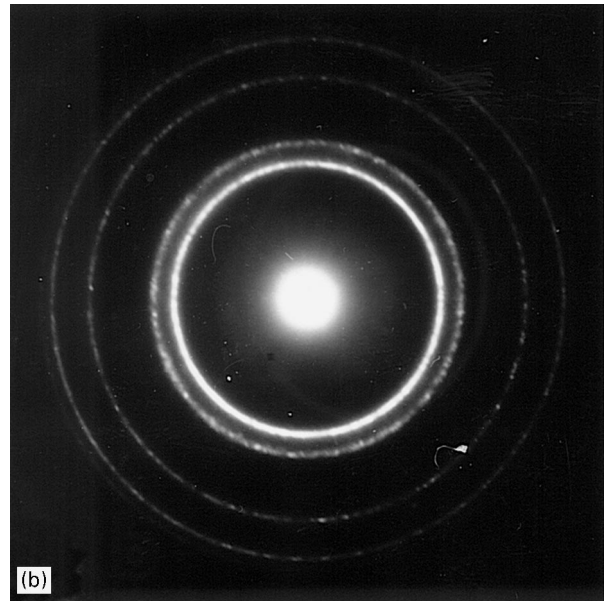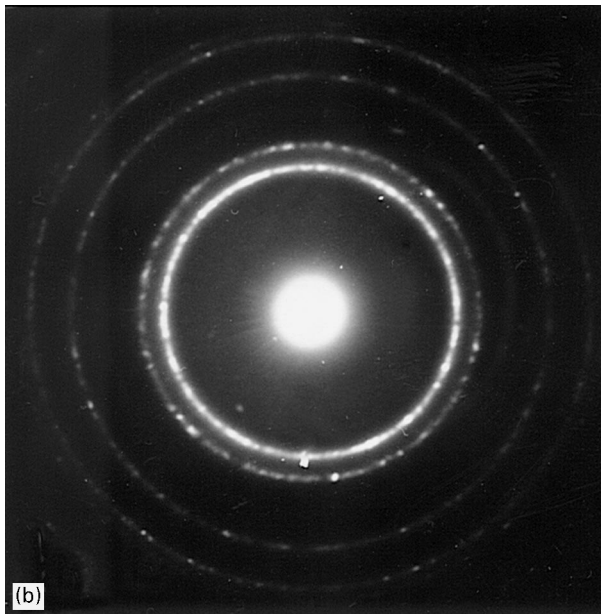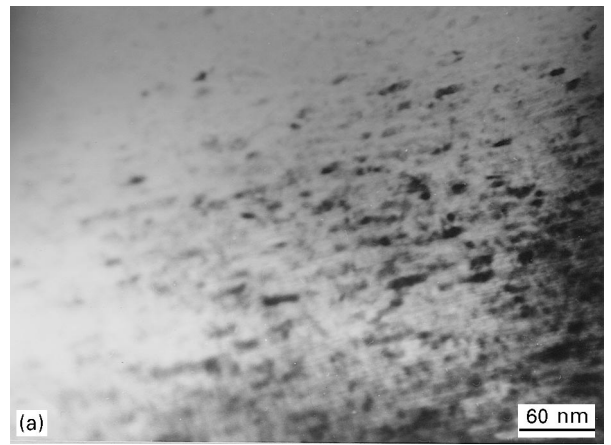
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Figure 6 TEM micrograph of $Ni_{76}Si_{24}$ powder mixture milled for 8 h; (a) bright field image, (b) electron diffraction pattern, and (c) dark field image of (1 1 1) reflection.
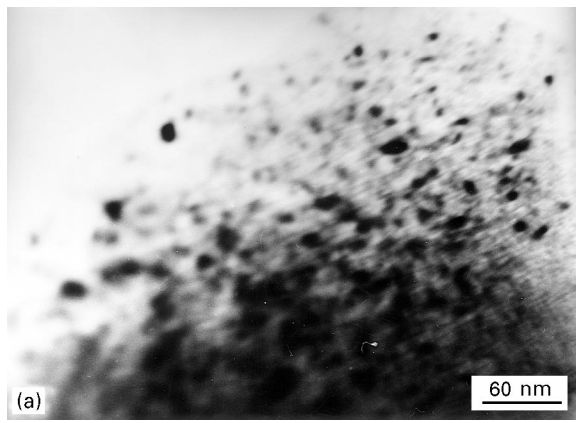
Figure 7 TEM micrograph of $Ni_{76}Si_{24}$ powder mixture milled for 24 h; (a) bright field image, (b) electron diffraction pattern, and (c) dark field image of (1 1 1) reflection.

A number of methods have been used to estimate the free energy of the phases, e.g. the CALPHAD approach [13]. Calculations of the enthalpy of formation, which can be applied to estimate the free energy of intermediate phases include Miedema's model [14] and the embedded atom method [15]. These methods were used with standard thermodynamic relations to calculate the free energy diagram for Ni–Si at 300 K. The free energy curves for various stable and metastable phases in the Ni–Si system are given in Fig. 10 [11]. From the free energy curve of Fig. 10, the free energy difference, ΔG^{0-ss}, between ideal solution state and f.c.c. solid solution states, is estimated to be about $-40 \, kJ \, mol^{-1}$. This is much larger than the
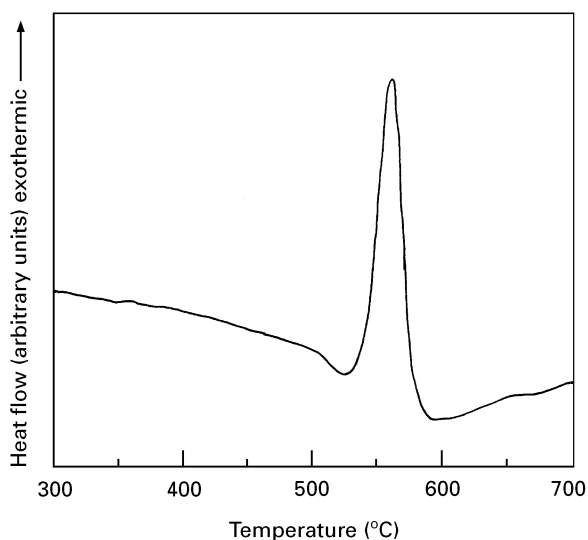
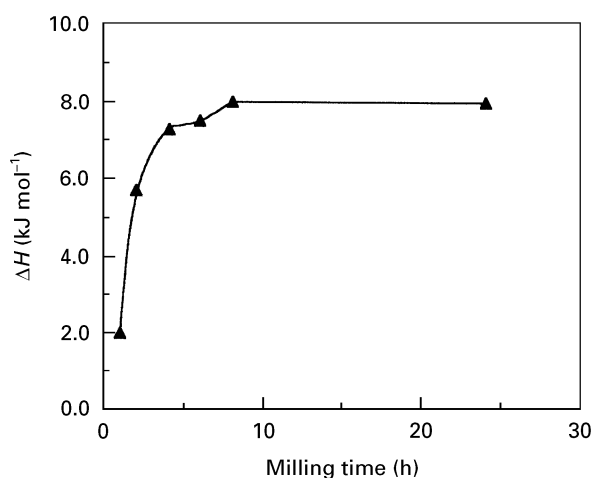Figure 8 DSC scan for $Ni_{76}Si_{24}$ powder mixture milled at room temperature for 24 h.

Figure 9 Enthalpy of 530 °C peak of DSC as a function of milling time for $Ni_{76}Si_{24}$ powder mixture milled at room temperature.

Figure 10 Calculated free energy diagram for the Ni–Si alloy system.

free energy difference, ΔG^{0-a}, between the ideal solution state and amorphous state (about $-3\,kJ\,mol^{-1}$). Therefore, the driving force for the transformation from the mixture of pure elements to the f.c.c. solid solution is much stronger than that from the mixture of pure elements to the amorphous state. This probably explains why the f.c.c. solid solution is more easily obtained by mechanical alloying Ni–Si powders in our experiment, by comparing the results of mechanical milling Ni_3Si compound in our previous work [11].

For the $Ni_{76}Si_{24}$ powder mixture after 4 h milling, a large exothermic peak is observed in the DSC at about 530 °C. The enthalpy values for these peaks (MA 4 h, 6 h, 8 h and 24 h) are all about $8\,kJ\,mol^{-1}$. This can be compared with the difference in free energy between the ordered and disordered f.c.c. Ni_3Si of about $8.5\,kJ\,mol^{-1}$. It appears to be in good agreement between experimental and calculated ΔG. However, this stored energy is smaller than the results of energy storage for milling Ni_3Si compound. Perhaps these two transition paths can reach different f.c.c.
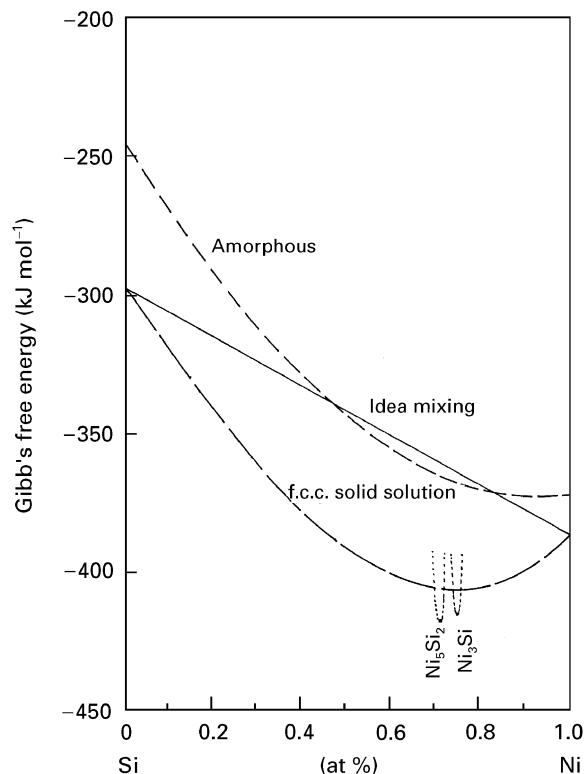
solid solution states and exhibit little difference in the DSC results. Meanwhile, according to the results of TEM observation, the final grain/cell size for both of these two transformation paths are 10 nm and 12 nm; this implies that the dynamic recovery effect seems similar between the mechanical alloying of $Ni_{76}Si_{24}$ powder mixture and the mechanical milling of Ni_3Si compound.

Jang and Koch [10] had reported on the partial amorphization of Ni_3Al intermetallic compound by high energy ball milling. The microstructure after very high deformations was found to be formed of a cell structure of about 2 nm diameter. In some volumes of the material an image and selected area electron diffraction pattern consistent with an amorphous structure were observed. Veprek et al. [16] also have noted a crystalline-to-amorphous transition in Si with decreasing grain size in chemical vapour-deposited Si films. An abrupt transition from microcrystalline to amorphous Si was observed when the grain size was reduced to about 3 nm. Both of the above authors suggested that when the nanocrystalline grain size falls below some critical value, the increase in grain boundary energy can act as the driving force for the crystalline-to-amorphous transformation. Even after milling the $Ni_{76}Si_{24}$ powder mixture for a long time (4 h and longer), its grain (cell) size only reaches a saturated value of about 10 nm, even after 24 h milling. This value is much higher than the assumed critical value of 2 nm. Comparing this result with the DSC enthalpy, this implies that no amorphous state will be obtained on the mechanical alloying of Ni_3Si powder mixture. This is also analogous to the results of our previous work and the results of Koch and his colleague [17].

5. Conclusions

High energy ball milling can transform the $Ni_{76}Si_{24}$ powder mixture into a f.c.c. solid solution with a very fine grain/cell (about 10 nm) microstructure. The evolution of these transformations with milling time was followed by XRD, TEM and DSC. Complete f.c.c. solid solution occurred at milling times of 4 h and kept the saturated ΔH of the DSC peak (about $8\ kJ\ mol^{-1}$) which is comparable with the calculated ordering enthalpy, even after 24 h milling. This terms out smaller than the results of energy storage for milling Ni_3Si compound. Perhaps these two different transition paths can reach different f.c.c. solid solution states and exhibit little difference in the DSC results. Meanwhile, the dynamic recovery effect seems similar between the mechanical alloying of $Ni_{76}Si_{24}$ powder mixture and the mechanical milling of Ni_3Si compound. This might be explained by the evidence of the TEM observation that reveals an average grain diameter of 10 to 12 nm after longer milling times, respectively. However, the structural development during milling of the f.c.c. solid solution for both Ni_3Si and Ni_3Al were analogously to be dominated by the formation and refinement of fine microcrystallites which eventually reached nanometer dimensions.

Acknowledgements

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