Thermodynamic Study of Magnetic Field-Enhanced Nanocrystallisation in Amorphous Fe-Si-B(-Nb-Cu)

Victoria A. Yardley, Sadahiro Tsurekawa^{*1}, Hiromichi Fujii^{*2} and Takashi Matsuzaki

Department of Nanomechanics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Recent work has shown that annealing amorphous alloys under an applied magnetic field can enhance the fraction of nanocrystalline phase formed and induce a strong texture. This effect has been attributed to the displacement of thermodynamic equilibrium by the energetic contribution from the applied field. In the present paper, an attempt is made to test the validity of this proposition in the Fe-Si-B(-Nb-Cu) system using equilibrium calculations in the framework of the CALPHAD (CALculation of PHAse Diagrams) methodology and a simple estimate of the energy supplied by the field. However, it is found that the magnetic energy term thus obtained is too small to produce the observed change in nanocrystalline phase fraction. Possible reasons for this discrepancy are discussed. [doi:10.2320/matertrans.MI200704]

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1. Introduction

The Fe-Si-B system forms the basis of a number of alloys that can be prepared in an amorphous state by melt-spinning or other rapid cooling processes and then heat-treated to give a nanocrystalline body-centred cubic (BCC) Fe-Si phase within a residual amorphous matrix. Such materials are of great technological interest because of their magnetic softness. In contrast to conventional, micro-scale behaviour, the coercivity decreases with decreasing grain size below a critical grain size.¹⁾ A 'random anisotropy' model, originally proposed to describe amorphous ferromagnets,²⁾ has been applied to amorphous-nanocrystalline two-phase systems to account for this behaviour.^{3,4)} According to this model, if the nanocrystals are smaller than the ferromagnetic exchange length, the effective magnetocrystalline anisotropy will be the average of the anisotropies over several crystals, and will consequently be lower than that of a bulk sample of the same material, leading to the low values of coercivity observed.

Previous work by some of the present authors has demonstrated that annealing Fe78Si9B13 and Fe_{73 5}Si_{13 5}B₉Nb₃Cu₁ amorphous ribbons under a d.c. magnetic field at an appropriate temperature can increase the fraction of crystalline phase formed and promote a strong (101) texture perpendicular to the ribbon surface.^{5,6)} The only crystalline phase observed to form under the experimental annealing conditions was the BCC Fe-Si phase. The critical temperatures determined for the Fe₇₈Si₉B₁₃ and Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁ alloys are summarised in Table 1. Observations of induced texture can be found in Table 2 and data on crystalline phase fraction in Table 3. In both alloys a 6T applied field causes an increase in BCC phase fraction. This field-induced effect appeared only in temperature ranges where the amorphous material was paramagnetic and the crystalline phase ferromagnetic. It has thus been attributed to the energetic contribution of the interaction between the

Table 1 Critical temperatures of $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ measured by DSC at a heating rate of 0.33 Ks^{-1} .

Composition	$Fe_{78}Si_9B_{13} \\$	$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$
Curie temp. of amorphous (K)	680	586
Crystallisation temp. (K)	800	750
Curie temp. of BCC (K)	940	920

Table 2 Effect of magnetic annealing conditions on texture formation.

Composition and annealing conditions	Fe ₇₈ Si ₉ B ₁₃ 853 K, 1.8 ks	Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁ 823 K, 1.8 ks
No field	Random	Random
2T, 4T // surface	Random	Degree of (101) texture increases with increasing field strength
6T // surface	Strong (101) texture in normal direction	Strong (101) texture in normal direction
$6T \perp surface$	Some $\langle 101 \rangle$ texture, but less than in parallel case	

Table 3 Phase fraction of BCC as estimated from EBSD micrographs $(Fe_{78}Si_9B_{13})^{5)}$ or X-ray diffraction data $(Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1)^{.6)}$

Fe ₇₈ Si ₉ B ₁₃ 853 K, 1.8 ks H // surface	Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁ 823 K, 1.8 ks H // surface
0.49	0.65
	0.68
	0.68
0.62	0.7
	Fe ₇₈ Si ₉ B ₁₃ 853 K, 1.8 ks H // surface 0.49 0.62

applied field and the magnetised material. This energy term is more negative for more strongly magnetised bodies, so an applied field will lower the free energy of a ferromagnetic phase more than that of a paramagnetic phase, resulting in a displacement of the position of equilibrium and increased stability of the ferromagnetic phase.

Table 4 summarises the effects of the applied field on the hysteresis parameters. A 6T magnetic annealing treatment

^{*1}Present address: Department of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

^{*2}Graduate Student, Tohoku University

Table 4 Effect of magnetic annealing conditions on saturation magnetisation and coercivity.

Composition and annealing conditions		Fe ₇₈ Si ₉ B ₁₃ 853 K, 1.8 ks H // surface	Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁ 823 K, 1.8 ks H // surface	
Saturation magnetisation	0 < H < 4T	Same as for as-spun	Increases monotonically with increasing H	
	H = 6T	Lower than for as-spun	Lower than for $H = 4T$	
Coercivity	0 < H < 4T	Greater than for as-spun	Extremely low	
	H = 6T	Greater than for as-spun	Extremely low	

caused a decrease in saturation magnetisation compared to that given by heat treatment under lower or zero applied field. This has been attributed to the increased fraction of BCC phase, in which boron has a very low solubility, and the consequent increase in the boron content of the remaining amorphous matrix. In Fe-B amorphous alloys, the saturation magnetisation was found to be maximum for a boron content of $15-16 \text{ at.}\%^{7}$ and to decrease beyond this.

Previous studies have considered the effect of a magnetic field on phase transformations in terms of magnetic contributions to Gibbs free energy, for example in Fe-C⁸⁾ and Fe-C-Si-Mn.^{9,10)} In the present paper, an investigation is made as to whether it is possible to simulate the observed effects on Fe-Si-B (Nb, Cu) alloy systems using similar considerations. Thermodynamic data and software using the CALPHAD framework are used to study the phase stabilities in these alloy systems and an estimate of the magnetic energy contribution is made using the same methods as in Refs. 8–10). One main motivation of this work is to determine whether the interpretation in terms of a magnetic free energy contribution is sufficient to explain the observed experimental results, or whether other effects need to be considered due to the nanocrystalline nature of this system. In addition, it would be useful to investigate whether the changes in saturation magnetisation can be related to the calculated phase compositions. If so, this would open the possibility for thermodynamic modelling to be used as a tool to design appropriate magnetically enhanced heat-treatments, reducing the need for costly and time-consuming experimentation.

2. Modelling Methodology

2.1 Calphad method

The CALPHAD (CALculation of PHAse Diagrams) methodology, first introduced by Kaufman and Bernstein,¹¹⁾ is described in detail in Refs. 12–15). In essence, it is a method of modelling the dependence of the Gibbs free energy of the phases in a system on temperature, pressure and composition. The expressions for the Gibbs free energy of binary and ternary interactions, are obtained from experimental data and *ab-initio* calculations and collated into a standard database format. This can then be used in a Gibbs energy minimisation program to determine the equilibrium phases and their phase fractions and compositions under a given set of conditions.

2.2 Data sources and model details

The utility of the CALPHAD method depends critically on

the existence of reliable thermodynamic data for the system of interest. Data and models from the literature were used to construct a database for the Fe-Si-B-Nb-Cu system. The "MatCalc" program from Graz University of Technology, Austria, was used to perform the equilibrium calculations.¹⁶) The majority of the thermodynamic data used in the calculations in this paper were taken from "IWS_Steel. tdb",¹⁷ a database supplied with "MatCalc", but the original sources of the data are detailed below.

2.2.1 Pure elements

Expressions for the free energy of the pure elements Fe, Si, B, Nb and Cu in the phases FCC, BCC and liquid were taken from Dinsdale,¹⁸⁾ apart from the parameters for metastable pure B in the form of BCC and FCC, which are listed in Hallemans *et al.*¹⁹⁾ and based on work by Pan and Saunders.²⁰⁾

2.2.2 Fe-B binary system and modelling of amorphous phase

Various authors have considered the extent to which thermodynamic analysis can be applied to supercooled liquid phases and the transition to a glassy state at the glass transition temperature T_g .^{21–26)} This transition is accompanied by an abrupt change in heat capacity but a continuous change in extensive properties such as volume and enthalpy, and has therefore been considered as a thermodynamic second-order transition analogous to the magnetic transition seen at the Curie temperature.^{27,28)} Shao has used this analogy to develop a model for use in CALPHAD-based calculations^{27,28)} with the same form as the existing model used for the magnetic transition (see Section 2.2.8^{29–31)}).

However, the glass transition temperature is also dependent on the rate of heating or cooling used to measure it, so it is clear that there is also a kinetic component involved.²¹⁾ An ideal glass transition temperature has been postulated based on thermodynamic arguments alone³²⁾ but to achieve this would require such a slow cooling that, in practice, crystallisation would intervene first.

Palumbo *et al.*³³⁾ assessed the Fe-B system, considering both the stable equilibrium phase diagram and metastable equilibria involving the amorphous phase. Their metastable assessment termed "Met 1" considers a liquid/amorphous phase with a transition at a glass transition temperature T_g ; above this, the phase has an excess heat capacity, but this becomes zero at T_g as ordering takes place. Parameters from the "Met 1" assessment have been used in the present paper to describe the Fe-B interactions. Since T_g values were not available from experimental DSC data, Palumbo *et al.* used an estimated value of 800 K; this value has likewise been used in the present paper.

2.2.3 Fe-Si binary system

Parameters for the Fe-Si interactions were taken from the reassessment by Miettinen³⁴⁾ of earlier work by Lacaze and Sundman.³⁵⁾ Since these assessments do not consider amorphous behaviour, parameters describing the liquid phase were used for the liquid/amorphous phase over the whole temperature range.

2.2.4 B-Si binary system

Parameters for the liquid phase in the B-Si system have been taken from Tokunaga *et al.*,³⁶⁾ and for the BCC phase from Miettinen.³⁷⁾ The liquid phase parameters were used across the whole temperature range to model the liquid/ amorphous phase.

2.2.5 Fe-Si-B ternary system

A thermodynamic description of a phase in a ternary system such as Fe-Si-B is obtained by first using an extrapolation method to estimate the free energy using the energy terms for the same phase in the constituent binary systems (Fe-Si, Fe-B and B-Si), as explained in Ref. 13). The result is then compared with experimental data to determine the ternary parameter for interactions between the three elements Fe, Si and B. An expression for the Fe-Si-B ternary interaction in the liquid phase can be found in Ref. 38). However, this was not obtained using the "Met 1" Fe-B parameters from Palumbo et al.33) but instead used a different model for the Fe-B system. It was therefore considered that using this expression in conjunction with the "Met 1" Fe-B parameters could result in inaccuracies, especially in the region around T_g where the excess heat capacity term has been introduced. The ternary term from Ref. 38) was thus excluded, and only the binary parameters were used. No ternary parameters were found in the literature in either the BCC or the FCC phase of the Fe-Si-B system. 2.2.6 Interactions involving Nb and Cu

Data are available in Ref. 17) for the liquid, BCC and FCC phases in the binary systems Fe-Cu (data listed in Ref. 39) and taken ultimately from Ref. 40)), Fe-Nb⁴¹⁾ and Cu-Nb.⁴²⁾ The parameters for the liquid phase were used in the model for the liquid/amorphous phase across the whole temperature range.

2.2.7 Stoichiometric phases

A number of intermetallic phases are included in the assessments in the literature, where they have been modelled as stoichiometric phases with fixed compositions.^{33,38)} These include the metastable iron boride Fe₃B,³³⁾ and the stable boride Fe₂B, which appears after a sufficiently long annealing treatment at temperatures above around 873 K in samples with Si content below about 12 at.⁶.⁴³⁾ However, since these phases were not observed in the experimental results of interest, they were excluded from the thermodynamic calculations to enable only the metastable equilibria between the liquid/amorphous and BCC phases to be considered.

2.2.8 Magnetic contributions to free energy

The intrinsic magnetic nature of phases such as BCC iron, which undergoes a ferromagnetic to paramagnetic transition at the Curie temperature, contributes to the Gibbs free energy. A model for this effect has been developed,^{29–31)} requiring parameters of Curie temperature and magnetic moment per atom to be included in the database descriptions for "magnetic" phases. In this system, BCC and FCC were

treated as magnetic and the magnetic parameters for the Fe-B and Fe-Si binary interactions were taken to be the same as those for pure Fe. The amorphous phase also goes through a ferromagnetic to paramagnetic transition at a lower Curie temperature than BCC,⁵⁾ but this was not considered explicitly in the model for Fe-B by Palumbo *et al.*³³⁾

2.3 Estimation of magnetic energy contribution

The general expression for the energy per mole of a body of magnetisation \underline{M} in an applied field \underline{H} is:

$$U_{mag,mol} = -\mu_0 V_m \left[\int \underline{M} \cdot d\underline{H} - \frac{N_d M^2}{2} \right] \tag{1}$$

where μ_0 is the permeability of free space, V_m is the molar volume expressed in m³, N_d is the demagnetising factor and <u>M</u> and <u>H</u> are in SI units of Am⁻¹. In the case of a paramagnetic material, Equation (1) becomes:

$$U_{para,mol} = -\mu_0 V_m \left[\frac{H^2 C}{T - T_C} - \frac{N_d M^2}{2} \right]$$
(2)

where *C* is the Curie constant and T_C is the Curie temperature. The ferromagnetic case is more complex because <u>*M*</u> is not a single-valued function of <u>*H*</u> and a number of energetic terms contribute to the free energy. Detailed accounts of the energetics of ferromagnets can be found in Refs. 44) and 45), but to obtain an order-of-magnitude estimate of the maximum magnetic free energy contribution in a ferromagnet, the following simplified case is considered:

i. the easy axis of magnetisation lies parallel to the direction of the applied field.

ii. the specimen is magnetised to saturation (\underline{M}_s) and so comprises a single domain.

iii. the applied field is much greater than that required for magnetic saturation, such that the path-dependent part of the magnetisation curve can be neglected.

This allows eq. (1) to be approximated to:

$$U_{ferro,mol} = -\mu_0 V_m \left[\underline{M}_s \cdot \underline{H} - \frac{N_d M^2}{2} \right]$$
(3)

3. Results

3.1 Test against unseen experimental data

Figure 1 shows a comparison between thermodynamic calculation and experiment for the dependence of the BCC phase fraction on boron content x in alloys of composition $Fe_{73.5}Si_{22.5-x}B_xNb_3Cu_1$ at 813 K. This is very close to the temperature T_g of 800 K chosen by Palumbo *et al.* for the transition between 'liquid' and 'amorphous' behaviour in their liquid/amorphous phase. Since there is some doubt about whether the 'liquid' or 'amorphous' state may be the most appropriate description of the behaviour at this temperature, curves for both the liquid and the amorphous state (extrapolated to 813 K) were calculated. The crosses are data points from Herzer¹⁾ giving the volume fraction of crystalline phase, the solid line represents the calculated phase fraction of BCC in equilibrium with the liquid/amorphous phase in its 'liquid' state, and the broken line is the fraction of BCC in equilibrium with this phase in its 'amorphous' state. There is good agreement between the experimental data and the



Fig. 1 Comparison of BCC phase fraction predicted using data for liquid phase (solid line), data for amorphous phase (dotted line) and experimental data from Herzer.¹⁾



Fig. 2 Phase fraction of BCC in equilibrium with the liquid/amorphous phase. The solid line represents $Fe_{78}Si_9B_{13}$ and the broken line represents $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$.

'liquid' curve, which successfully reproduces the decrease in BCC phase fraction with increasing boron content. This test helps to confirm the validity of both the model for the liquid phase and the applicability to the Fe-Si-B-Nb-Cu system of the value of T_g chosen by Palumbo *et al.*³³ which, being set at 800 K, implies that the material should be in its 'liquid-like' state at 813 K.

3.2 BCC phase fractions

Calculations of the metastable equilibrium between BCC, FCC and liquid/amorphous phases over the range 500–1000 K were made for the $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ systems, including the interaction terms for Nb and Cu, where appropriate.

The FCC phase was not observed experimentally, and the calculated results were in agreement, finding it to be unstable over the temperature range of interest. Figure 2 is a plot of the fraction of the BCC phase in equilibrium with the liquid/ amorphous phase for both alloys; the solid line represents $Fe_{78}Si_9B_{13}$ and the broken line, $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$. In $Fe_{78}Si_9B_{13}$, the stable fraction at the annealing temperature of 853 K is 0.58, and in $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ at 823 K, it is 0.72. In both cases, annealing took place above 800 K, and therefore in the region of liquid-type behaviour according to



Fig. 3 Compositions of phases in $Fe_{78}Si_9B_{13}$ alloy: (a) Boron content in liquid/amorphous phase; (b) boron content in BCC phase; (c) silicon content in liquid/amorphous phase.

the model. At the transition temperature T_g , the stable fraction of BCC changes abruptly from 0.46 below T_g to 0.58 above it in Fe₇₈Si₉B₁₃, and from 0.64 below T_g to 0.70 above it in Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁. These differences correspond quite closely to the differences in BCC fraction determined in magnetic annealing experiments (0.49 without a field and 0.62 with a 6T field in Fe₇₈Si₉B₁₃; 0.65 without a field and 0.7 with a 6T field in Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁). This may, of course, be coincidental, but a possible interpretation is attempted in Section 4.

3.3 Partitioning of boron and silicon in Fe₇₈Si₉B₁₃

Figure 3(a) shows the boron content in the liquid/ amorphous phase of the $Fe_{78}Si_9B_{13}$ alloy, and 3(b) shows

Table 5 Calculated values of magnetic moment per iron atom in Fe7₈Si₉B₁₃ samples annealed without and with a magnetic field.

Applied field	x_{Si}	x_B	f_{bcc}	а	b	$\mu_{Fe,bcc}$	$\mu_{Fe,amo}$	$\mu_{Fe,mix}$
0	0.09	0.13	0.49	0.18	0.25	1.81	2.05	1.94
6T	0.09	0.13	0.62	0.15	0.34	1.99	1.68	1.87

that in the BCC phase in metastable equilibrium with it. The observation that the BCC phase was effectively (Fe, Si)⁵) is successfully replicated by the calculation. B has a negligible solubility in the amorphous region and slight solubility, increasing with temperature, in the liquid region.

In the liquid/amorphous phase (Figure 3(a)), the boron content is between 0.3 and 0.31 for the FeSiB alloy in the liquid region, and between 0.24 and 0.28 in the amorphous region. These values are higher than that of 0.15–0.16 which gave a maximum of magnetic saturation as reported by Cowlam and Carr⁷⁾ and as a result, one would expect a monotonic decrease in saturation magnetisation of the amorphous matrix with increasing phase fraction of BCC in this range.

In Fig. 3(c), it can be seen that the solubility of silicon in the liquid/amorphous phase is also rather small, although greater than that of B in BCC. To a reasonable approximation, the metastable equilibrium phases can be considered as a BCC Fe-Si phase of composition FeSi_a and a liquid/amorphous Fe-B phase of composition FeB_b , with the fractions *a* and *b* given by:

$$a = x_{Si}/f_{bcc}$$

$$b = x_B/(1 - f_{bcc})$$
(4)

where x_{Si} and x_B are the atom fractions of Si and B, respectively, in the bulk composition, and f_{bcc} is the phase fraction of BCC.

The observed decrease in magnetic saturation at higher applied fields could be due to the competing effects of an increased fraction of BCC, which has a higher magnetic moment, and of boron enrichment of the amorphous phase, leading to a lower magnetic moment.

Data for the magnetic moment of Fe-Si alloys as a function of Si content can be found in Ref. 46). Although these data did not follow a linear trend over all the composition range, they were linear in the range $0.14 \le a \le 0.24$ and a straight line was fitted to them to obtain the magnetic moment per Fe atom, $\mu_{Fe,bcc}$, in BCC:

$$\mu_{Fe,bcc} = -4.61a + 2.66\tag{5}$$

The expression obtained by Cowlam and Carr for the magnetic moment per atom of amorphous Fe-B ribbons as a function of B content⁷) was used to obtain $\mu_{Fe,amo}$, the magnetic moment per Fe atom of the amorphous phase.

$$\mu_{Fe,amo} = 2.17 - 17.04 \times 10^{-4} (100b - 17.2)^2 \qquad (6)$$

An estimate of the average moment per iron atom of the bulk material can be obtained by applying a simple rule of mixtures and ignoring any differences in density between the two phases:

$$\mu_{Fe,mix} = \mu_{Fe,bcc} f_{bcc} + \mu_{Fe,amo} (1 - f_{bcc}) \tag{7}$$

This calculation, although it may be excessively simplistic, correctly predicts that the average magnetic moment per

atom is lower in the sample of $Fe_{78}Si_9B_{13}$ annealed under a field of 6T, with a BCC phase fraction of 0.62, than in the sample annealed under zero field, with a BCC phase fraction of 0.49 (Table 5).

3.4 Modelling of magnetic contribution

Using eq. (3), a value for the saturation magnetisation of $1.71 * 10^{6} \text{ Am}^{-1}$ for pure Fe from Ref. 47) and a molar volume for pure Fe of $7.09 \times 10^{-6} \text{ m}^3$ from Ref. 48), the energy contribution $U_{ferro,mol}$ was estimated as $-50 \,\mathrm{J}\,\mathrm{mol}^{-1}$ for a magnetic induction $\underline{B} = -\mu_0(\underline{M} + \underline{H})$ of 6T and a demagnetising field of zero. This value is of a similar order of magnitude to that determined by Jaramillo et al.^{9,10)} A value for $U_{para,mol}$ is more difficult to estimate because this requires a knowledge of the paramagnetic susceptibility of the liquid/ amorphous phase. Hysteresis loops were measured for the asspun amorphous material^{5,6)} but these were taken at room temperature, at which this phase is ferromagnetic. Jiles⁴⁹⁾ states that typical paramagnetic susceptibilities range from $\sim 1 * 10^{-3}$ to $\sim 1 * 10^{-5}$. This would give a magnetic energy term of $\sim -1 * 10^{-1}$ to $\sim -1 * 10^{-3} \,\text{J}\,\text{mol}^{-1}$. Since these terms are much smaller than those for the ferromagnetic free energy, only $U_{ferro,mol}$ is considered. A $U_{ferro,mol}$ term was added to the expression for the Gibbs free energy of Fe in the BCC phase, ignoring any temperature-dependence of this magnetic energy term, and the equilibrium was re-calculated. It was found that the estimated magnetic energy term was of insufficient magnitude to reproduce the experimentally observed changes in phase fraction of BCC. By making calculations with various different values, it was found that an energy offset term of approximately twice this (~ -0.1 $kJ mol^{-1}$) was necessary to give a discernible change in the fraction of BCC (Fig. 4(a)); this would require an applied field of around 9T. To obtain the changes in BCC fraction observed experimentally, much larger terms would be needed. Even a term of -2 kJ mol^{-1} , corresponding to an applied field of 180 T according to this calculation, is insufficient to produce the experimentally observed change of around 10% in BCC phase fraction. Additional energy terms do, as expected, increase the predicted fraction of boron in the liquid/amorphous phase (Fig. 4(b)).

4. Discussion

The good agreement of the thermodynamic calculations with the experimental data of Herzer¹⁾ in Section 3.1 allows confidence that the database used here can give reasonable predictions of phase stability in the equilibrium between the liquid/amorphous and BCC phases despite the lack of a ternary ordering term. The model for magnetic energy used here is very simple, but even in a more rigorous treatment of magnetic effects (in the Fe-C-X system), the calculated modifications of phase stability were small; ferrite-austenite phase boundary temperatures were modified by up to 3 K, at



Fig. 4 Effects of modifying the energy of Fe in BCC phase: (a) effect on phase fraction of BCC; (b) effect on B content of liquid/amorphous phase. Energy terms are given in $kJ \text{ mol}^{-1}$.

the most, per T of applied field.⁵⁰⁾ However, both the Fe-C-X phase boundary calculation, and that in the present paper, considered the energy of a bulk sample, and several effects that may influence magnetic energy in nanocrystalline/ amorphous systems have been disregarded. In particular, no attempt has been made to take into account the 'random anisotropy' effects expected for small nanocrystals,¹⁾ or the modification of the domain structure induced by annealing under a magnetic field.⁵¹⁾ In addition, the origin and energetic implications of the observed strong (101) texture perpendicular to the ribbon surface after magnetic annealing^{5,6)} have not been considered. Some or all of these effects could account for the observed increase in BCC phase fraction after annealing under a magnetic field.

Another possibility is that the applied field does indeed have only a small effect on the position of equilibrium, but a strong effect on reaction kinetics. It is possible that if the magnetic field enhances transformation kinetics, the sample annealed under a field is close to equilibrium after the end of the heat-treatment, while in the sample annealed for the same length of time without a field, transformation is still incomplete. The validity of this interpretation could easily be tested by annealing for longer times to determine whether any further change in phase fraction occurs.

A further possible interpretation is suggested by the observation in Section 3.2 that in both the alloys studied here, the BCC phase fraction after non-magnetic annealing is near that predicted by an equilibrium between BCC and the

'amorphous' ($T < T_g$) part of the liquid/amorphous phase. The fraction after magnetic annealing at 6T is closely approximated by an equilibrium with the 'liquid' $(T > T_{g})$ part of the liquid/amorphous phase. This does not seem to be easily explicable in terms of the effect of the magnetic field on the liquid/amorphous matrix itself; it appears unlikely that an applied field would favour the higher-volume liquidlike state over the lower-volume amorphous state. The calculations discussed above have considered the liquid/ amorphous matrix as an equilibrium phase for which the thermodynamic parameters of free energy, enthalpy, heat capacity etc. are single-valued functions of temperature (with the exception of the discontinuity at T_g). However, as discussed in Section 2.2.2, the glass transition temperature, and thus the state of the system at temperatures near T_g , varies with the rate of temperature change. The measured crystallisation temperature also depends on heating rate.⁵²⁾

Metallic glasses produced by melt-spinning, which involves quenching rates of the order of 10^6 Ks^{-1} , can contain a significant amount of structural disorder.⁵³⁾ The measured tracer self-diffusivity of as-spun amorphous alloys in the Fe-Si-B system decreases with increasing annealing time, finally reaching a plateau value.⁵⁴⁾ This is evidence of relaxation from a structure with quenched-in excess volume, giving a higher atomic mobility, to a more stable, lower-volume structure. The characteristic timescales for structural relaxation and for crystallisation can be similar at temperatures near the glass transition.55) The activation energy for crystallisation measured by Horváth et al. for Fe₇₈Si₉B₁₃⁵⁴⁾ was rather higher than that for tracer self-diffusion. This suggests that, on annealing, structural reorganisation could occur at least to some extent before the onset of crystallisation, and the crystals would form from a relaxed, nearequilibrium matrix. On the other hand, if the activation energy for crystallisation were reduced, crystal formation could begin before sufficient time had elapsed for structural relaxation, and in this case, the BCC phase would form from a higher-energy, non-equilibrium matrix. The higher energy of this phase would make it less thermodynamically stable and favour a greater fraction of BCC phase than would be the case for the relaxed matrix. Recent results show a greater nucleation rate of BCC in Fe_{73 5}Si_{13 5}B₉Nb₃Cu₁ on annealing with a magnetic field⁶⁾ so it is clear that applied fields can enhance crystallisation kinetics. If the difference in the kinetics of the two processes is small, then even a small energetic contribution from the applied field may be enough to change the relative rates of crystallisation and relaxation.

A possible criticism of this explanation is, however, that even if the stability of the matrix phase from which the BCC phase forms is initially different, there will be time for structural relaxation of the remaining matrix during the annealing treatment. In the case of an initially high-energy matrix which subsequently relaxes, the fraction of BCC phase formed will then be greater than that required by equilibrium, and some redissolution of BCC crystals may be expected. At sufficiently long annealing times, the magnetically and non-magnetically annealed specimens would tend to the same fraction of BCC phase.

The interpretation proposed above could be tested by performing a relaxation anneal on the ribbons at a low temperature before conducting a comparison between magnetic and non-magnetic crystallisation annealing treatments. If the interpretation is correct, the BCC phase fraction precipitated should be approximately the same irrespective of whether a field is applied.

5. Conclusions

Phase equilibrium calculations in the Calphad framework, using a database of thermodynamic parameters obtained from the literature, have been used to model metastable equilibria between the amorphous and crystalline BCC phases in the $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ systems. The predicted phase fractions of BCC gave good agreement with experimental data from the literature. The thermodynamic model predicted that the BCC phase would contain negligible B and the amorphous matrix only a small amount of Si. It was thus straightforward to estimate the dependence of the magnetic moment per unit volume as a function of the compositions of the two phases. A calculation using this method and a simple rule of mixtures successfully replicated the observed decrease in average magnetic moment of the material after magnetic annealing of $Fe_{78}Si_9B_{13}$.

The energetic contribution from a 6T applied magnetic field was estimated, but found to be insufficient to predict the large changes in BCC phase fraction observed experimentally. Several possible reasons for this have been proposed, including a consideration of the relative rates of relaxation and crystallisation processes. This interpretation is only a suggestion at present, but a simple experiment has been proposed to test whether or not it is viable.

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