Comments on 'Character of transformations in Fe-Co system'

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Abstract

The existence of an ordering reaction in FeCo alloys has recently been challenged. The compatibility of new and published results with the alternative explanation is examined. It is shown that the existence of an ordering reaction remains the best explanation for most observations to date.

1   Introduction

Near equiatomic FeCo based alloys are face-centred cubic (fcc) (γ) above $\sim$983 °C, and body-centred cubic (bcc) (α) below this temperature. It is generally accepted that α orders to a B2 structure (α_2) below $\sim$730 °C (figure 1).

The existence of an ordering reaction in $Fe_{1-x}Co_x$ alloys (with x in the range 29-70 wt% [2]) has been widely accepted for more than 50 years. Early evidence for ordering were presented by Kussmann in 1932 [3], Rodgers and Maddocks in 1939 [4] and Shull and Siegel in 1949 [5].

The ordering reaction, and particularly its kinetics, subsequently attracted considerable attention [6–21] because of the presumed relationship between order and the severe intergranular brittleness of these alloys. Such studies have used a variety of methods to follow the evolution of the long range order parameter S as a function of time and/or temperature. These methods have been summarised in a recent review, co-written by the author [22].
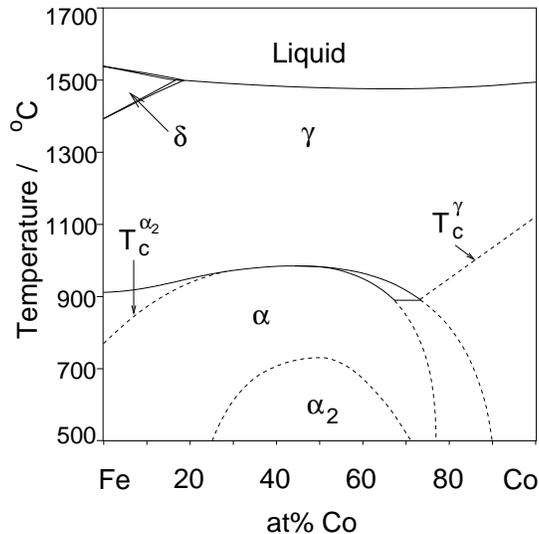
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Figure 1: The binary phase diagram for FeCo, after [1].

Recently however, Ustinovshikov and Tresheva [23] have suggested that the ordering reaction does not occur in the bulk, but rather at the surface of samples, provided that these are heat-treated in air. They further suggested that the heat-capacity peak observed in all studies at $\sim$730 °C relates to a change in the sign of the interaction between Fe and Co rather than to the ordering reaction. The elusive $\sim$ 550 °C secondary peak [2], sometimes referred to as '550 °C anomaly', would on the contrary correspond to an as yet undocumented phase-transition.

In the present work, we examine the evidence put forward by Ustinovshikov and Tresheva in the light of a number of studies overlooked by these authors, and new results obtained so as to test directly the validity of their alternative explanation.

2 Evidence for the ordering reaction

As mentioned in the introduction, Ustinovshikov and Tresheva proposed that the ordered α_2 phase only forms in a thin surface layer, provided that heat-treatments are carried out in air. In an attempt to make this claim compatible with the vast number of studies reporting the formation of α_2, the authors emphasised that most of these studies involved heat-treatments in air (for example, Ref. [15]), and used X-

ray diffraction (for example, Ref. [6]) as a method to estimate the long-range order parameter. Because this method only provides a relative measure of the order parameter (that is, a sample of known degree of order is required), it can only estimate the relative extent of the transformation (that is, the extent of the transformation compared to that in the sample assumed to be fully ordered).

While these arguments are certainly valid, they only concern a few of the majority of results reporting the existence of α_2. For example, Smith and Rawlings [11] carried out heat-treatments in a salt bath and used neutron diffraction, which allows an estimation of the absolute value of the long-range order parameter. Additional evidence of ordering using neutron diffraction is provided by Yu *et al.* [21, 24, 25] or Zhu *et al.* [26], for example. Neutron diffraction does not suffer from the problems associated with X-rays: low penetration, and very weak superlattice peaks (as discussed later). For example, while for X-rays, the ratio of intensities of $I_{\{100\}_{\alpha_2}}/I_{\{110\}_\alpha}$ is 1/1390, it is 1/6 in neutron diffraction [5].

Clegg and Buckley [6, 17] also reported ordering with samples heat-treated in salt bath. Other methods have involved heat-treatments in Pyrex capsules filled with argon [15], and most studies have used at least two different experimental methods to establish the degree of order.

It seems clear, therefore, that Ustinovshikov and Tresheva's hypothesis faces considerable difficulties to fit past studies. Nevertheless, there remains the need to explain their own experimental results.

3 α_2 as a surface layer

3.1   Experimental evidence

In their study, Ustinovshikov and Tresheva used rectangular plates of 3 mm thickness which they aged at 700 °C in air and in vacuum. X-ray diffraction showed that a surface layer produced peaks 'consistent' with the ordered phase α_2, only for the samples heat-treated in air. Once this layer was removed, the peaks disappeared. The authors reported a logarithmic time dependency for the penetration into the bulk, and an increased amount of α_2 in Fe-49Co-2V when compared to Fe-50Co.

The above authors also noted that this surface B2 structure has a lattice parameter which is hardly dependent on the composition of the alloy, with 0.2902 nm for Fe-35Co, 0.2905 nm for Fe-50Co and 0.2909 for Fe-65Co. In addition, its hardness was found to be different (lower) than that of the bulk.

3.2 Alternative explanation

It is proposed that the observed layer was an oxide, previously reported by Rogers *et al.* [15]. Rogers underlined that the peaks corresponding to this oxide are close enough to the peaks of the α_2 phase so as to make its identification impossible if the order is low.

The rate of penetration and the absence of the layer from samples heat-treated in vacuum also strongly support this hypothesis. In addition, the growth of a stoichiometric oxide could result in a phase of lattice parameter relatively independent of the bulk composition, as observed by Ustinovshikov and Tresheva. The lattice parameter of the ordered α_2 phase, on the contrary, is expected to depend on composition as follows [1]:

$$a_{\alpha_2}/\text{nm} = 0.28250 + 6.4231 \times 10^{-5}[\text{at\%Fe}] \qquad (1)$$

After heat-treatments at 700 °C, the authors indicate that diffraction peaks for the B2 structure never appear in the vacuum heat-treated samples, and only in a surface layer in those heat-treated in air. The choice of 700 °C to perform the comparison is rather surprising as the degree of order is known to be low at this temperature (figure 2).

It is therefore not impossible that the order parameter was too low in both cases to give clear superlattice diffraction peaks. The similarity between the X-ray atomic factors of Fe and Co means that the superlattice peaks are very weak, even when anomalous scattering effects are used to enhance their intensity (by using Fe or Co radiations) [6]: a value of $I_{\{100\}_{\alpha_2}}/I_{\{200\}_\alpha} = 1/66.1$ has been reported for Fe-50Co at its maximum degree of order [17], using cobalt K_α radiations as in the study of Ustinovshikov and Tresheva. Other authors have underlined the impossibility of distinguishing any superlattice line except for the $\{100\}_{\alpha_2}$ [6].
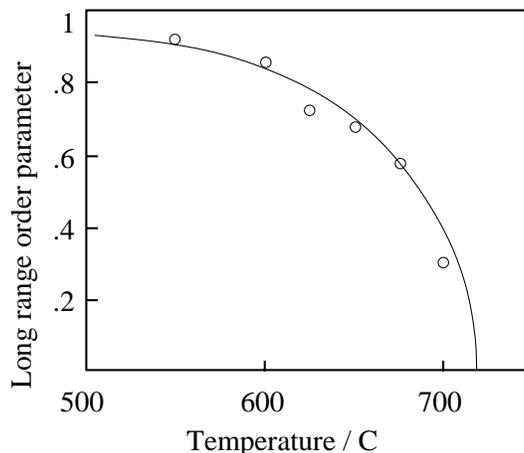
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Figure 2: The long range order parameter as a function of temperature in FeCo, after [7].

In contrast, in the results reported by Ustinovshikov and Tresheva [23], the peaks interpreted as superlattice peaks (for example, $\{110\}_{\alpha_2}$) have intensities similar to those of the α structure.

Therefore, neither the position nor the intensity of the peaks reported by Ustinovshikov and Tresheva are in agreement with what they identify as α_2. It is surprising that the comparison between air/vacuum heat-treatment was not repeated at temperatures lower than 700 °C where the degree of order is expected to be higher.

Finally, increased vacancy supersaturation have been observed in vanadium containing alloys when compared to binary alloys [8]. This could explain the faster oxidation of the former as the vacancy supersaturation would enhance diffusion.

4 Separation in pure components

4.1 Experimental evidence

Having postulated that there is no bulk ordering in FeCo alloys, Ustinovshikov and Tresheva attempted to explain the transition observed at 730 °C. For this purpose, they proposed that the interactions between Fe and Co become repulsive above ∼730 °C. That is to say, the interaction parameter changes sign. This, in turn, is argued to lead to separation in pure elements.

In samples held 4 h at 900 °C or 1000 °C and water quenched, Ustinovshikov and Tresheva reported disappearance of the original solid solution peaks and apparition of two sets of peaks consistent with an fcc phase of lattice parameter 0.3564 nm and a bcc phase of lattice parameter 0.2848 nm. These are argued to correspond to 'pure' cobalt and 'pure' iron, respectively.

4.2   Comparison with previous results

Evidence based on X-ray measurements in Ustinovshikov and Tresheva's work are discussed with an accuracy of about 0.0001 nm. However, as for the identification of α_2, the parameters reported differ significantly from previously reported values (0.287 nm for bcc iron and 0.3544 nm for fcc cobalt).

The lattice parameters of the α and high-temperature γ Fe-Co solid solutions have been reported as [1]:

$$
\begin{aligned}
a_\alpha/\text{nm} &= 0.28236 + 6.4514 \times 10^{-5}[\text{at\%Fe}] \\
a_\gamma/\text{nm} &= 0.35438 + 1.0233 \times 10^{-4}[\text{at\%Fe}] \quad (2)
\end{aligned}
$$

While these appear to provide a slightly better match for the results of Ustinovshikov and Tresheva, difficulties remain.

The existence of an fcc phase at high temperature is well documented (for example, [1,2]), but it is equally well established that this phase cannot be retained at room temperature, and undergoes a martensitic transformation to the bcc structure (for example, see Ref. [27]).

If a sample is quenched from the high temperature two-phase domain, it is possible to distinguish between the martensite (α', previously γ), and the high temperature α because of their different morphology.

This has been used to estimate the width of the $\alpha + \gamma$ field at high temperature (for example, [28]), by measurement of the α' and α compositions. Some of these works used identical procedures as those described by Ustinovshikov and Tresheva. For example, Bennett and Pinnel [29, 30] or Mahajan *et al.* [31] aged samples of FeCo-2V for 6 h at 900, 925 and 950 °C, in flowing Ar-10%H$_2$ then quenched the samples in ice-brine before measuring the composition.

None of these results report separation in two components at these temperatures. Therefore, Ustinovshikov and Tresheva's observations cannot be explained by supposing that the high-temperature heat-treatment fell in the two-phase region, not only because of the narrowness of this domain, but also because the austenite would in any case not have been retained at room temperature where the measurements were performed. On the other hand, previous measurements of the composition at high temperature do not support the hypothesis of a separation in pure components.

5   Magnetic properties

According to Ustinovshikov and Tresheva, the ordering reaction occurs only on the surface of samples that have been heat-treated in air, and therefore cannot be of any consequence for the magnetic or mechanical properties.

On the contrary, the authors suggest that the magnetic properties are 'grossly changed' by the formation of the hypothetical λ-structure at 550 °C. This, however, is only supported by measurement of the saturation at 700 and 500 °C (which are reported as points in figure 3).

Interestingly, past experiments have never claimed that the ordering reaction had a strong impact on the saturation magnetisation, and the exact influence of the ordering reaction upon the mechanical properties is still discussed [22]. Measurements of the saturation magnetisation show an increase of about 4% upon ordering [6, 32–34], as illustrated in figure 3. It is clear that, while one of the measurements by Ustinovshikov and Tresheva is in good agreement with typical values, the saturation at 700 °C is widely different from any previously reported value.

Rather than examining whether details of past experiments could explain the discrepancies, it was decided to perform a direct test of Ustinovshikov and Tresheva's hypothesis.

For this purpose, a sample of Rotelloy 8 was used. This is an equiatomic FeCo alloy with 1V, ∼0.2 Ta wt%, made by Carpenter Ltd, and was provided as a sheet of 150 μm thickness. The sample had been cold-rolled and was therefore given a recrystallisation heat-treatment of 2 h at 800 °C. The length of the heat-treatment ensures
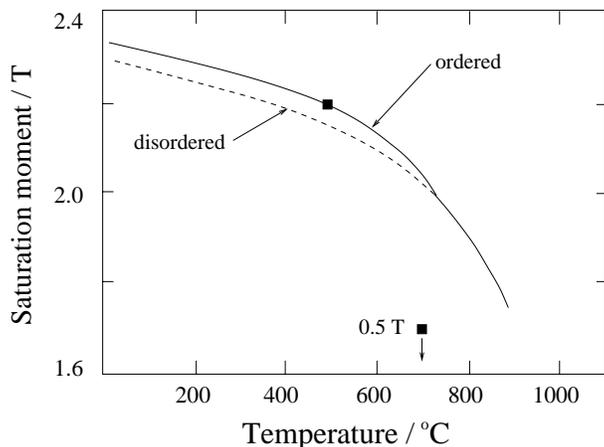
Figure 3: The variation of the saturation magnetisation for FeCo-2V as a function of temperature, after [6]. The two points obtained by Ustinovshikov and Tresheva [23] are superimposed. Note that the measurement at 700 °C is of 0.5 T.

that there are no residues of texture [35–37]. The heat-treatment was performed in a silica capsule filled with a partial pressure of argon.

A sample 2×2 mm was then obtained by electro-erosion, to avoid any deformation during the cutting process, and the magnesium oxide surface layer (used as an insulator in laminate products) was removed by careful polishing.

A vibrating sample magnetometer was used to measure the saturation moment as a function of temperature. The sample temperature is controlled by a flow of helium, therefore protecting the sample from oxidation.

In a first experiment, the saturation moment was measured after maintaining the sample at 750 °C for a few minutes, then decreasing the temperature at a rate of 8 °C/s. In a second experiment, the sample was held a few minutes at 750 °C, then quenched to 560 °C where the saturation moment was measured and found to be similar to that obtained in the previous experiment. The sample was then quenched to 540 °C to follow the evolution of the saturation moment as a function of time for 10 minutes. This is because, according to Ustinovshikov and Tresheva, the transformation to the λ-structure only happens after 5 minutes. Because no significant variation occurred, the measurement was repeated at 500 °C. The results are shown in figure 4.
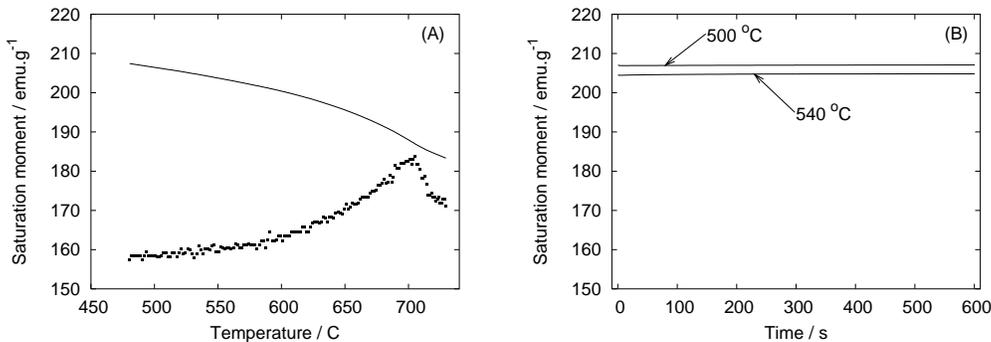
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Figure 4: (A) The saturation moment as a function of temperature for a sample cooled at 8°C/s. The first derivative is also shown as points, without scale. (B) The saturation moment at 540 and 500 °C as a function of time, showing no significant evolution. Note that the peak in (A) is slightly below the temperature generally agreed for the onset of ordering, which is to be expected given the relatively high cooling rate used.

Clearly, neither of the measurements undertaken in the present work support the existence of a phase-transition at 550 °C.

6   Conclusions

The hypotheses put forward by Ustinovshikov and Tresheva are difficult to reconcile with a number of studies overlooked by these authors. In addition, part of their results can be understood without rejecting ordering, while another part could not be reproduced. For example, Ustinovshikov and Tresheva report a saturation magnetisation of 0.5 T at 700 °C, but 2.20 T at 500 °C. All of the published literature and our present results fail to confirm such a large change between 500 and 700 °C.

Furthermore, the alternative explanation put forward for the 730 °C transition is dubious: if this peak was the result of separation into pure elements, one would expect a significant cooling rate dependency, and relatively slow overall kinetics, as the process would involve long-range diffusion. However, regardless of the nature of the transformation occurring at 730 °C, its kinetics [2] are clearly not compatible with a reaction involving long-range diffusion.

7 Acknowledgements

References

[1] I. Ohnuma, H. Enoki, O. Ikeda, R. Kainuma, H. Ohtani, B. Sundman, K. Ishida, Acta Mater. 50 (2002) 379–393.

[2] A. S. Normanton, P. E. Bloomfield, F. R. Sale, B. B. Argent, Metal Sci. 9 (1975) 510–517.

[3] L. Kussmann, Zeit. Techn. Physik 13 (1932) 449–460.

[4] J. W. Rodgers, W. R. Maddocks, Tech. rep., Second alloy steels report-Section VIII (1939).

[5] C. G. Shull, S. Siegel, Phys. Rev. 75 (1949) 1008–1010.

[6] D. W. Clegg, R. A. Buckley, Metal Sci. J. 7 (1973) 48–54.

[7] N. S. Stoloff, R. G. Davies, Acta Metall. 12 (1964) 473–485.

[8] P. Grosbras, J. P. Eymery, P. Moine, Acta Metall. 24 (1976) 189–196.

[9] M. Rajkovic, R. A. Buckley, Metal Sci. (1981) 21–29.

[10] P. Grosbras, J. P. Eymery, P. Moine, Scripta Metall. 7.

[11] A. W. Smith, R. D. Rawlings, Phys. Stat. Sol. A 34 (1976) 117–123.

[12] R. A. Buckley, Metal Sci 19 (1975) 243–247.

[13] J. P. Eymery, P. Grosbras, P. Moine, Phys. Stat. Sol. A 21 (1974) 517–528.

[14] A. T. English, Trans. Met. Soc. AIME 236 (1966) 14–18.

[15] J. A. Rogers, H. M. Flower, R. D. Rawlings 9 (1975) 32–35.

[16] J. F. Dinhut, H. Garem, J. P. Eymery, P. Moine, Scripta Metall. 8 (1974) 307–312.

[17] R. A. Buckley, Metal Sci. 13 (1979) 67–72.

[18] R. V. Major, C. M. Orrock, IEEE Trans. Magn. 24 (1988) 1856–1858.

[19] A. I. C. Persiano, R. D. Rawlings, J. Mat. Sci. 26 (1991) 4026–4032.

[20] A. I. C. Persiano, R. D. Rawlings, J. Mater. Eng. 12 (1990) 21–27.

[21] R. H. Yu, S. Basu, Y. Zhang, J. Q. Xiao, J. Appl. Phys. 85 (8) (1999) 6034–6036.

[22] T. Sourmail, H. K. D. H. Bhadeshia, Microstructure, magnetic and mechanical properties of FeCo based alloys, Tech. rep., Advanced Aerospace Materials DARP, Rolls-Royce (2004).

[23] Y. Ustinovshikov, S. Tresheva, Mat. Sci. Eng. A A248 (1998) 238–244.

[24] R. H. Yu, S. Basu, Y. Zhang, A. Parvizi-Majidi, J. Q. Xiao, J. Appl. Phys. 85 (9) (1999) 6655–6659.

[25] R. H. Yu, S. Basu, R. Y. Zhang, A. Parvizi-Marjidi, K. M. Unruh, J. Q. Xiao, IEEE Trans. Magn. 36 (5) (2000) 3388–3393.

[26] Q. Zhu, L. Li, M. S. Masteller, G. J. D. Corso, Appl. Phys. Lett. 69 (25) (1996) 3917–3919.

[27] J. A. Ashby, H. M. Flower, R. D. Rawlings, Metal Sci 11 (1977) 91–96.

[28] K. Kawahara, J. Mat. Sci. 18 (1983) 3427–3436.

[29] J. E. Bennett, M. R. Pinnel, J. Mater. Sci 9 (1974) 1083–1090.

[30] M. R. Pinnel, J. E. Bennett, Metall. Trans. 5 (1974) 1273–1283.

[31] S. Mahajan, M. R. Pinnel, J. E. Bennett, Metall. Trans. 5 (1974) 1263–1272.

[32] C. W. Chen, J. Appl. Phys. 32 (3) (1961) 348S–355S.

[33] L. Li, J. Appl. Phys. 79 (8) (1996) 4578–4580.

[34] J. E. Goldman, R. Smoluchowski, Phys. Rev. 75 (1949) 310–311.

[35] M. M. Borodkina, E. I. Detalf, Y. P. Selisskiy, Fiz. Metal. Metalloved. 7 (1959) 214–224.

[36] A. A. Goldenberg, Y. P. Selliskiy, Fiz. Metal. Metalloved. 15 (5) (1963) 717–724.

[37] Y. P. Selliskiy, M. N. Tolochko, Fiz. Metal. Metalloved. 13 (4) (1962) 587–590.