

Brief Reports

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Intermediate phases of the α - σ phase transition in the Fe-Cr system

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(Received 24 September 1992)

(Fe_{100-x}Cr_x)_{100-y}Sn_y alloys with $42.0 \leq x \leq 44.7$ and $0 \leq y \leq 5.6$ were annealed at 700 °C for a period of up to 1000 h in order to cause a transformation of the α phase into the σ phase. Room temperature ⁵⁷Fe Mössbauer spectra registered on the samples consist of a magnetic subspectrum, related to the α phase, and a nonmagnetic subspectrum, related to the σ phase. Evidence is found that the isomer shift of the nonmagnetic subspectrum changes continuously with the amount of its relative contribution in the spectrum and it reaches the value characteristic of a pure σ phase only when its contribution in the two-phase sample is larger than about 30%.

The σ phase describes an intermetallic compound with a complex crystal structure that was identified for the Fe-Cr system in 1954 by Bergman and Shoemaker¹ as tetragonal with 30 atoms per unit cell. According to Hall and Algie,² 53 examples of binary σ phases had been identified up to 1966; all of them are characterized by the important feature that they contain only transition elements.

A greater understanding of these intermetallic compounds is therefore desirable from a theoretical standpoint. In the case of some systems and in particular, in the case of Fe-Cr, the σ phase is also very important for technological reasons since its presence drastically deteriorates properties of the material.

Both of these interests in the σ phase have stimulated many investigators to study the problem. The main goal of theoreticians has been to establish the mechanism and kinetics of the formation of this phase, while experimentalists have been rather interested in finding a remedy to prevent its precipitation. As a result of these studies, it was established that the undesired phase forms predominantly on grain boundaries and it grows through a process of nucleation.³ The kinetics of its formation can be described in terms of the Johnson-Mehl equation, and the addition of a third element promotes its formation either by an acceleration of its kinetics or by an extension of the range of its occurrence.

It is known that electronic and atomic size factors play an important role in the transformation process.^{4,5} Some attempts have been made to clarify the transformation mechanism.^{6,7} However, no satisfactory solution has

been found so far. Consequently, further theoretical and experimental investigations of the problem are needed and justified.

In this Brief Report, results of a Mössbauer-effect study on a series of nearly equiatomic Fe-Cr alloys containing up to 5.6 at. % Sn are reported. As presented elsewhere,⁸ addition of tin into the alloys significantly retards the precipitation of the σ phase.

The advantage of using Mössbauer-effect spectroscopy (MES) for this purpose is that it permits a detection of the σ phase in the earliest stages of its formation, i.e., in the region that normally is not accessible to methods traditionally used in such studies such as x-ray diffraction or electron microscopy. The distinction between the α and σ phases in MES is based on the fact that (a) the former is magnetic at room temperature (RT), while the latter is not; hence, the Mössbauer spectrum of the former shows a six-line pattern and the spectrum of the latter consists of a pseudo-single-line and (b) the isomer shift of the spectrum characteristic of the σ phase is by factor 2.5 larger in magnitude than the one characteristic of the α phase.⁹ As the isomer shift is sensitive to the composition of a given phase and to an arrangement of atoms in space, it can be used to identify different states of the α - σ transition, if such happen to occur.

In order to transform the samples from the α to the σ phase, they were vacuum annealed at 700 °C for various periods of time up to 10³ h. One of the samples studied, the Mössbauer spectrum which consisted of pseudo-single-line only, was characterized by x-ray diffraction. The resulting pattern confirmed that the sample was in

the σ phase.

Typical RT ^{57}Fe Mössbauer spectra registered in a transmission geometry by means of a standard spectrometer are presented in Figs. 1(a)–1(e). The spectrum shown in Fig. 1(a) is characteristic of a pure α phase while the spectrum shown in Fig. 1(e) is characteristic of a pure σ phase. All other spectra show that the corresponding samples consist of the two phases.

Our goal in the present study was to see whether or not properties of the nonmagnetic phase depend on its age. For this purpose the spectra were computer analyzed by means of a model-independent fitting method outlined elsewhere.¹⁰ It yielded spectral parameters such as the

average hyperfine field, the average isomer shift of the α phase, and the average isomer shift (IS) of the nonmagnetic phase, as well as the relative contributions of both phases. (The spectrum corresponding to the nonmagnetic phase was treated as consisting of five doublets with different quadrupole splittings, corresponding to five possible nonequivalent Fe sites in the σ phase.)

To illustrate how the properties of the two phases depend on their age, we plot in Fig. 2 the values of the IS for the magnetic phase (open symbols) and for the nonmagnetic phase (solid symbols) versus the relative abundance of the nonmagnetic phase A_σ for all the samples studied [A_σ values are correlated with the annealing time

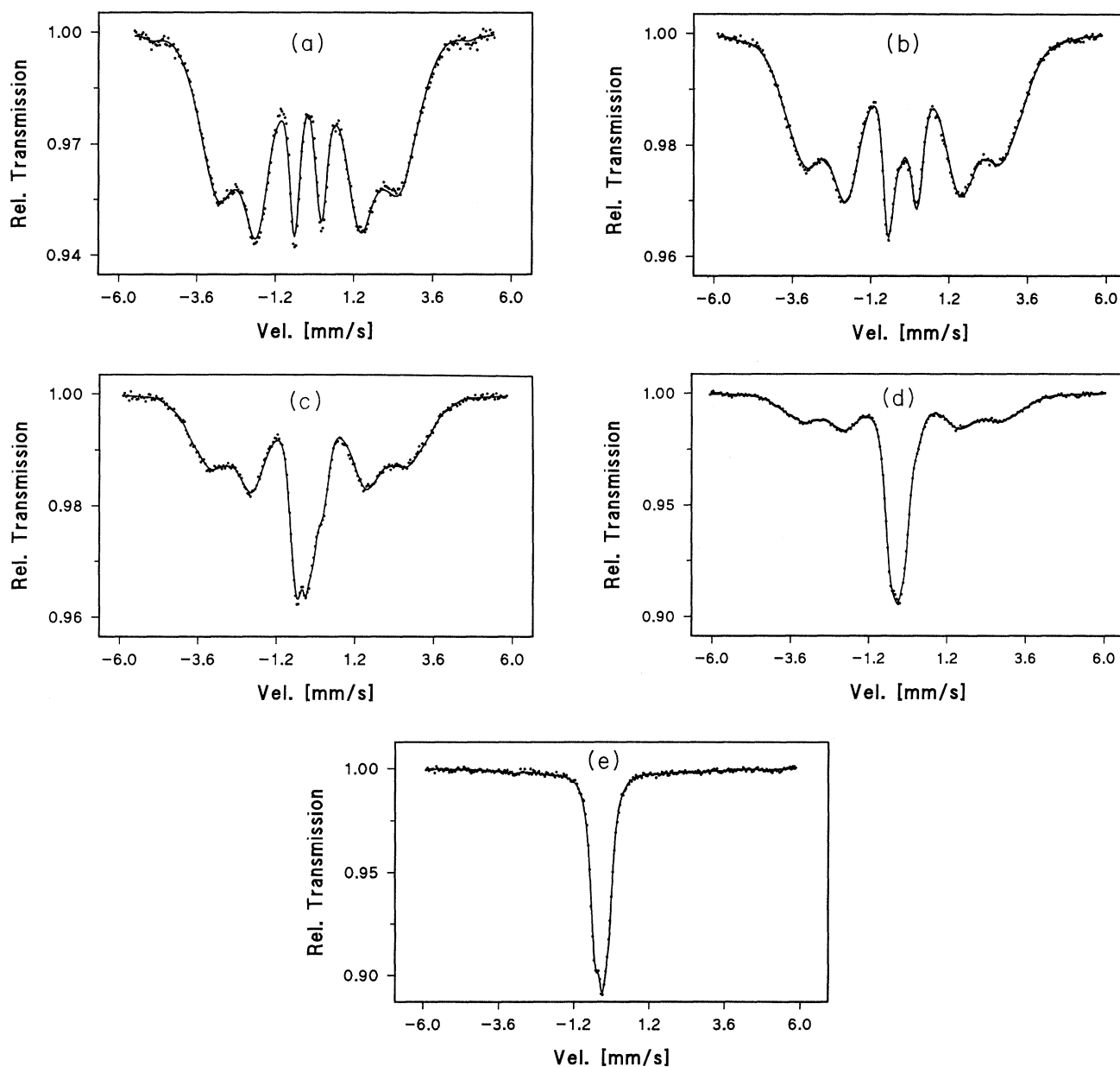


FIG. 1. RT ^{57}Fe Mössbauer spectra of an $(\text{Fe}_{55.4}\text{Cr}_{44.6})_{99.1}\text{Sn}_{0.9}$ alloy subjected to annealing at 700°C for (a) 0 h, (b) 1 h, (c) 2 h, (d) 5 h, and (e) 8 h. Solid lines represent the best-fit spectra.

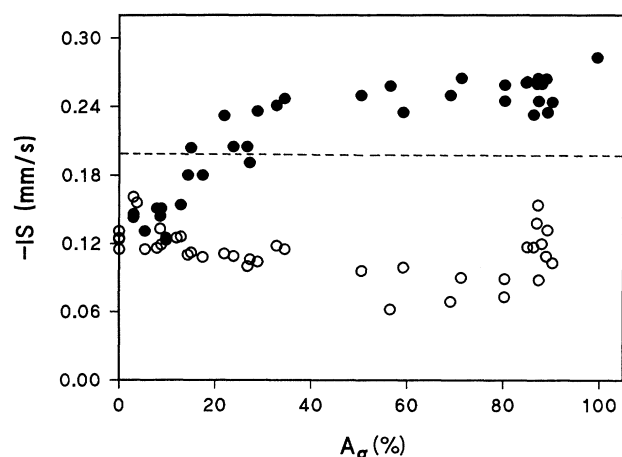


FIG. 2. Isomer shift of the nonmagnetic subspectrum (solid symbols) and that of the magnetic subspectrum (open symbols) vs the relative abundance of the nonmagnetic phase A_σ . The dashed line represents the value of the IS expected for the $B2$ -type ordered phase. Note that the negative values of the IS, relative to a Co/Rh source, are plotted.

as shown in Fig. 3 for the sample $(\text{Fe}_{55.4}\text{Cr}_{44.6})_{99.1}\text{Sn}_{0.9}$.

Figure 2 gives a clear evidence that the α - σ transformation is a continuous process. In particular, it can be noticed that the value of the isomer shift of the nonmagnetic subspectrum in the two-phase spectra has a lower value than the value characteristic of a pure σ phase, unless the relative abundance of this phase is larger than about 30%. In other words, it has been revealed that the transformation from a simple α phase, with only two atoms per unit cell, needs a definite time to result in a very complex σ phase, with 30 atoms per unit cell [in the case of the sample $(\text{Fe}_{55.4}\text{Cr}_{44.6})_{99.1}\text{Sn}_{0.9}$, this time is equal to ~ 8 h; see Fig. 3] and this transformation is realized through a variety of intermediate states.

A question appears on the nature of these intermediate states or "phases" as well as on the mechanism that drives the transformation.

Concerning the first question, there is already some suggestion for equiatomic Fe-V alloys^{11,12} that such a transformation occurs through a metastable ordered phase of a $B2$ -type structure. Such an intermediate phase seems to be possible also in the case of Fe-Cr alloys, as

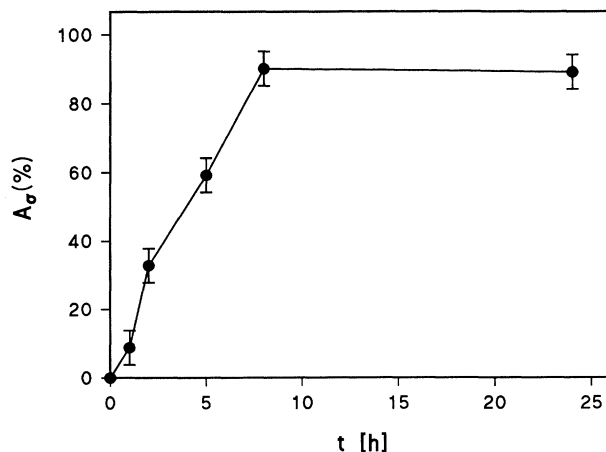


FIG. 3. Relative abundance of the nonmagnetic phase A_σ vs time of annealing for a $(\text{Fe}_{55.4}\text{Cr}_{44.6})_{99.1}\text{Sn}_{0.9}$ alloy.

the estimated value of the isomer shift for such a structure, $\text{IS}_{B2} \approx -0.20$ mm/s (relative to a Co/Rh source), if one takes into account the data from Ref. 9 and assumes that the effect of Cr atoms on the isomer shift is additive. This value of IS_{B2} is marked in Fig. 2 as a dashed line. One can readily note that it lies "on the way" from the α to the σ phase; hence, it can occur. However, as can be seen from this picture, there are many other values of the IS that lie between the two extreme values. This obviously means that the transformation in the Fe-Cr system goes through several metastable states until it finally results in the σ phase.

The nature of the mechanism that drives the α - σ phase transformation remains open. Recent theoretical calculations show that virtual phases may temporarily appear at intermediate stages of precipitation.^{13,14} However, as those calculations do not directly depict the transformation described in the present Brief Report, they cannot be used in order to discuss our results in terms of them.

It is hoped, nevertheless, that the results shown here will stimulate proper theoretical calculations that will shed more light on the α - σ phase transformation.

This work was supported in part by the Calouste Gulbenkian Foundation, Lisbon.

¹B. G. Bergman and D. P. Shoemaker, *Acta Crystallogr.* **7**, 857 (1954).

²E. O. Hall and S. H. Algie, *Metall. Rev.* **11**, 61 (1966).

³P. A. Blenkinsop and J. Nutting, *J. Iron Steel Inst.* **205**, 953 (1967).

⁴D. P. Shoemaker and B. G. Bergman, *J. Am. Chem.* **72**, 5793 (1950).

⁵D. I. Bardos, R. K. Malik, F. X. Spiegel, and P. A. Beck, *Trans. AIME* **236**, 40 (1966).

⁶W. J. Kitchingman, *Acta Crystallogr. A* **24**, 282 (1968).

⁷W. J. Kitchingman and G. M. Bedford, *Met. Sci. J.* **5**, 121

(1971).

⁸B. F. O. Costa and S. M. Dubiel (unpublished).

⁹S. M. Dubiel and J. Zukrowski, *J. Magn. Magn. Mater.* **23**, 216 (1981).

¹⁰G. Le Cäer and J. M. Dubois, *J. Phys. E* **12**, 1083 (1979).

¹¹K. Bunghardt and W. Spyra, *Arch. Eisenhüttenw.* **30**, 95 (1959).

¹²M. Deire, *C. R. Acad. Sci.* **259**, 2640 (1964).

¹³Long-Qing Chen and A. G. Khachatryan, *Phys. Rev. B* **44**, 4681 (1991); **46**, 5899 (1992).

¹⁴P. E. A. Turchi and A. Finel, *Phys. Rev. B* **46**, 702 (1992).