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High-temperature creep and structure investigation of nearly stoichiometric Fe_3Si

Part 2 *Structure investigation of Fe–26at% Si alloy*

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X-ray diffraction measurements were carried out on powdered single crystals of nearly stoichiometric Fe_3Si. The experimental data obtained in the temperature range from room temperature up to 750° C in terms of long-range order, thermal expansion, phase transition and Debye temperature (together with values of the Curie temperature) support the existence of two modifications of the DO_3 structure for Fe–26at% Si alloys and a phase transition in the DO_3 structure field at 595° C. The high-temperature modification has a smaller thermal expansion coefficient, a higher Curie temperature and a higher Debye temperature.

1. Introduction

In Part 1 [1] we studied the creep behaviour of Fe–Si single crystals. In this part we present some results of X-ray diffraction experiments on Fe–Si alloy (26 at % Si) and we discuss the interpretation of the experimental data obtained in the temperature range from room temperature up to 750° C mainly in terms of long-range order, thermal expansion, phase transition, Debye temperature and Curie temperature determinations.

2. Experimental procedure

The investigated alloy Fe–26 at % Si was prepared as a powder sample (particle size $\leqslant 40\,\mu$m) from a single crystal. The X-ray diffraction measurements were performed with a standard diffractometer (Co$K\alpha$ radiation with an iron filter) and an evacuated high-temperature chamber ($\Delta T = \pm 2$ K, pressure 0.13 Pa). The annealing of the powdered single crystal was carried out in this chamber. The diffraction pattern was measured during each annealing series at high temperature and at room temperature after cooling.

The several annealing experiments are summarized in Table I. The annealing referred to in Column E was carried out from 450° C up to 700° C in steps of $\Delta T = 10$ K ($\dot{T} = 0.5\,\mathrm{K\,min^{-1}}$) in about 30 min for each temperature. The computation of the lattice constant as a function of the temperature was performed after measurement of the Bragg angle for the (440) line during Annealing E.

Long-range order estimates were obtained from computation of the occupation probabilities for the structure positions. The DO_3 superlattice can be represented by four interpenetrating fcc sublattices A, B, C, D, each having four equivalent atomic positions. At 25 at % Si ($x^{Si} = 0.25$) and in the case of an ideal ordered structure, the occupation probabilities of these sublattices are given by

$$\begin{array}{llll} p_A^{Si} = 0 & p_B^{Si} = 0 & p_C^{Si} = 1 & p_D^{Si} = 0 \\ p_A^{Fe} = 1 & p_B^{Fe} = 1 & p_C^{Fe} = 0 & p_D^{Fe} = 1 \end{array} \qquad (1)$$

At compositions $0.25 < x^{Si} < 0.50$ in the ordered DO_3-type structure, the silicon atoms prefer to occupy the C sublattice and they also enter positions in the B sublattice (ideally $p_C^{Si} = 1$; $p_B^{Si} > 0$). Departure from the ideally ordered DO_3 structure, or transitions into the lower-ordered B2 and A2 structures, are presented by modifications in the values of the occupation probabilities.

Measurements of the occupation probabilities are

TABLE I Structure properties after annealing

	Annealing*				
	a	b	c	d	e
$(\overline{u^2})^{1/2}(10^{-10}\,\mathrm{m})$	0.155	0.154	0.238	0.154	0.297
Θ_D (K)	337	339	375	338	250
$p_{A,D}^{Si}$	0	0	0	0	0
p_B^{Si}	0.25	0.10	0.14	0.14	0.15
p_C^{Si}	0.79	0.94	0.90	0.90	0.89
Structure	DO_3	DO_3	DO_3	DO_3	DO_3

*a: room-temperature measurements after 3 h annealing at 450° C; b: room-temperature measurements after short-time annealing at several termperatures up to 610° C (plus a); c: high-temperature measurements ($T = 610°$ C) after 6 h annealing at 610° C (plus a + b), d: room-temperature measurements after Annealing c (plus a + b); e: room-temperature measurements after a slow temperature increase from 450 up to 700° C and additional annealing at several temperatures up to 750° C.

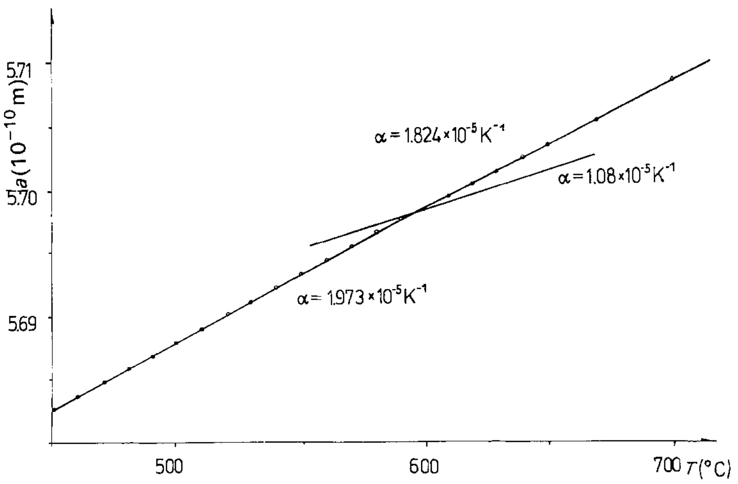

Figure 1 Measured values of the lattice constant as a function of the temperature.

obtained from the sample using X-ray powder patterns. The structure factors $F(hkl)$ of the fundamental lines $h + k + l = 4n$ are independent of the occupation probabilities and they are given by

$$F(hkl) = 16(x^{\mathrm{Si}}f_{\mathrm{Si}}(hkl) + (1 - x^{\mathrm{Si}})f_{\mathrm{Fe}}(hkl)) \quad (2)$$

whereas for superlattice lines of the type $h + k + l = 4n + 2$

$$F(hkl) = 16(f_{\mathrm{Fe}}(hkl) - f_{\mathrm{Si}}(hkl))(x^{\mathrm{Si}} - p^{\mathrm{Si}}_{A,D}) \quad (3)$$

and for superlattice lines of type $h + k + l = 4n + 3$

$$F(hkl) = 4(f_{\mathrm{Fe}}(hkl) - f_{\mathrm{Si}}(hkl))(p^{\mathrm{Si}}_C - p^{\mathrm{Si}}_B) \quad (4)$$

It is supposed that

$$p^{\mathrm{Si}}_C > p^{\mathrm{Si}}_B \quad \text{and} \quad p^{\mathrm{Si}}_A = p^{\mathrm{Si}}_D = p^{\mathrm{Si}}_{A,D} \quad (5)$$

Two ratios $F(hkl)$ (superlattice line)/$F(hkl)$ (fundamental line) follow from the measured values of the integrated line intensities. They represent equations for p^{Si}_B, p^{Si}_C and $p^{\mathrm{Si}}_{A,D}$. The occupation probabilities are calculated from these two equations and from the additional condition

$$p^{\mathrm{Si}}_B + p^{\mathrm{Si}}_C + 2p^{\mathrm{Si}}_{A,D} = 4x^{\mathrm{Si}} \quad (6)$$

The atomic scattering factors $f(hkl)$ were computed after Cromer and Mann [2] and corrected for dispersion. The computations of the Debye–Waller factor, the values of the thermal atomic displacements $(\overline{u^2})^{1/2}$ and the (X-ray) Debye temperature Θ_D were carried out using the well-known Debye–Waller theory as approximated for biatomic cubic structures [3].

3. Results and discussion

After a short time of annealing at 450° C, the powder sample has a well built-up DO_3 structure as shown from the values of the occupation probabilities of the lattice position in Column a, Table I. Further annealing produces no change in the structure type but rather variations in the values of the occupation probabilities (see Columns b, c, d and e in Table I). Up to the annealing referred to in Column d there is no measurable variation in the line width, and thus no indication of a phase transition or of a two-phase region, even in the Debye temperature at 610° C is noticeably higher than at room temperature (Columns b and c, Table I). However, it was possible to demonstrate under the already-described temperature conditions for the first part of the annealing in Column e (Table I) a second-order phase transition at $T = 595°$ C. Fig. 1 shows the measured values of the lattice constant as a function of the temperature in the temperature region from 450 to 700° C as measured during the annealing, and Fig. 2 shows the computed values of the thermal expansion coefficient of the sample. In both curves there is a noticeably abrupt jump at $T = 595°$ C.

The powder sample of the Fe–26 at % Si alloy under an almost stationary temperature regime undergoes a phase transition in the DO_3 structure field at $T = 595°$ C. The phase transition seems to be similar to the experimentally found phase transitions in the B2 structure field for Fe–Al alloy [4–6], i.e. an abrupt variation of the physical properties of the sample by the transition temperature without variation of the structure type measured by X-ray methods.

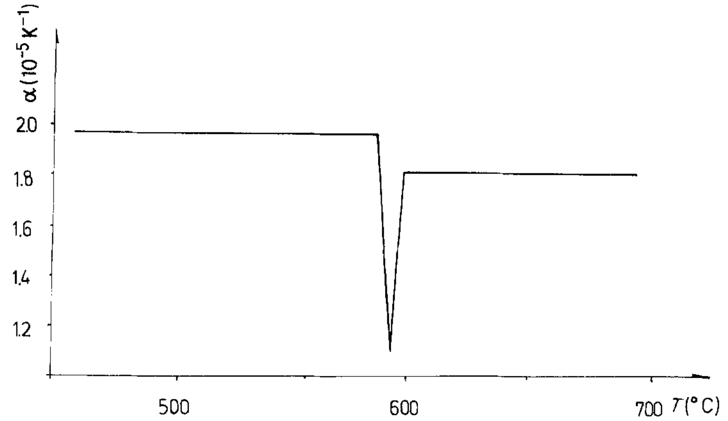

Figure 2 Computed values of the thermal expansion coefficient.

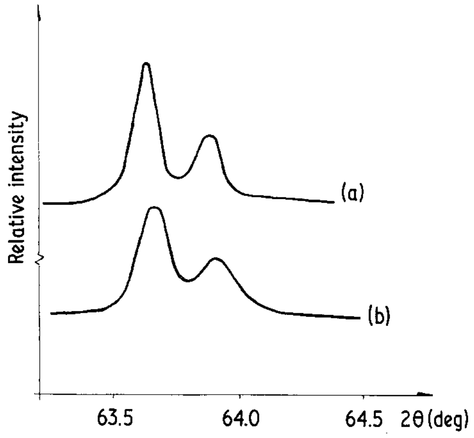

Figure 3 The width of the (440) line (a) before and (b) after annealing. Half-widths are (a) 0.12°, (b) 0.16°.

Further experimental evidence on this transition was obtained from measurements of the Curie temperature. The sample after undergoing the phase transition has a Curie temperature $T_C = (576 \pm 4)°$ C. Another sample after a first annealing of 10 h at $T = 610°$ C has a Curie temperature $T_C = (556 \pm 4)°$ C. This result supports the existence of two modifications of the DO_3 structure for Fe–26 at % Si alloys. Furthermore, this result shows that the phase transition does not occur merely by annealing the sample (short-time annealing), even at temperatures higher than the transition temperature. The phase transition requires a slow, almost stationary rise in the annealing temperature through the transition point. Once the transition occurs, the sample retains a sort of memory after cooling and thus has easier transition properties on further annealing. More exact experimental proof of this behaviour was gained by further annealing of the sample in the high-temperature chamber. Each short annealing (of 1 to 2 h) in the temperature region 450 to 590° C now produces a growth in the line width. The growth reduces and disappears on short-time annealing to higher temperatures and further heating after cooling. Column e in Table I shows the results of measurements of the sample at room temperature after several of these further anneals. Fig. 3 compares the width of the (440) line before and after these anneals ($\Delta_{HW} = 0.04°$).

4. Conclusions

The experimental evidence obtained in this work demonstrates the existence of two modifications of the DO_3 structure in Fe–26 at % Si alloy. The value of the transition temperature is 595° C. The high-temperature modification has a smaller thermal expansion coefficient, a higher Curie temperature and a higher Debye temperature. This indicates that this phase is probably one with a higher degree of electron binding and with higher interactions between electron spins. The transition requires well-defined thermal treatment. After a first transition, the alloy has a different behaviour on thermal annealing. In the temperature region 450 to 590° C the alloy now undergoes transition from the first into the second modification, with a relatively long relaxation time. It is to be assumed that both modifications differ but little in the lower limit of free energy, and that nuclei of the high-temperature modification continue cooling after the first transition, thus allowing such a transition at temperatures other than the first transition temperature. The decrease in value of the Debye temperature shown in Column e of Table I is an indication of the instability of the crystal lattice during this transition process.

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