Ordering phenomena in Fe-Si alloys with variable Si-content (0.2-11.7 wt. %) and thermomechanical processing

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Abstract

Fe-Si electrical steel around 6.5 wt. % Si is an optimum material for soft magnetic applications. Nevertheless, the brittleness appearing above 3.5 wt. % Si makes the cold processing very difficult to carry out. It is generally believed that the embrittlement is caused by order/disorder phenomena. Mössbauer spectroscopy was used to investigate the ordering processes in several Fe-Si-alloys with up to 11.7 wt. % Si. Type and degree of ordering were determined and results show that the alloys are never random solid solutions and their order degree increases with the silicon content. In addition, the effect of the thermomechanical processing was analysed. It is shown that slow cooling promotes B2 ordering while fast cooling does the opposite. On the other hand, cold rolling tends to cause disordering on the alloys.

Keywords

High Si-steel. Electrical steel. Mössbauer spectroscopy. Order-disorder.

Fenómenos de ordenamiento en aleaciones Fe-Si con contenido variable de Si y tratamiento termomecánico

Resumen

El acero eléctrico al silicio, en torno al 6,5 %, en masa de Si, es un material óptimo para aplicaciones de materiales magnéticos suaves. Sin embargo, la fragilidad que aparece por encima del 3,5 % de silicio hace muy difícil el procesamiento en frío. Generalmente, se cree que la fragilidad es causada por fenómenos de orden/desorden. Para estudiar los procesos de ordenamiento en aleaciones Fe-Si de, hasta 11,7 %, en masa de Si, se usó la espectroscopía Mössbauer. Se ha determinado el tipo y grado de orden y los resultados muestran que las aleaciones estudiadas nunca son soluciones desordenadas y que su grado de orden aumenta con el contenido en silicio. Además, se analizó el efecto del procesamiento termomecánico, incluyendo etapas de laminado en caliente y frío. Se muestra que el enfriamiento lento favorece el orden B2, mientras que el enfriamiento rápido hace lo contrario. Por otra parte, la laminación en frío tiende a causar desorden en las aleaciones.

Palabras clave

Acero con alto contenido en silicio. Acero eléctrico. Mössbauer. Orden-desorden.

1. INTRODUCTION

Fe-Si alloys constitute suitable materials for saving energy in electrical applications like transformers and motor cores. It is a fact that the soft magnetic properties of Si-electrical steels are improved with high Si-contents. Moreover, 6.5 wt. % seems to be the ideal content to obtain an optimum compromise between high electrical resistivity, low core losses, high magnetic polarization and almost no magnetostriction. Nevertheless, mass production in a conventional way keeps restricted to steels below 3.5 wt.% Si, due to a drastically reduction in the steel ductility which makes not possible the cold rolling processing into a sheet thin enough. For this reason, alternative production methods have arisen, avoiding the rolling stages, like CVD (chemical vapour deposition), hot dipping and diffusion annealing[1] and ribbon production by rapid solidification from the melt, being all of them much more expensive. It is generally believed that this ductile-brittle transition is related to an ordering phenomenon. Literature shows a large amount of research work concerning the phase diagram of the Fe-Si alloys in the Fe-rich part. It has been usually predicted by

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TEM experiments that Fe-Si alloys form a ferritic random solution below 5 wt. % Si, while a mixture of B2 and DO_3 ordered phases appears in the 5-7.5 wt. % Si zone[2-4]. Above this Si-content, DO_3 prevails as the ordered phase present. However, below 5 wt. % Si, Mössbauer and neutron diffraction studies are contrary to these results, stating the presence of order ($Fe_{15}Si$ [5] and DO_3[6], respectively) for these concentrations and doubting about the existence of the B2 phase[7]. We can conclude that ordering processes in Fe-Si alloys are not completely figured out yet, and this study is an attempt to do so. Moreover, recent research in our group has succeeded in showing a proper processing way in order to laminate Si-steel up to 6.3 wt. % [8]. The present study involves the determination of the ordering present in the Fe rich-Si alloys and its dependence and evolution with the Si-content and the thermomechanical processing. Mössbauer spectroscopy was the technique chosen for this purpose, since hyperfine parameters are highly sensitive to the local atomic environments of the Fe-atoms and consequently the technique is able to yield information about the short and long-range ordering present in the material[9 and 10].

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Experimental alloys were produced by casting at a laboratory scale and followed by diffferent thermomechanical treatments, in order to obtainthe most adequate microstructure[11]. Alloys with Si-contents varying from 1.9 to 11.7 wt. % were cast and in addition, two commercial steels (A and G) were studied. Table I summarizes their chemical compositions.

Table I. Chemical composition of the studied alloys

Tabla I. Composición química de las aleaciones estudiadas

Sample	Si wt.%	Si at.%	C wt.%	Al wt.%
Alloy A (commercial quality)	0.17	0.44	0.02	0.05
Alloy B (experimental)	1.9	3.73	0.02	0.05
Alloy C (experimental)	3.3	6.39	0.03	0.04
Alloy D (experimental)	4.2	8.05	0.09	0.03
Alloy E (experimental)	5.0	9.42	0.02	0.06
Alloy F (experimental)	5.6	10.55	0.06	0.02
Alloy G (CVD by NKK)	6.5	12.17	-	-
Alloy H (experimental)	7.7	14.18	-	-
Alloy I (experimental)	11.6	20.69	-	-

Experimental alloys C, D, E and F were hot rolled after a reheating at 1150 °C during 1 h. Then, sheets were air-cooled, except alloys D and F: additional cooling procedures were applied on them (See Results and Discussion). In a next stage, these materials were cold rolled until a thickness of 0.5-0.6 mm.

Thin foils of the samples were prepared by mechanical grinding down to a thickness of 30-35 µm in order to obtain good Mössbauer quality spectra. The measurements were carried out in transmission geometry at room temperature. The spectrometer was periodically calibrated using pure iron foils. The experimental spectra were fitted using a least square computer fit developed in the Dept. Subatomic and Radiation Physics of Ghent University. The program uses a discrete distribution of sextets with the chance to restrict hyperfine parameters. Line area ratios are set to be the same for all individual components of a spectrum while line broadening is supposed to be linear. In some cases, oxides present in the samples were fitted with a doublet.

3. RESULTS AND DISSCUSSION

Mössbauer spectra were fitted with a discrete number of sextets, each of them identifying one type of Fe-atoms, concerning their environment. Figure 1 shows Mössbauer spectra of four alloys in their as-cast state. Two subspectra represent the Fe-atoms with no Si-atoms as nn (nearest neighbours): one corresponds to 0 atoms as nnn (next-nearest neighbours) while the other corresponds to a variable number (1-6) of atoms[10]. The remaining subspectra correspond to Fe-atoms with 1, 2, 3 and 4 Si-atoms as nn respectively.

3.1. Evolution of ordering with Si-content

As a first step, Mössbauer results of all alloys in their as-cast state were analysed in order to study the effect of the Si-content on the ordering. Figure 2 shows the probabilities for a Fe-atom to have different neighbourhood configurations in some order/disorder situations: besides the random distribution, DO_3 and B2 preferential arrangements (lines) are also compared with the experimental results given by the Mössbauer spectra analysis (points) because they are widely present in literature as the possible appearing phases. A_i denotes the Fe-atoms with i Si-atoms as nn. The comparisons shown in the graphs may lead to the
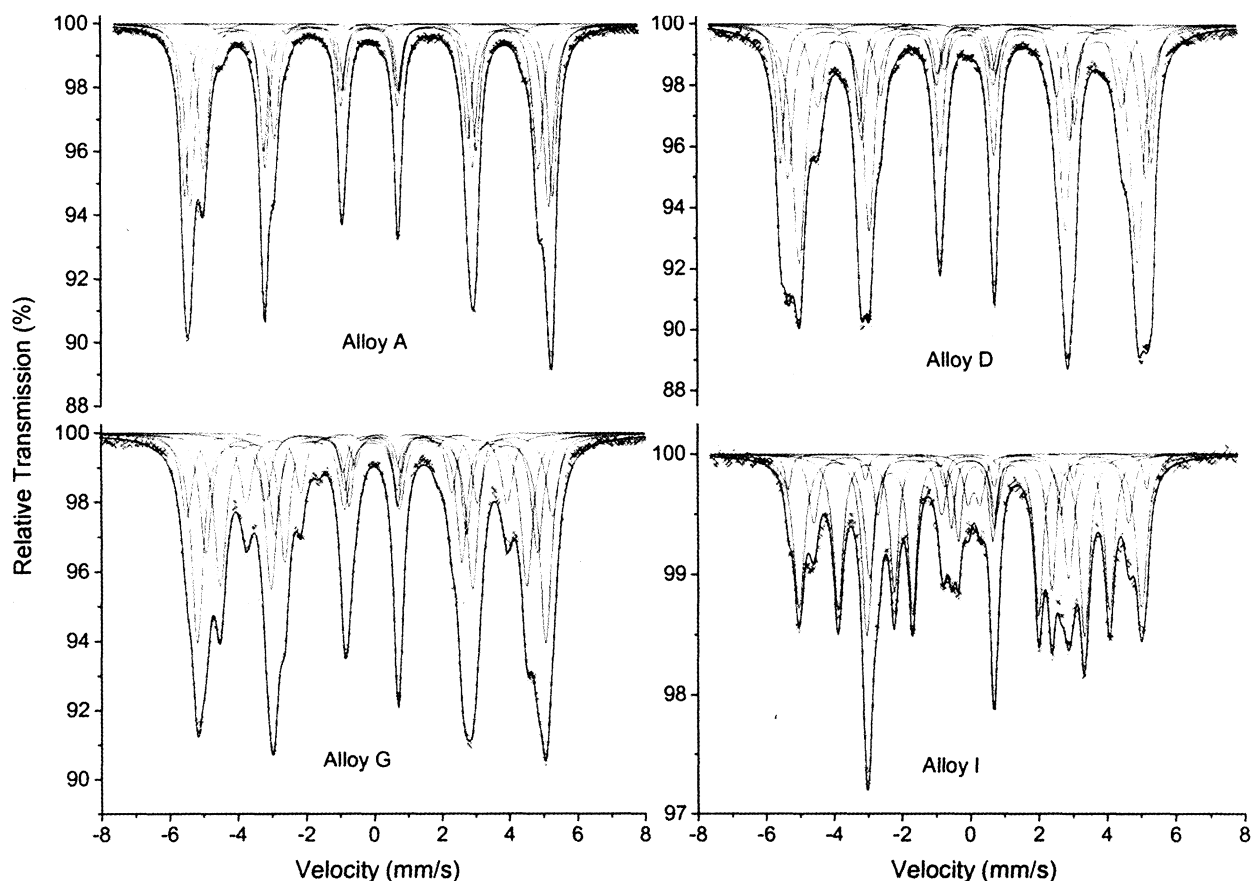
Figure 1. Mössbauer spectra of Fe-Si alloys in their as-cast state.

Figura 1. Espectros Mössbauer de las aleaciones Fe-Si en estado de colada.

following conclusions: the content of Si in alloy A is too low to detect any ordering. Alloys B and C show values for the site occupations very close to the disordered state. However, the high value of P_2 may be a sign of some $Fe_{15}Si$ ordering. Alloys D, E, F and G present a higher degree of DO_3 ordering, as can be seen from the P_2 value. Nevertheless, the high value of P_1 and the very low one of P_3 raise some doubts about the order present in these alloys. A possible explanation may be the presence of some $Fe_{15}Si$ or Fe_7Si order. Alloys H and I have values that correspond nearly to the DO_3 distribution, as it was expected. The discrepancies appearing when the experimental results are compared with ideal arrangements of the atoms (random, DO_3, B2) can be partially solved considering other types of order. As it is shown in the literature, structures like $Fe_{15}Si$ and Fe_7Si have to be taken into account for low Si-contents[5, 12 and 13]. Figure 3 summarizes the unit cells of these structures and also the well known DO_3 and B2.

They are realized when the order is complete and the compositions are the stoichiometric ones.

Then, 1, 2, 4 or 8 Si-atoms respectively, occupy the D sites of the lattice. However, for other Si-contents and/ or incomplete order situations the Si-atoms will not occupy fully the D-sites required for the different structures. It is possible to characterize these intermediate order situations defining parameters, which represent the partial concentrations of Si on the right sites for the different structures. Then the theoretical Mössbauer intensities, P_i, can be calculated as a function of these parameters and, by comparison with the experimental ones, it is plausible to obtain the order situation, which approaches the most to the experimental intensities of the Mössbauer lines. In this way for alloys B and C, considering that a high fraction of Si-atoms arranged following the $Fe_{15}Si$ structure and a fraction do so following Fe_7Si, it is possible to reach a good agreement with the experimental values. On the other hand, for alloys D, E, and F, considering that a high fraction of the atoms follows the Fe_7Si and the B2 distribution, it is also possible to reach a good result. For alloys G, H and I, a mixture of DO_3 and
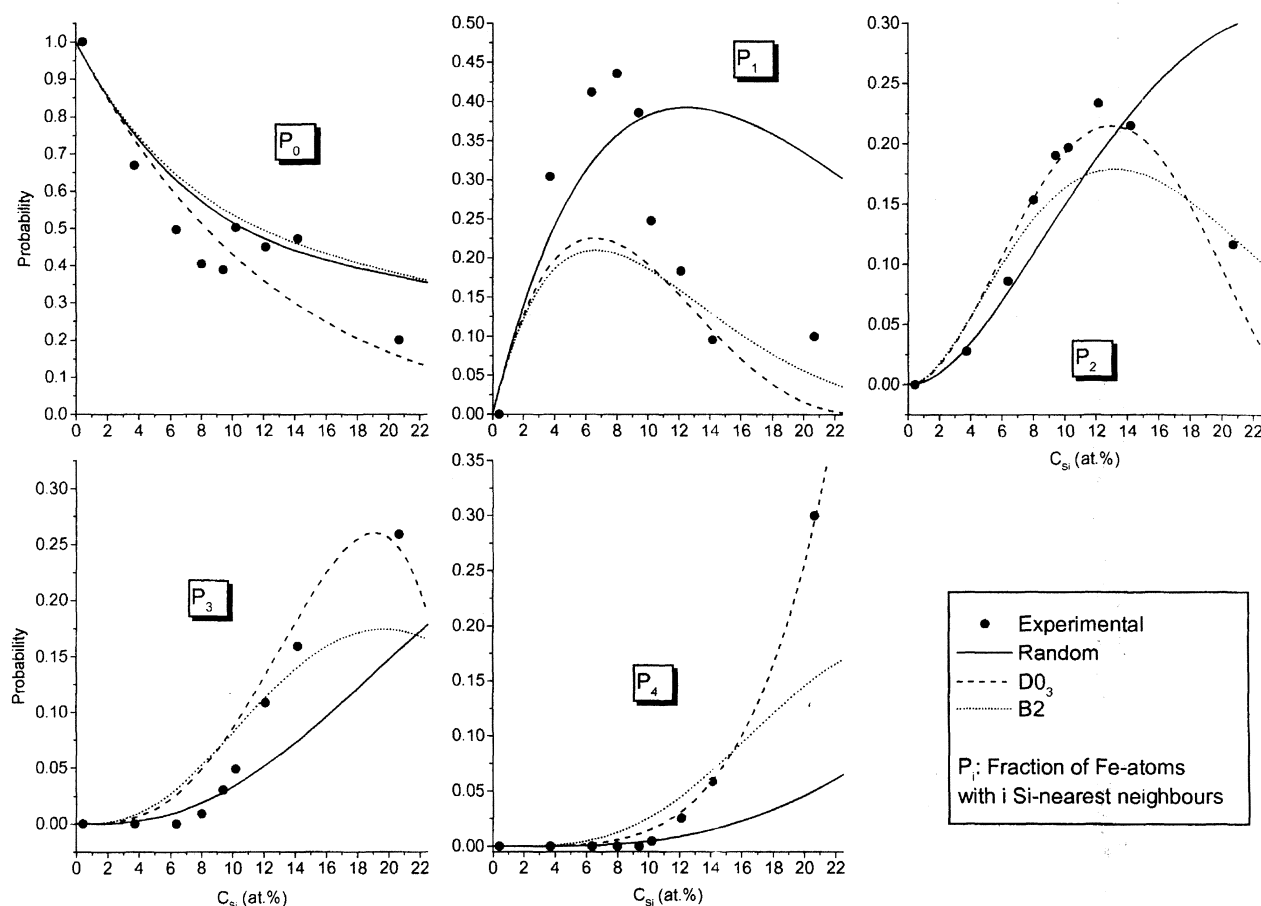
Figure 2. Experimental and theoretical values of the probabilities of the various sites (depending on number of Si-atoms as nn) to be occupied as a function of the Si-concentration (at. %).

Figura 2. Valores experimentales y teóricos de las probabilidades de ocupación de los distintos sitios (dependiendo del número de átomos de Si como primeros vecinos) en función del contenido de Si (% at.).
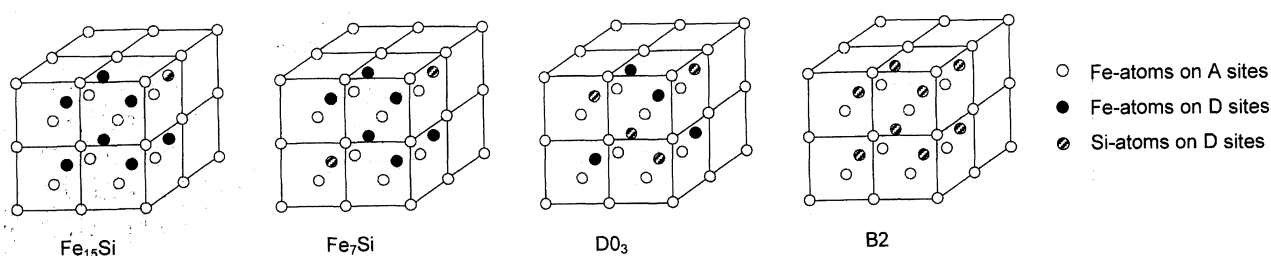

Figure 3. Unit cells for the different ordered structures of the Fe-Si alloys.

Figura 3. Celdas unidad para las distintas estructuras ordenadas de las aleaciones Fe-Si.

B2 ordering gives the best agreement with the experimental results. Table II gives the results of the fractions of Si-atoms arranged following the different ordered structures for the alloys in their as-cast state. With disorder, it is meant the fraction of Si-atoms arranged on other sites of the lattice, different from the ones that represent order. For

low Si-content (alloys B and C), $Fe_{15}Si$ is the predominant ordering (around 80 % of the Si-atoms arranged following this structure), also with some Fe_7Si. For "medium" Si-contents (alloys D, E and F) atoms mostly follow the Fe_7Si structure (around 70 % do so following Fe_7Si), however some B2 ordering is appearing and increasing with

Table II. Fractions of Si-atoms arranged following the different ordered structures for the as-cast Fe-Si alloys

Tabla II. Fracciones de átomos de Si situados de acuerdo a las las distintas estructuras ordenadas para las aleaciones Fe-Si después de colada

Sample	Si wt.%	Si at. %	$Fe_{15}Si$	Fe_7Si	DO_3	B2	Disorder
Alloy B	1.9	3.73	0.83	0.17	-	-	0
Alloy C	3.3	6.39	0.81	0.18	-	-	0.01
Alloy D	4.2	8.05	-	0.77	-	0.04	0.19
Alloy E	5	9.42	-	0.70	-	0.12	0.18
Alloy F	5.6	10.55	-	0.71	-	0.22	0.07
Alloy G	6.5	12.17	-	-	0.95	0	0.05
Alloy H	7.7	14.18	-	-	0.95	0.05	0
Alloy I	11.6	20.69	-	-	1	0	0

Table III. Fractions of Si-atoms arranged following the different ordering types for alloys C, D, E and F after different thermomechanical treatments

Tabla III. Fracciones de átomos de Si situados de acuerdo a los distintos tipos de orden para las aleaciones C, D, E y F después de diferentes tratamientos termomecánicos

Sample		$Fe_{15}Si$	Fe_7Si	B2	Disorder
	TM1	0.83	0.17	-	0
Alloy C	TM2	0.81	0.18	-	0.01
	TM4	0.76	0.20	-	0.04
	TM1	-	0.77	0.04	0.19
	TM2	-	0.76	0.06	0.18
Alloy D	TM3	-	0.69	0.04	0.27
	TM4	-	0.71	0.05	0.24
	TM5	-	0.69	0.16	0.15
	TM1	-	0.70	0.12	0.18
Alloy E	TM2	-	0.69	0.12	0.19
	TM4	-	0.66	0.04	0.30
	TM1	-	0.71	0.22	0.07
	TM2	-	0.74	0.19	0.07
Alloy F	TM3	-	0.71	0.20	0.09
	TM4	-	0.67	0.12	0.21
	TM5	-	0.67	0.28	0.05

the Si-content. Finally, the highest Si-alloys (G, H and I) possess without any doubts, the DO_3 ordering (more than 90 % of Si-atoms follow this structure).

3.2. Evolution of ordering with the thermomechanical processing

For alloys E and G, the materials after the different thermomechanical routes, including hot and cold rolling stages was analysed. The summary of the treatments performed on the steels is as follows:

TM1: material after casting and hot rolling to 25 mm thickness, considered as the starting base material in the work by Ros et al.[8].

TM2: hot rolling from 25 mm to approximately 1,5 mm in 4 steps followed by air-cooling at a rate of 450 °C/min.

TM3: as TM2, but with water quench as the cooling procedure.

TM4: material cold rolled after hot rolling to approximately 0.5-0.6 mm.

TM5: as TM2, but with slow cooling in a furnace to room temperature in 48 h.

Following the same ordering models shown above, table III gives types and amounts of order for alloys C, D, E, F after the different TM. Results show that alloy C experiences no changes along its processing: it keeps the same degree value of $Fe_{15}Si$ + Fe_7Si order. On the other hand, for the other alloys changes are noticeable. B2 ordering is favoured by slow cooling after hot rolling (TM5) while disorder is favoured by cold deformation (TM4). The differences between the air-cooled (TM2) and the water-quench (TM3) samples are

slight and only for alloy D is possible to conclude that water-quench promotes a higher disordering.

CONCLUSIONS

By means of this study, it has been shown that Fe-Si alloys are close to be a random solution only for very low Si-contents. Ordering becomes first apparent for low Si-contents (1.9-3.3 wt. %) in the $Fe_{15}Si$ form. As Si-content is increased, ordering shifts to Fe_7Si and DO_3 types, and a presence of B2 is noticeable in the 4.2-5.6 wt. % Si range. For these reasons, it can be concluded that there is always a tendency to large interatomic distances for the Si-Si pairs, due probably to a strong repulsion force between them. On the other hand, the reason of the embrittlement of these alloys may lie on the DO_3 and/ or B2 enhancement, being difficult to distinguish which one is more prevalent on this phenomenon. About the influence of the thermomechanical processing, the order in the low Si-alloys is not influenced by the thermomechanical route. For higher Si-concentrations, the most important parameter is the cooling rate after the hot rolling. In this sense, fast cooling is more convenient in order to avoid

the ordering reaction, being this fact in agreement with former experimental work[8 and 14].

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