Chemical Diffusion in L1₀-Ordered FePt

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Diffusion in FePt has been studied with emphasis on the effect of order-disorder transition by interdiffusion experiments below and above the L1₀–A1 transition temperature. The chemical diffusion coefficient in the disordered state obeys the Arrhenius law with the effective activation energy of 3.1 eV (1 eV = 1.6 × 10^{−19} J). Anisotropy of diffusion in the ordered state has been examined using monovariant single-crystals of the tetragonal L1₀ structure. The coefficient of diffusion in the *a*-axis direction is slightly lower than the extrapolation of the diffusivity from the disordered state, while that of diffusion in the *c*-axis direction deviates significantly toward lower values. The apparent activation energy for the diffusion in the two directions is 3.2 and 3.8 eV, respectively.

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1. Introduction

Ordered alloys in iron-group metal and platinum-group metal systems, such as FePt, FePd, CoPt, attract much attention in recent years for their unique magnetic properties (see, *e.g.*, Ref. 1) and references therein). To optimise fabrication processes and also to assess long-term performance, knowledge of the diffusion behaviour is essential. From a fundamental viewpoint of atomic diffusion, the effect of the order-disorder transition on diffusion is also of significant interest. Careful experiments from this aspect were made on tracer diffusion and chemical diffusion in CuZn,^{2,3)} which undergoes B2–A2 (bcc solid-solution) transition. However, no such investigations have so far been made in fcc-based alloys. In the last few years a study of diffusion in the Fe–Pt system, in which L1₀ and L1₂ ordering take place at compositions around 1 : 1 and 1 : 3, respectively, from the fcc solid-solution (the A1 phase), has been undertaken by the present authors.^{4–7)} This paper reports the results of the measurements of chemical diffusion in L1₀-ordered FePt. From the atomic arrangement in the structure shown in Fig. 1, anisotropy in diffusion is expected in the ordered state: the diffusion in the *c*-axis direction must be slower than in perpendicular directions. Evolution of the anisotropy with the development of order has been verified in the present study.

2. Experimental Procedure

2.1 Specimen preparation

Fe–Pt alloys of various compositions close to Fe₅₀Pt₅₀ were prepared by argon arc melting. Single-crystals were grown by unidirectional solidification in a Bridgman furnace using alumina crucibles, and were subsequently annealed in a vacuum for homogenisation. The composition of each alloy was determined by electron-probe microanalysis (EPMA). Discs or rectangular parallelepiped (RP) pieces were cut out from the crystals by spark erosion in such a way that the normal of the disc surface or of one face be parallel to one of

Fig. 1 Atomic arrangement in the L1₀ ordered structure. Solid lines and dashed lines indicate respectively the crystallographic unit cell with the lattice parameters *a'* and *c'* and the cell based on the face-centred cubic structure with *a* and *c*. At room temperature, *a* = 0.385 nm, *c* = 0.372 nm (*c/a* = 0.966).

the {001} directions of the parent fcc crystal. Pieces to be used for experiments in the ordered state were then subjected to a thermomechanical treatment described below to let them consist of a single variant of the L1₀ structure.

The treatment was done using a high-temperature mechanical testing machine with a specially designed equipment by which a constant compressive load can be applied to the specimen. A disc or RP-shaped piece was mounted with its {001} faces being normal to the loading axis, and was heated up to 1523 K in a vacuum under a uniaxial compressive stress of 8–10 MPa. After being kept at that temperature for 5 min, it was cooled down to room temperature. This procedure, which is an adaptation from the method developed for FePd,⁸⁾ leads to strong preference of the L1₀ variant whose *c*-axis is parallel to the stress axis, as the *c/a* value is less than unity in FePt⁹⁾ as well as FePd. The volume fraction of the favoured variant was evaluated by X-ray diffraction, from relative intensities of 002 and 200 diffraction lines: when successful it was always more than 90%.

2.2 Interdiffusion experiments

Diffusion couples were prepared by diffusion bonding of two pieces of different compositions by vacuum annealing at

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1273 K for 30 min under a compressive stress of 15 MPa. The compositions of the pieces consisting a couple were (in mol%Fe) 47/55 for experiments in the disordered state and 42/54 for those in the ordered state. The 47%Fe alloy in the former was a coarse-grained polycrystal (grain size ≈ 0.1 mm). For the latter, two types of couples were prepared. Type 1 consists of two single-variant single crystals with their *c*-axes parallel to the bonded interface, while type 2 with those normal to the interface. The chemical diffusion in the direction normal to the *c*-axis and that in the direction parallel to the *c*-axis can be measured by the two types of couples, respectively. To examine the Kirkendall effect, alumina particles of 0.3 μm diameter were placed at the interface. It was verified beforehand that the bonding treatment did not cause any significant modification of the single-variant structure. No recrystallisation was found to have occurred at the interface after the bonding treatment, and neither after the heat-treatment for diffusion described below.

Diffusion annealing was done at a temperature in the range between 1333 K and 1713 K in a vacuum for a period of time leading to a spreading of the concentration profile of the order of 100 μm . The diffusion that had occurred during the bonding treatment turned out to be less than 1/100 in the diffusion distance and thus can be neglected. Concentration profiles were measured by EPMA using JEOL JXA-8800 by repeated point analyses across the bonding interface with several μm intervals. Intensities of Fe $K\alpha$ and Pt $M\alpha$ characteristic X-rays were measured simultaneously and were converted to concentrations by the ZAF method using an FePt alloy of a predetermined composition (54.8 ± 0.8 mol%Fe) as a reference.

3. Results and Discussion

In most of the results, the concentration profile obtained by EPMA were symmetrical about the centre and its probability plot exhibited a straight line within the experimental accuracy, and consistently no measurable shift of the markers was observed. Analyses have been made on a concentration profile obtained by averaging three or four measured profiles. The chemical diffusion coefficient, D , was determined by directly fitting the error-function solution of the diffusion equation,

$$c(x) = c_0 + \frac{c_1 - c_0}{2} [1 + \text{erf}(a_1(x - a_0))], \quad (1)$$

to the averaged concentration profile with four adjustable parameters c_0 , c_1 , a_0 and a_1 . The diffusion coefficient is immediately obtained from a_1 as

$$D = \frac{1}{4ta_1^2}, \quad (2)$$

where t is the annealing time. The origin of the distance ordinate, x , is chosen at the original position of the bonding interface determined from the locations of physical gaps found at the surface of the diffusion couple, very often at the side edges; they are due to incomplete bonding and no diffusion must have taken place there. Therefore, the parameter a_0 in eq. (1) may indicate the marker shift (although it does not directly give the displacement), but in

Fig. 2 Concentration profile (a) and its probability plot (b) in the diffusion couple of type 1 annealed at 1423 K (in the ordered state) for 92 h. Circles: experimental data. Solid curve: error-function profile fitted to the data.

practice it was always negligibly small.

Figure 2 shows an example of the concentration profile (a) and its probability plot (b). The latter is a transformation of the former according to the following formula:

$$q(x) = \text{erf}^{-1} \left(2 \frac{c(x) - c_0}{c_1 - c_0} - 1 \right). \quad (3)$$

The data points in Fig. 2(b) follow the straight line that represents the error-function profile in Fig. 2(a). Some of the data at low temperatures showed slight deviations from the error-function profile. However, since no systematic trend was recognised, they were not considered significant; such profiles have also been analysed in terms of eq. (1). The values of the diffusion coefficient thus determined are listed in Table 1.

In highly ordered alloys and intermetallic compounds the chemical diffusion coefficient varies sensitively with composition through the correlation effects in the tracer diffusion and the thermodynamic driving force,^{10–13} the latter being termed the thermodynamic factor for diffusion. In the present case, however, such effects do not appear much on the diffusion in the $L1_0$ ordered state. This is considered reasonable, as the range of temperatures examined, 1333–1493 K, is very close to the order-disorder transition temperature, 1553 K, where the degree of the long-range order is appreciably less than unity.⁹⁾

Figure 3 shows an Arrhenius plot of the chemical diffusion coefficient, together with the tracer-diffusion coefficient of Pt

Table 1 Chemical diffusion coefficient in FePt. D_a and D_c refer respectively to the diffusion in the a -axis direction and in the c -axis direction.

A1 (disordered fcc)		L1 ₀ ordered		
T/K	D_d/m^2s^{-1}	T/K	D_a/m^2s^{-1}	D_c/m^2s^{-1}
1713	$(3.47 \pm 0.12) \times 10^{-13}$	1493	$(1.11 \pm 0.09) \times 10^{-14}$	$(9.18 \pm 0.35) \times 10^{-15}$
1683	$(2.57 \pm 0.08) \times 10^{-13}$	1423	$(4.95 \pm 0.10) \times 10^{-15}$	$(2.72 \pm 0.08) \times 10^{-15}$
1643	$(1.69 \pm 0.05) \times 10^{-13}$	1393	$(2.50 \pm 0.09) \times 10^{-15}$	$(1.79 \pm 0.05) \times 10^{-15}$
1603	$(8.14 \pm 0.39) \times 10^{-14}$	1333	$(5.88 \pm 0.20) \times 10^{-16}$	$(2.51 \pm 0.07) \times 10^{-16}$

Fig. 3 Arrhenius plot of the chemical diffusion coefficient in FePt in the disordered state, D_d , and in the ordered state, D_a (in the a -axis direction) and D_c (in the c -axis direction). The Pt tracer diffusion coefficient in FePt is due to Ref. 14).

in FePt in the literature.¹⁴⁾ The diffusion coefficient for the a -axis direction in the ordered state, D_a , is slightly smaller than the extrapolation from the high-temperature disordered state, and exhibits a slightly steeper slope. The deviation from the extrapolation is much more remarkable for the diffusion coefficient for the c -axis direction, D_c , which shows sharper decrease with temperature. The diffusion parameters D_0 and Q in the expression $D = D_0 \exp(-Q/kT)$ have been determined by linear regression and are summarised in Table 2.

While the atomic ordering barely affects the diffusion in the a -axis direction, a noticeable effect is observed in the diffusion in the c -axis direction. This can be understood qualitatively from the atomic arrangement in the L1₀

structure (Fig. 1): atomic migration can occur in the (001) plane without disturbing the ordered arrangement, whereas migration in the c -axis direction must be associated with formation of antistructure atoms. The diffusion in the c -axis direction must therefore be related closely to the degree of order, as the concentration of the antistructure atoms, c_i , is linearly related to the long-range order parameter, η , namely, at the equiatomic composition

$$c_i = \frac{1}{2}(1 - \eta), \quad (4)$$

where i is either of the antistructure atom species. The concentration of antistructure atoms in FePt has been calculated from the long-range order parameter reported in the literature⁹⁾ according to this formula and is plotted against reciprocal temperature in Fig. 4. At temperatures close to the order-disorder transition, the data points appear to follow a straight line, and from its slope the formation energy of antistructure atoms is found to be effectively 1.56 ± 0.06 eV. Unexpectedly it is significantly larger than the difference in the activation energy for D_c and D_a , which is only 0.6 eV (see Table 2). This discrepancy seems to indicate a failure of such a simple interpretation that the formation of antistructure atoms is the single governing factor. In systems where the degree of order is prominently reduced, the movements of atoms must be inseparably related to their configuration. Explanations should thus be provided in such a way that their close relationship is properly taken into account; an appropriate method of approach is probably the path-probability

Fig. 4 Concentration of antistructure atoms in equiatomic FePt calculated from the long-range order parameter.⁹⁾

Table 2 Arrhenius parameters for diffusion in equiatomic FePt.

	Temperature range/K	D_0/m^2s^{-1}	Q/eV^*
Chemical diffusion in A1, D_d	1603–1713	$10^{-3.38 \pm 0.90}$	3.08 ± 0.30
Chemical diffusion in L1 ₀ , D_a	1333–1493	$10^{-3.17 \pm 1.30}$	3.17 ± 0.36
Chemical diffusion in L1 ₀ , D_c	1333–1493	$10^{-1.12 \pm 1.62}$	3.80 ± 0.45
Pt tracer diffusion ¹⁴⁾	1173–1663	$10^{-3.7 \pm 0.5}$	3.03 ± 0.13

*1 eV is equal to 1.6021×10^{-19} J and corresponds to 96.485 kJ mol⁻¹.

method.¹⁵⁾

In any case, for better understanding of the phenomenon, properties of point defects, thermodynamics and tracer-diffusion behaviour have to be studied in much more detail. Measurements of the tracer diffusion coefficient of Fe are in progress; a preliminary report has been made.⁶⁾

4. Conclusions

The chemical diffusion coefficient in FePt above and below the L1₀-A1 order-disorder transition has been measured by interdiffusion experiments. The diffusion coefficient for the *a*-axis direction in the ordered state is slightly smaller than the extrapolation from the disordered state, while the diffusion coefficient for the *c*-axis direction is markedly smaller and decreases more rapidly with temperature. The apparent activation energy is 3.1 eV in the disordered state, 3.2 eV and 3.8 eV for the *a*-axis direction and for the *c*-axis direction, respectively, in the ordered state. The anisotropy in diffusion can be understood, at least qualitatively, from the atomic arrangement of the ordered structure.

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REFERENCES

- 1) H. Kanazawa and T. Suzuki: J. Magn. Soc. Japan **25** (2001) 671–674.
- 2) A. B. Kuper, D. Lazarus, J. R. Manning and C. T. Tomizuka: Phys. Rev. **104** (1956) 1536–1541.
- 3) Y. Funamizu and K. Watanabe: J. Japan Inst. Metals **39** (1975) 1087–1092.
- 4) Y. Nosé, H. Numakura, M. Koiwa, T. Ikeda and H. Nakajima: Defect Diffus. Forum **194–199** (2001) 559–564.
- 5) A. Kushida: Master thesis (Graduate School of Engineering, Kyoto University, Kyoto 2001).
- 6) Y. Nosé, A. Kushida, T. Ikeda, H. Nakajima and H. Numakura: *Proc. Int. Conf. on Designing of Interfacial Structures in Advanced Materials and their Joints, DIS'02* (Osaka University, Osaka, 2002), in press.
- 7) Y. Nosé, T. Ikeda, H. Nakajima and H. Numakura: Mater. Trans., this issue.
- 8) K. Tanaka, T. Ichitsubo and M. Koiwa: Mater. Sci. Eng. A **312** (2001) 118–127.
- 9) H. Kudielka and P. Runow: Z. Metallk. **67** (1976) 699–703.
- 10) I. V. Belova and G. E. Murch: Philos. Mag. A **73** (1996) 117–129.
- 11) I. V. Belova and G. E. Murch: Philos. Mag. A **73** (1996) 1223–1235.
- 12) I. V. Belova and G. E. Murch: Philos. Mag. A **73** (1996) 1699–1713.
- 13) T. Ikeda, H. Numakura and M. Koiwa: Acta Mater. **46** (1998) 6605–6613; corrigendum at **47** (1999) 1993.
- 14) J. Kučera and B. Million: Phys. Status. Solidi. (a) **31** (1975) 275–282.
- 15) H. Sato and H. Zhang: Defect Diffus. Forum **95–98** (1993) 57–74.