

# Phase Transformations and Properties of Fe–Co Alloys

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**Abstract.** The development of advanced motors and generators for airspace and special power applications requires the use of soft magnetic materials which have high mechanical strength. In the search for these high strength soft magnetic alloys, a great number of investigations have been done in the last decade, and as a consequence, important advances have been obtained. The Fe–Co alloys present excellent magnetic properties and have been indicated as candidate materials for these power applications. In this work a brief review of the work published in the last 30 years in Fe–Co–V alloys is presented, and new routes for research on Fe–Co–X and Fe–Co–V–X alloys (X is an alloy element) are pointed out.

## INTRODUCTION

Interest in the investigation of binary Fe–Co alloys has been noticeable since the discovery of Preuss [1] and Weiss [2] that alloys of this system present the highest saturation magnetization of ferromagnetic materials. In 1926, Elmen [3] patented the equiatomic Fe–Co alloy named Permendur. However, severe restrictions on the fabrication of thin plates of that alloy were faced due to its extreme brittleness. White and Wahl [4] in 1932 solved this difficulty with the addition of 2% V to the equiatomic alloy with excellent results. This particular alloy was named 2 V–Permendur, or Supermendur when high purity Fe and Co are used as starting material for the fabrication of the alloy.

The iron–cobalt alloys constitute a family of magnetic materials that can present properties characteristic of soft or hard magnetic materials by changes in the alloy composition or by thermal–mechanical treatments. In the present work, attention will be focused on the soft Fe–Co–2% V alloy with good mechanical strength. These properties recommend this alloy for applications on advanced rotors and generators where high rotation speeds are involved, requiring, as a consequence, high mechanical strength.

The Fe–Co–V alloys are fabricated using electrolytic grade Fe and Co, Fe–V as a master alloy for

vanadium addition, and vacuum melting and remelting procedures. The ingots are generally hot worked followed by cold working to obtain thin plates. Before cold working the alloy is usually heat treated at temperatures above 993 K (720° C) and quenched in iced brine solution to remove brittleness. Recommended commercial heat treatment of plates is performed at temperatures around 1023 K (750° C) in hydrogen, followed by a slow cooling to room temperature. This treatment leads to an alloy with excellent soft magnetic properties but with a mechanical strength not adequate for advanced power applications (motors and generators). The main objective of this work is to briefly review the characteristics of Fe–Co–2% V alloys for advanced applications as well as to indicate the new routes being taken to improve the magnetic and mechanical properties of alloys of this system, related to the macroaddition of further elements to Fe–Co and Fe–Co–V alloys.

## PHASE TRANSFORMATIONS IN THE Fe–Co–2% V ALLOYS

A great amount of effort was made in the last 15 years to identify the phases present in this alloy and several reports are available in the literature [5–13]. At temperatures above 1223 K (950° C) the equilibrium, non-magnetic phase has a face centered cubic (fcc) structure. On quenching the alloy from temperatures in this range, the microstructure is characterized by the presence of a metastable martensitic phase with body centered cubic (bcc) structure. If the alloy is slowly cooled

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from temperatures above 1223 K (950° C), the fcc phase transforms to a bcc structure, and the transformation is completed at the temperature of 1123 K (850° C). Below temperatures around 983 K (710° C), the order-disorder transformation temperature, the cubic phase changes to a B2 (CsCl type) ordered structure. The order-disorder phenomena that occurs in this alloy has been the subject of several investigations [14-33] where kinetics, structure, critical temperature, and equilibrium value of the long range order parameter  $S$  were analyzed. When the Fe-Co-V alloy is heat treated at temperatures below the order-disorder transformation temperature, the precipitation of a nonmagnetic phase occurs. Research performed on the precipitation behavior of this phase [5,7,8,34] has shown that the precipitate has a fcc structure with some controversy about the possibility of an ordered  $L1_2$  type structure. The chemical composition of the precipitate is of the form  $Co_3V$  with some iron atoms substituting cobalt atoms. The precipitate is known to be semicoherent and the habit planes in the ordered matrix are known to be of the  $\{110\}$  family. The precipitation of this nonmagnetic phase in the cold worked material occurs preferentially on dislocations. According to Rawlings et al. [5], nucleation of this phase in the recrystallized material occurs homogeneously through an initial segregation of vanadium to anti-phase domain boundaries. The precipitation kinetics shows a classical C type curve behavior on a time-temperature transformation (TTT) diagram.

The martensitic transformation in Fe-Co-2% V alloy was examined by many authors [5,11,45,46]. This phase, when obtained after quench from the single fcc high temperature phase, presents a blocky morphology, while the martensite produced from the two-phase field (austenite + ferrite) has a lath type morphology.

Various nomenclatures have been used to name the phases present in the Fe-Co alloys, with differences between the authors. In this paper the following nomenclature will be used:

- $\gamma_1$  = fcc equilibrium phase at high temperatures
- $\alpha'_1$  = bcc martensitic phase
- $\alpha_1$  = bcc disordered phase
- $\alpha_2$  = bcc ordered-B2 structure phase
- $\gamma_2$  = fcc precipitate- $Co_3V$  type phase

## MICROSTRUCTURE AND PROPERTIES OF 49Fe-49Co-2V(at%) ALLOY

The knowledge of the effects of phase transformations on the mechanical and magnetic properties of equiatomic Fe-Co alloys is of fundamental importance for practical applications. In this context, a great number

of investigations have been done, since the pioneer work of C.W. Chen [35], that opened new routes for research on this alloy system.

H.C. Fiedler [36], D.R. Thornburg [37], D.M. Pavlovic [38], A.J. Moses [39], and E. Josso [40,41] have investigated the effects of isochronal heat treatments on the mechanical and magnetic properties of an initially cold worked Fe-Co-2% V alloy. Thornburg [37] obtains a considerable improvement of those properties by controlling the amount of recrystallization; as an example, average yield strengths in excess of 621 MPa (90 ksi) together with elongation values of 13% as well as reasonable values of magnetic induction  $B$  and coercive force  $H_c$  [ $B(100 \text{ Oe}) = 22.5 \text{ kG}$ ;  $H_c \cong 6.3 \text{ Oe}$ ] were cited. The investigations developed by Josso [40,41] on 90% cold worked alloy showed that annealing at 823 K (550° C) for 1 hr led to residual induction of 19 kG, coercive force of 25 Oe and  $(BH)_{\max} = 3 \times 10^5 \text{ G} \cdot \text{Oe}$ ; that is, semihard magnetic properties. Though the alloy presented an ultimate tensile strength of 897 MPa (130 ksi), the elongation to fracture was only 5% after this heat treatment. Improved ductility with slight variations on mechanical and magnetic properties was observed by Josso after 1 hr heat treatments at 953-973 K (680-700° C) interrupted by fast quenching the alloy. Annealing temperatures higher than 1173 K (900° C) however, led to severe degradation of that magnetic performance.

A good combination of mechanical and soft magnetic properties has been obtained by Fiedler [36] using high temperature short time heat treatments to obtain a single phase fine grained material. This author reported values of yield strength in the range of 483 MPa-552 MPa (70-80 ksi) and induction values of 20 kG at 13 Oe and 22.4 kG at 85 Oe, of the order of those required for advanced rotors applications. However, the heat treatments used are very difficult, if not impossible, to realize in a commercial basis. Attempts to explain all these experimental findings were made but, as noted by Josso, better understanding of the phase transformations occurring in the alloy was lacking.

To illustrate the evolution of the strength of an initially cold worked Fe-Co-2% V alloy after heat treatments, microhardness results obtained by the present authors [42] are presented in Figure 1, together with previous results by E. Josso [41]. As can be seen, strengthening of the cold worked alloy is noticed up to annealing temperatures of 823 K (650° C) and is followed by a strong softening at higher temperatures. This large microhardness decrease with annealing temperature is associated with recovery and recrystallization process. Above around 1023 K (750° C) where recrystallization is completed, only

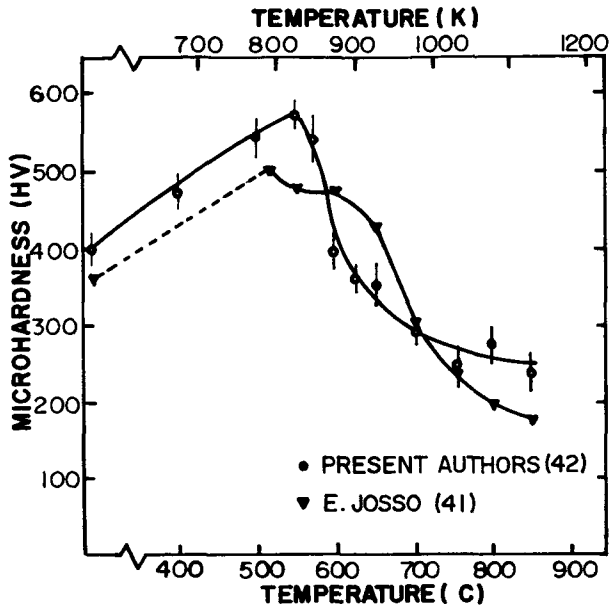


Fig. 1. Vickers microhardness of an initially 90% cold worked Fe-Co-2% V alloy as a function of the heat treatment temperature; isochronal heat treatments: [42] 2 hr, [41] 1 hr.

minor variations of microhardness are noted. The observed hardening at lower temperatures is due to the precipitation of  $\gamma_2$  ( $\text{Co}_3\text{V}$ ) phase. The same behavior is verified for the yield stress and ultimate tensile strength as shown in Figure 2. Though many aspects of  $\gamma_2$  precipitation reaction were investigated [2,4,5,7,8,34,54], its effects on the mechanical and magnetic properties were not systematically studied to the present. Figure 3 shows preliminary data obtained by the present authors illustrating the evolution of the

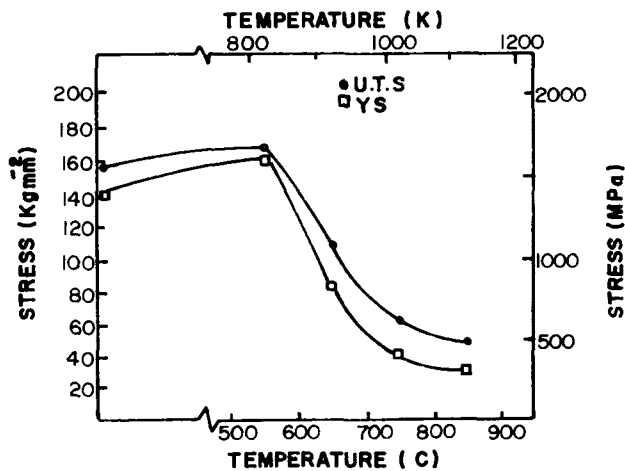


Fig. 2. Variation of the 0.2% yield stress (YS) and of the ultimate tensile strength (UTS) as a function of heat treatment temperature, for an initially 90% cold worked Fe-Co-2% V alloy; heat treatment time = 2 hr.

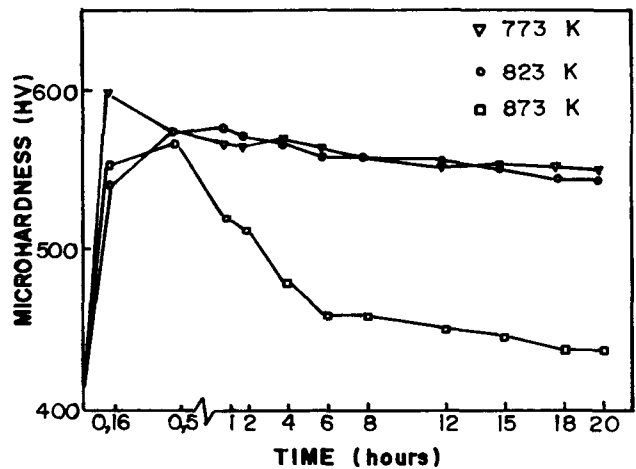


Fig. 3. The course of hardening during isothermal heat treatments at three different temperatures, for an initially 90% cold worked Fe-Co-2% V alloy.

microhardness of an initially 90% cold worked Fe-Co-2% V alloy, after isothermal heat treatments performed at 773, 823, and 873 K (500, 550, and 600°C) in argon. The hardening occurring at short aging times is mainly due to the very fine precipitation of  $\gamma_2$ . At long aging times softening occurs associated with  $\gamma_2$  coarsening as well recovery and recrystallization of the cold worked structure as exemplified in Figure 4 obtained for the sample heat treated at 873 K (600) for 18 hr. Figure 4(a) is a transmission electron microscope observation of an extraction replica of  $\gamma_2$  precipitates, and Figure 4(b) is a dark field TEM micrograph showing a grain boundary coarse precipitate. The effects of these thermal treatments on the mechanical and magnetic properties are under investigation and will be the subject of a future publication.

The order-disorder phenomenon in Fe-Co and Fe-Co-V alloys has received considerable attention due to its technological importance. Also, since the ordered state is based in the equiatomic composition, and the crystal structure of both the ordered (B2) and disordered (bcc) states are cubic, the theoretical analysis is more tractable. The evolution of the long range order parameter  $S$  was studied as a function of temperature and time using x-rays and neutron diffraction in a number of publications [14,16,21,52,53]. The influence of variables such as the disordering temperature and degree of cold work on the ordering kinetics was also addressed in many studies. It has been observed [16] that the degree of cold work retards the ordering kinetics but this retardation is independent of the amount of cold work for deformations higher than 25%; the activation energy for ordering is not sensitive to the degree of cold work. Disordering temperature seems to play an important role on the ki-



**Fig. 4.** Transmission electron micrographs obtained for an initially 90% cold worked Fe-Co-2% V alloy after 18 hr heat treatment at 873 K: (a) extraction replica; (b) thin foil dark field micrograph showing coarse precipitate; (c) thin foil bright field micrograph illustrating partially recrystallized structure.

netics of early stages of ordering, up to  $S = 0.5$ . Eymery et al. [14] have investigated the influence of quenching temperature and amount of cold work on ordering kinetics; in specimens quenched from temperatures higher than the critical transformation temperature  $T_c$ , the ordering process occurs by nuclea-

tion, growth, and coalescence of ordered domains, but in specimens quenched from temperatures a little below  $T_c$  the ordering phenomena is homogeneous inside very large domains.<sup>5</sup>

A great number of studies were made to understand the effect of the order-disorder transformation on the mechanical and magnetic properties of Fe-Co alloys [20-29]. A common result of these works is the verification that an increased brittleness is associated with increasing degrees of order. To improve alloy ductility, the inclusion of a third alloying element (V, Cr, Mn, etc.) is one way, and the use of fast quenching from the disordered state is commonly utilized.

The effects of the ordering phenomena on the magnetic properties of Fe-Co alloys were addressed in several studies [30-33, 40-42]. For the binary equiatomic Fe-Co alloy, ordering has little influence on the magnetic saturation induction [33]. Though the magnetic permeability, the coercive force, and saturation magnetization are all altered by ordering in ternary alloys [40-42], the reduced number of available data makes the interpretation very difficult.

#### Fe-Co-X AND Fe-Co-V-X ALLOYS

More recently, two investigation routes are being pursued for the Fe-Co alloys: the substitution of vanadium [43,44,48] (ternary alloys) and the addition of a fourth alloying element to the Fe-Co-2% V alloy (quaternary alloys) [50,51,29].

The interest in the new ternary alloys has its origin in two basic experimental observations:

- First, besides vanadium, other elements such as Cr, C, Mo, W, Ta, Nb, and Ni are also effective in improving the ductility and mechanical strength of the alloy [43,48].
- Second, above a certain critical degree of cold working (~72%) a simultaneous amelioration of the ductility and mechanical strength are obtained even for alloys submitted to ordering heat treatments [46].

The origin of this improved ductility of these ternary alloys has been investigated by Kawahara [43,48]. After addition of various alloying elements to the equiatomic Fe-Co alloy, he found that the elements that can combine with Co to form intermetallics of the type  $Co_3X$  are those responsible for increased ductility. These intermetallics can be formed by diffusion and are  $Co_3C$ ,  $Co_3Y$ ,  $Co_3Cr$ ,  $Co_3Ni$ ,  $Co_3Nb$ ,  $Co_3Mo$ ,  $Co_3Ta$ , and  $Co_3W$ . The elements: aluminum, beryllium, boron, copper, gold, manganese, silver, titanium, and zirconium, which are ineffective to increase ductility, do not form cobalt intermetallics. An explanation for this effect has been suggested by Ka-

wahara [46]. According to his ideas, small clusters containing Co and X, with composition close to  $\text{Co}_3\text{X}$  would be formed during the solidification of the alloy. In the vicinity of these clusters, the alloy would be locally impoverished of Co, forming zones where ordering would be difficult to develop. These zones are referred to as local concentration disordered (LCD) zones, shown in figure 10 of reference [41]. Cold working of the alloy would make the distribution of these LCD zones more dense and homogeneous, leading to a filament-like structure which is more ductile and strong.

Though the investigations related to the addition of a third alloying element to Fe-Co alloys have been done extensively, its main objective was to improve the alloy ductility; the effects of these additions on the magnetic properties has been only briefly touched on in these studies. The results by Kawahara, in fact, suggest the possibility of obtainment of high mechanical strength and ductility in these alloys without considerable degradation of the soft magnetic properties characteristic of the equiatomic Fe-Co alloys.

Another investigation route, though incipient, is being followed, after the observations of Branson et al. [5] that the addition of Ni to the Fe-Co-V alloy resulted in higher ductility without damage to the magnetic properties. After this work, Pitt and Rawlings [5] investigated the microstructure of Fe-Co-V and Fe-Co-V-Ni alloys submitted to various thermal-mechanical heat treatments and concluded that the presence of Ni induced an increase in the volume fraction of  $\gamma_2$  precipitate and the acceleration of the precipitation kinetics. Also, the presence of a fine  $\gamma_2$  dispersed in the matrix affects grain growth leading to an additional contribution to strength. This latter point has been studied by Pitt and Rawlings in another publication [29] for alloys containing up to 7.4wt% Ni. They found that  $\gamma_2$  can dissolve nickel playing an important, though indirect role, in the improvement of the ductility of the alloy.

## REFERENCES

1. A. Preuss, dissertation, University of Zurich, 1912.
2. P. Weiss, *Trans. Faraday Soc.* 8, p. 148, 1912.
3. G.W. Elmen, U.S. Patent 1739752, 1929.
4. J.H. White and C.V. Wahl, U.S. Patent 1862559, 1932.
5. R.D. Rawlings, H.M. Flower, and J.A. Ashby, *Met. Sci.* 11 p. 91, 1977.
6. M.R. Pinnel and J.E. Bennett, *The Bell System Tech. J.*, v. 52, No. 8, October 1973, 1325.
7. S. Mahajan, M.R. Pinnel, and J.E. Bennett, *Met. Trans.* 5, 1974, p. 1263.
8. M.R. Pinnel and J.E. Bennett, *Met. Trans.* 5, 1974, p. 1273.
9. S. Mahajan and K.M. Olsen, Proceedings of the Conference on Magnetism and Magnetic Materials, San Francisco, 1974 (American Institute of the Physics, New York, 1975) p. 743.
10. M.R. Pinnel and J.E. Bennett, *IEEE Trans. on Magnetics*, vol. MAG-11, No. 3, May 1975, p. 901.
11. M.R. Pinnel, S. Mahajan, and J.E. Bennett, *Acta Metall.* 24, 1976, p. 1025.
12. J.A. Rogers, H.M. Flower, and R.D. Rawlings, *Met. Sci.* 9, p. 32, 1975.
13. J.A. Ashby, H.M. Flower, and R.D. Rawlings, *Phys. Status Solidi* (a) 47, 1978, p. 407.
14. J.P. Eymery, P. Grosbras, and P. Moine, *Phys. Status Solidi* (a) 21, 1974, p. 517.
15. P. Grosbras, J.P. Eymery, and P. Moine, *Scripta Metall.*, vol. 7, 1973, p. 959.
16. A.W. Smith and R.D. Rawlings, *Phys. Status Solidi* (a) 34, 1976, p. 117.
17. M. Rajkovic and R.A. Buckley, *Met. Sci.* 15, 1981, p. 21.
18. L.A. Alekseyev, D.M. Dzhavadov, Yu. D. Tyapkin, and R.B. Levi, *Phys. Met. Metallog.* 43(6), 1977, p. 99.
19. M.I. Glazyrina, A.M. Glezer, B.V. Molotilov, S.M. Tret'yaHova, and V.I. Kleynerman, *Phys. Met. Metallog.*, vol. 56, No. 4, 1983, p. 93.
20. C.W. Chen and G.W. Wiener, *J. Appl. Phys.* 30, 1959, p. 199S.
21. N.S. Stoloff and R.G. Davies, *Acta Metall.* 12, 1964, p. 473.
22. M.J. Marcinkowski and H. Chessin, *Phil. Mag.* 10, 1964, p. 837.
23. T.L. Johnston, R.G. Davies, and N.S. Stoloff, *Phil. Mag.* 12, 1965, p. 305.
24. K.R. Jordan and N.S. Stoloff, *Trans. of the Metall. Soc. of AIME*, vol. 245, 1969, p. 2027.
25. P. Moine, J.P. Eymery, and P. Grosbras, *Phys. Status Solidi* (b) 46, 1971, p. 177.
26. Y.G. Koynu, G.F. Hancock, and R.D. Rawlings, *Phys. Status Solidi* (a) 16, 1973.
27. J.F. Dinhut, H. Garen, J.P. Eymery, and P. Moine, *Scripta Metall.*, vol. 8, 1974, p. 307.
28. J. Eymery and P. Moine, *Scripta Metall.*, vol. 9, 1975, p. 467.
29. C.D. Pitt and R.D. Rawlings, *Met. Sci.*, June 1983, 17(6), p. 261.
30. R.C. Hall, *J. Appl. Phys.* 31, 1960, p. 157S.
31. D.R. Thornburg and D.A. Colling, *Met. Trans.* 5, 1974, p. 2241.
32. D.M. Dzhavadov and Yu. D. Tyapkin, *Phys. Met. Metallog.* 54(5), 1982, p. 84.
33. J.S. Kouvel, *Magnetism and Metallurgy*, vol. 2, 1969, A.E. Berkowitz and E. Kneller, eds.
34. H.C. Fiedler and A.M. Davis, *Met. Trans.* 1, 1970, p. 1036.
35. C.W. Chen, *J. Appl. Phys.* 32, 1961, p. 348S.
36. H.C. Fiedler, Proceedings of the Magnetism and Magnetic Materials Conference, San Francisco, 1974 (American Institute of Physics, New York, 1975), p. 739.
37. D.R. Thornburg, *J. Appl. Phys.* 40, 1969, p. 1579.

38. D.M. Pavlovic and F.G. Slone, IEEE Trans. on Magnetics, 09/69.
39. A.J. Moses, Proceedings of the Conference on Magnetism and Magnetic Materials, San Francisco 1974 (American Institute of Physics, New York, 1975) p. 741.
40. E. Josso, Memories Scientifiques, *Rev. Metallurg.* LXX No. 5, 1973.
41. E. Josso, IEEE Trans. on Magnetics, vol. MAG-10, No. 2, June 1974.
42. P.I. Ferreira, A.A. Couto, and W.A. Monteiro, Anais do 7o. CBECIMAT, UFSC, Florianópolis, SC (Dec. 1986), p. 43.
43. K. Kawahara, *J. Mater. Sci.* 18, 1983, p. 1709.
44. K. Kawahara, *J. Mater. Sci.* 18, 1983, p. 2047.
45. K. Kawahara, *J. Mater. Sci.* 18, 1983, p. 3427.
46. K. Kawahara, *J. Mater. Sci.* 18, 1983, p. 3437.
47. K. Kawahara, *J. Mater. Sci.* 19, 1983, p. 949.
48. K. Kawahara and M. Uehara, *J. Mater. Sci.* 19, 1984, p. 2575.
49. P.I. Ferreira and A.A. Couto, XI Colóquio da Sociedade Brasileira de Microscopia Eletrônica, to be published.
50. M.W. Branson, R.V. Major, C.D. Pitt, and R.D. Rawlings, *Journal of Magn. and Mag. Mat.* 19, 1980, p. 222.
51. C.D. Pitt and R.D. Rawlings, *Met. Sci.* 15, 1981, p. 369.
52. D.W. Clegg and R.A. Buckley, *Metal Sci. J.* 7, 1973, p. 48.
53. R.A. Buckley, *Metal Sci J.*, 9, 1975, p. 243.
54. C. Kuroda, *Japan J. Appl. Physics*, 5, 1966, p. 8.