Thermal stability of nanocrystalline fcc and hcp Ni(Si) synthesized by mechanical alloying of $Ni_{90}Si_{10}$

M. K. DATTA†, S. K. PABI and B. S. MURTY‡

Department of Metallurgical and Materials Engineering, Indian Institute of
Technology, Kharagpur 721 302, India

ABSTRACT

The thermal stability of nanocrystalline fcc and hcp Ni(Si), obtained by mechanical alloying of $Ni_{90}Si_{10}$, has been studied. The allotropic transformation from fcc to hcp Ni(Si) is accompanied by a volume expansion of 8.6% and is observed when fcc Ni(Si) reaches a critical crystallite size of 10 nm. The hcp phase transforms to stable fcc Ni(Si) at 573 K. It has been identified that the lattice distortion in nanometre-sized crystallites from the equilibrium configuration and the decrease in the interfacial energy with grain refinement act as self obstacles in controlling the grain growth of nanocrystalline materials.

§ 1. INTRODUCTION

The thermal stability of nanocrystalline materials against grain growth is of both scientific and technological interest because of a high density of interfaces, which provide a significant driving force for grain growth. Grain growth in polycrystalline materials is driven by the decrease in interfacial energy and hence decrease in the total energy of the system. According to the well-known Gibbs–Thomson equation (Shewmon 1969) regarding the grain-growth process in conventional polycrystals, it is expected that the driving force for grain growth increases with a reduction in grain size, and might be extremely large for nanometre-sized grains even at room temperature. However, contrary to expectation, experimental observations indicate that most nanocrystalline materials of either elements or compounds, synthesized by various methods, exhibit inherent grain-size stabilities up to reasonably high temperatures (Suryanarayana 1995, Lu 1996).

The grain-size stability in nanocrystalline materials has so far been found to be related closely to the structural characteristics of the material, such as the grain size and its a distribution, grain morphologies, triple junctions, presence of a second phase, porosity in the sample and so on (Suryanarayana 1995, Lu 1996, Novikov 1999). In addition, lattice distortion of the nanometre-sized crystallites (Liu et al. 1994b, Lu 1996, Ayyub 1998) and decrease in the interfacial energy with grain refinement (Lu et al. 1993, Lu 1996) also may play an important role in controlling the grain-size stability of nanocrystalline materials. The present letter reports the effects of lattice distortion and interfacial energy of nanometre-sized crystallites on

the grain-size stability of fcc and hcp Ni(Si) based on the results of isothermal annealing treatments after mechanical alloying (MA).

§ 2. EXPERIMENTAL DETAILS

Mixtures of elemental powders of Ni and Si of 99.5% purity, corresponding to a nominal composition $Ni_{90}Si_{10}$, were subjected to MA using a high-energy planetary ball mill (Fritsch Pulverisette-5). The MA was carried out at 300 rpm for 50 h with WC milling media using a ball-to-powder weight ratio of 10:1. The mechanically alloyed powders after 30 and 50 h of MA were annealed isothermally at various temperatures (373, 423, 473, 523, 573, 673 and 773 K) for 4 h in evacuated quartz ampoules (about 10^{-6} Torr). The milled and heat-treated powders were characterized by X-ray diffraction (XRD) using a Philips 1710 X-ray diffractometer with CoK_α radiation. The effective crystallite size and relative strain of different phases in mechanically alloyed powders as well as the heat-treated products were calculated using the Voigt function single-line method (de Keijser et al. 1982) after eliminating the instrumental broadening contribution, using the most intense peak in the XRD patterns.

§ 3. RESULTS

XRD patterns of $Ni_{90}Si_{10}$ after different durations of MA are shown in figure 1. The diffraction peaks of Si disappeared after 20 h of MA, suggesting the formation of a fcc solid solution of Si in Ni (Ni(Si)). The increased incorporation of Si into Ni is known to decrease the lattice parameter of the latter (Pearson 1958). However, it is interesting to note that the positions of Ni(Si) peaks continuously shifted to lower angles, accompanied by a gradual broadening with increase in milling time, indicating a continuous increase in the lattice parameter and, consequently, in the unit-cell volume with refinement of crystallite size. MA for 30 h has resulted in the formation of a fcc solid solution of Si in Ni with a molar volume 6.93 cm³ mol⁻¹ (11 nm crystallite size), which is different from the molar volume expected for 10 at.% Si in Ni
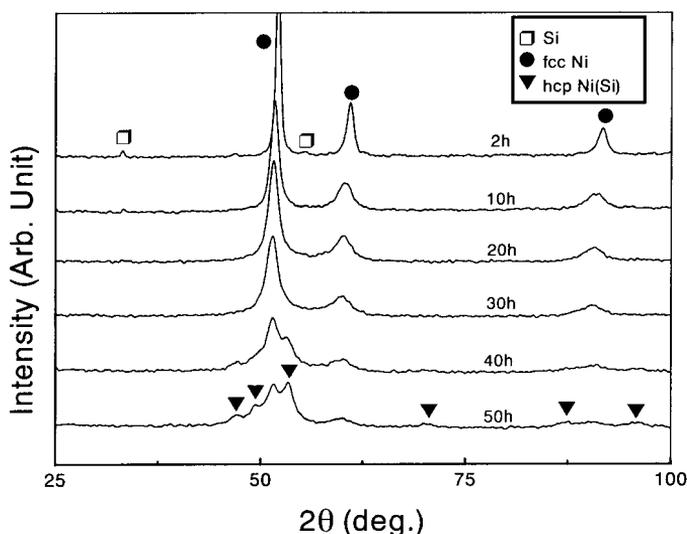

Figure 1.   XRD patterns of $Ni_{90}Si_{10}$ after different durations of MA.

($6.55 \, cm^3 \, mol^{-1}$). After 40 h of milling, new XRD peaks were detected (figure 1), which were successfully indexed as hexagonal Ni(Si) of molar volume $7.57 \, cm^3 \, mol^{-1}$ with a = 0.2601 and c = 0.4285 nm. Figure 2 shows the variation of molar volume of fcc and hcp Ni(Si) with the refinement of crystallite size. A molar volume expansion of $0.38 \, cm^3 mol^{-1}$ (5.8%) is evident for fcc Ni(Si) when the crystallite size decreased from the bulk state to 10 nm. At this stage, hcp Ni(Si) forms with a sudden increase in the molar volume by $0.60 \, cm^3 \, mol^{-1}$ (8.6%).

Figure 3 shows the XRD patterns of $Ni_{90}Si_{10}$ after 30 h of MA and after annealing at 423, 523, 573 and 673 K for 4 h. The positions of the Ni(Si) peaks shift to higher angles accompanied by a gradual sharpening with increase in temperature, indicating a continuous decrease of the unit-cell volume with increase in crystallite size. Figure 4 shows the variation of crystallite size and the molar volume of fcc Ni(Si) with increase in temperature. The crystallite size increases very slowly up to 523 K (22 nm at 523 K, in comparison with 11 nm in the as-milled state), while the molar volume drops from 6.93 to $6.57 \, cm^3 \, mol^{-1}$, which is close to the equilibrium molar volume of 10 at.% solid solution of Si in Ni ($6.55 \, cm^3 \, mol^{-1}$). Above this temperature (which is equivalent to $0.3T_1$, where T_1 is the liquidus temperature of $Ni_{90}Si_{10}$), substantial grain growth is observed (from 22 nm at 523 K to 39, 70 and 100 nm at 573, 673 and 773 K respectively), while the molar volume decreases only marginally to $6.55 \, cm^3 \, mol^{-1}$ after heating to 573 K and remains constant on further heating up to 773 K. The temperature for grain growth observed in the present study (greater than 523 K) agrees well with that reported by earlier workers (about 533 K by Knauth et al. (1993) and Cziraki et al. (1994)) for nanocrystalline Ni and fcc Ni(Si).

50 h of MA resulted in the formation of a mixture of fcc and hcp Ni(Si) of molar volume 6.97 and $7.61 \, cm^3 \, mol^{-1}$ respectively. The XRD patterns of a 50 h-milled sample and after annealing for 4 h at 423, 523, 573 and 673 K are shown in figure 5. It is clearly evident from the XRD patterns that the hcp phase is stable up to 523 K, and at 573 K it suddenly transforms back to the fcc phase. The variations of molar
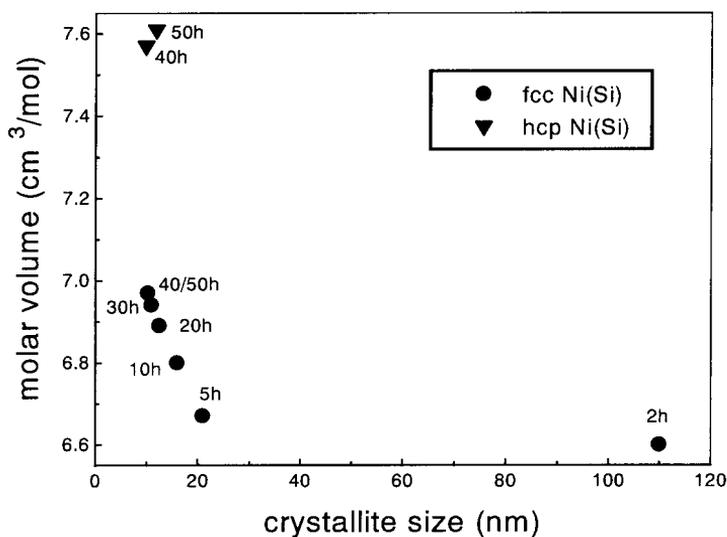

Figure 2. Variation of molar volume of fcc and hcp Ni(Si) with crystallite size after MA.
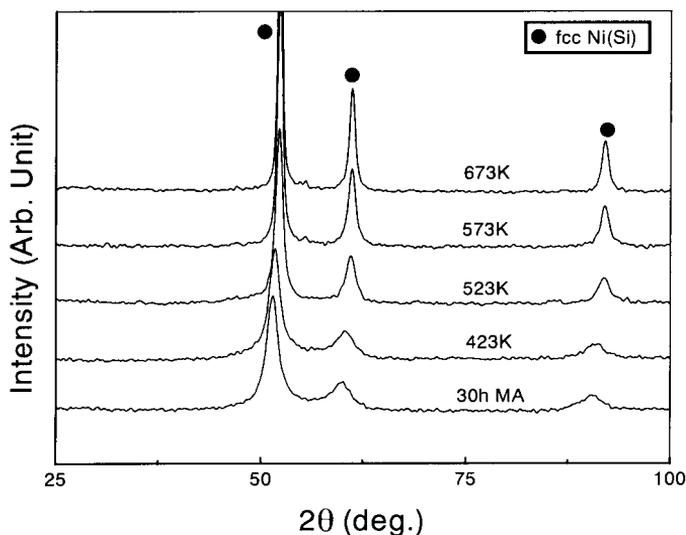
Figure 3. XRD patterns of $Ni_{90}Si_{10}$ annealed at different temperatures for 4 h and after 30 h of MA.
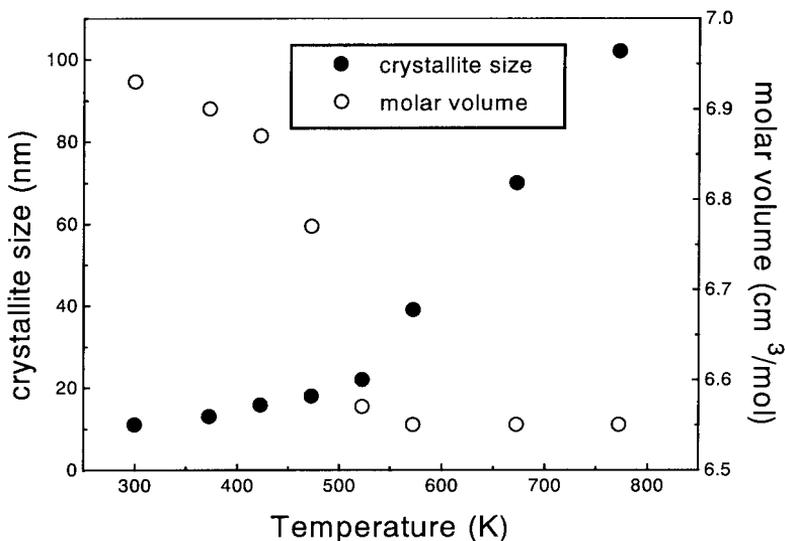

Figure 4. Variation of molar volume and crystallite size of fcc Ni(Si) with annealing temperature after MA for 30 h.

volume and crystallite size of fcc and hcp phases with annealing temperature are shown in figure 6. Similarly to the 30 h-milled sample, the crystallite sizes of both fcc and hcp phases increase very slowly up to 523 K (21 and 23 nm at 523 K, in comparison with 10 and 12 nm in the as-milled state for fcc and hcp phases respectively). The molar volume of the fcc phase drops from 6.97 to 6.56 cm^3 mol^{-1}, while that of the hcp phase increases from 7.61 to 7.82 cm^3 mol^{-1} when the milled sample is annealed at 523 K. When the crystallite size of the hcp phase reached 23 nm (at 523 K), it
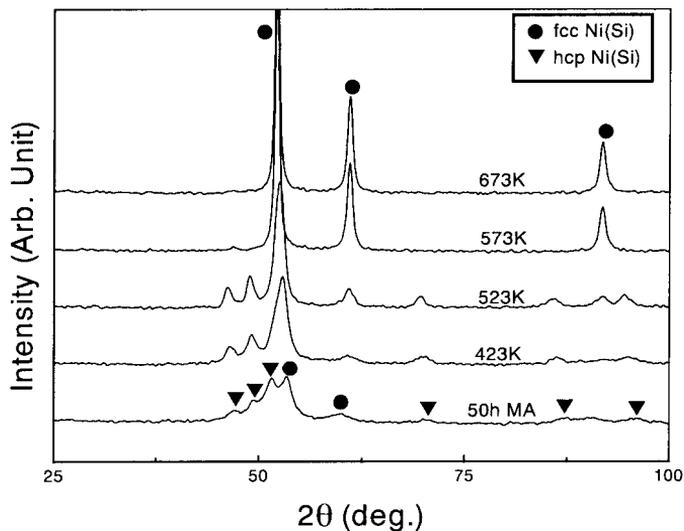
Figure 5.   XRD patterns of $Ni_{90}Si_{10}$ annealed at different temperatures for 4 h and after 50 h of MA.
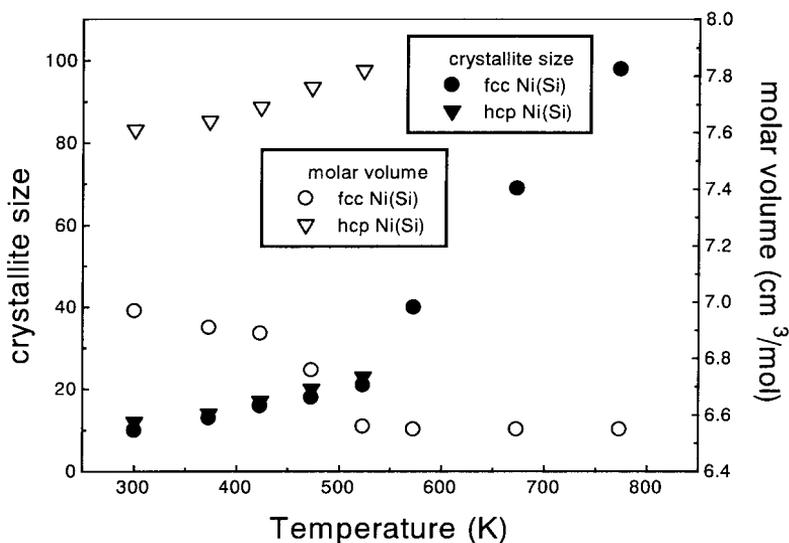

Figure 6.   Variation of molar volume and crystallite size of fcc and hcp Ni(Si) with annealing temperature after MA for 50 h.

appeared to become unstable and transformed back to the fcc phase. Above 523 K, substantial grain growth of fcc Ni(Si) was observed (from 21 nm at 523 K to 40, 70 and 100 nm at 573, 673 and 773 K respectively), while the molar volume remained more or less constant at 6.5 cm³ mol⁻¹, similar to the 30 h-milled sample. It is interesting to note that the crystallite size of fcc Ni(Si) at different annealing temperatures is insensitive to the previous milling time (30 h or 50 h) and also to whether the milled sample is single phase (fcc Ni(Si)) or a two-phase mixture (fcc + hcp Ni(Si)).

§ 4. DISCUSSION

The present results suggest that when fcc Ni(Si) reaches about 10 nm during MA, it suddenly transforms to the hcp phase, which transforms back to the equilibrium fcc phase on heating to 573 K. According to the mechanical instability model (Johnson et al. 1993, Ettl and Samwer 1994) of the crystal-to-amorphous transformation, there appears a common observation that the lattice atoms are displaced from their equilibrium lattice sites, causing lattice strain and softening of shear elastic constants to critical values during the course of amorphization, irrespective of the solid-state techniques used for this process. The prerequisites of this phase transformation (lattice strain and shear softening) could be met by the presence of static disorder in the parent crystal, which can be achieved either by the formation of a supersaturated solid solution or by accumulation of defects. Mechanical deformation during MA involves the creation and annihilation of a high density of dislocations in the material, leading to nanocrystalline grains with a special type of grain boundary (Fecht 1995). According to classical thermodynamic theory, the free energy of a crystallite relative to the perfect crystal will increase (by an amount σ_{gb}/d, where σ_{gb} and d are the grain-boundary energy and crystallite size respectively) when the crystallite size becomes smaller. Therefore, nanocrystallization is expected to enhance greatly the free energy of the system. The consequences of grain refinement into the nanometre scale may include either a supersaturated solid solution (owing to the enhancement of solubilities) or distorted lattice structures of crystallites (owing to supersaturation of defects) or both, in pure elements and intermetallics. As the equilibrium maximum solid solubility of Si in Ni is 10 at.% at room temperature, no extension of solid solubility is relevant in the present case, with the sample composition being $Ni_{90}Si_{10}$. Thus, any increase in the molar volume owing to the formation of a supersaturated solid solution can be ruled out. Hence, the increase in molar volume of the fcc phase with refinement of crystallite size can be attributed to an accumulation of defects. Once the molar volume of the fcc phase ($6.97 \, cm^3 \, mol^{-1}$) approaches the melting-point molar volume of pure Ni ($7.05 \, cm^3 \, mol^{-1}$), the grain boundary is expected to undergo defect-induced melting to an amorphous structure of zero shear modulus, which appears to relax immediately into a more compatible lower-density metastable hcp structure of molar volume $7.57 \, cm^3 \, mol^{-1}$, which is close to the molar volume of liquid at the melting point of Ni ($7.55 \, cm^3 \, mol^{-1}$). The mechanism of fcc-to-hcp transformation has been discussed thoroughly in terms of both mechanical and thermodynamic instability criteria in an earlier paper of the present authors (Datta et al. 2000).

The present results show that the increase in crystallite size with increase in temperature of fcc Ni(Si) is very small as long as the lattice is distorted from its equilibrium configuration. Once the lattice structure reaches the equilibrium configuration, substantial grain growth has been identified, suggesting that the lattice distortion of nanometre-sized crystallites also plays an important role in controlling the grain-size stability of nanocrystalline materials. In other words, an accumulation of defects, which is the main cause of lattice distortion, acts as an obstacle for the grain-growth process. The change of the distorted lattice to the equilibrium configuration is expected to arise through atomic diffusion, not only along the interfaces but also necessarily inside the crystalline lattice. Thus, grain growth in nanocrystalline materials is a result of both interface and volume diffusion. The distorted lattice reduces the volume diffusion coefficient and thus hinders the grain growth in nanocrystalline materials.

Grain growth in conventional materials is controlled mainly by atomic diffusion along grain boundaries. Knauth et al. (1993) have reported that the activation energy for the grain-growth process of fcc Ni(Si) is comparable with the activation energy for grain-boundary diffusion in Ni. The grain-boundary diffusion of an element depends on the interfacial energy, that is, the interfacial excess volume. Low-energy interfaces are generally more closely packed and consequently will present lower diffusivities, whereas high-energy interfaces are much more open and thus present easy paths for grain-boundary diffusion, resulting in faster grain growth. Thermodynamically (Datta et al. 2000), it is expected that the grains below a critical crystallite size always favour a lower interfacial energy, which can be achieved by the formation of either an amorphous grain boundary (Phillpot et al. 1995) (the crystal–amorphous interfacial energy is small in comparison with intercrystalline interfaces) or by the formation of a less dense phase (Datta et al. 2000), or by the segregation of a less dense element (such as Si in fcc Ni(Si)) (Cziraki et al. 1994) at the grain boundary. For nanocrystalline Ni, with average grain sizes ranging from a few nanometres to 60 nm, Liu et al. (1994a) have shown that the average interfacial excess energy decreases with a reduction in grain size in an approximately linear fashion. Therefore, it is expected that a decrease of the interfacial energy with grain refinement impedes interfacial diffusion and will reduce the driving force for grain growth.

In the present study, it has been shown that below a critical crystallite size (about 20 nm), the inherent characteristics of nanocrystalline materials, namely, lattice distortion from the equilibrium configuration and lower interfacial energy, act as self obstacles to grain growth. Above this critical crystallite size, the lattice distortion is minimal and the interfacial energy is expected to be high enough for normal grain-growth processes to prevail. It must be noted that, besides the lattice distortion and interfacial energy contribution, various kinds of drag due to the presence of a lower density second phase at the grain-boundary triple-junction porosities may also play an important role in inhibiting the grain growth in the nanocrystalline state.

§ 5. Conclusions

An hcp Ni(Si) phase forms during mechanical alloying with a volume expansion of 8.6%, when the crystallite size of fcc Ni(Si) becomes lower than a critical value (about 10 nm). This transformation is attributed to defect-induced melting of fcc Ni(Si) followed by relaxation to a lower density hcp phase. The hcp phase transforms back to the equilibrium fcc phase at 573 K when its crystallite size reaches about 20 nm. Lattice distortion in nanometre-sized crystallites from the equilibrium configuration and a decrease in the interfacial energy with grain refinement appear to act as self obstacles in controlling the grain growth of nanocrystalline materials.

References

AYYUB, P., 1998, Phys. Educ., **21**, 309.
CZIRAKI, A., TONKOVICS, Z., GEROCS, I., FOGARASSY, B., GROMA, I., TOTH-KADER, E., TARNOCZI, T., and BAKONYI, I., 1994, Mater. Sci. Engng. A, **179/180**, 531.
DATTA, M. K., PABI, S. K., and MURTY, B. S., 2000. J. Mater. Res., **15**, 1429.
DE KEIJSER, TH. H., LANGFORD, J. I., MITTEMEIJER, E. I., and VOGELS, A. B. P., 1982, J. appl. Crystallogr., **15**, 308.
ETTL, C., and SAMWER, K., 1994, Mater. Sci. Engng. A, **178**, 245.
FECHT, H. J., 1995, Nanostruct. Mater., **6**, 33.

JOHNSON, W. L., LI, M., and KRILL, III, C. E., 1993, J. non-crystalline Solids., **156–158**, 481.
KNAUTH, P., CHARAI, A., and GAS, P., 1993, Scripta metall. mater., **28**, 325.
LIU, X. D., LU, K., DING, B. Z., and HU, Z. Q., 1994a, Chin. Sci. Bull., **39**, 217.
LIU, X. D., LU, K., ZHANG, H. Y., and HU, Z. Q., 1994b, J. Phys.: condens. Matter., **6**, L497.
LU, K., 1996, Mater. Sci. Engng. R, **16**, 161.
LU, K., RUCK, R., and PREDEL, B., 1993, Scripta metall. mater., **28**, 1387.
NOVIKOV, V. V., 1999, Scripta. mater., **39**, 945.
PEARSON, W. B., 1958, A Handbook of Lattice Spacings and Structures of Metals and Alloys
        (London: Pergamon), p. 786.
PHILLPOT, S. R., WOLF, D., and GLEITER, H., 1995, Scripta metall. mater., **33**, 1245.
SHEWMON, P. G., 1969, Transformation in Metals (New York: McGraw-Hill), p. 300.
SURYANARAYANA, C., 1995, Inter. Mater. Rev., **40**, 41.