Phase analyses of the Co-Fe-Pd ternary alloys

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Abstract. Samples of different compositions of Co-Fe-Pd were made in a button arc furnace, under an argon atmosphere on a water-cooled copper hearth. They were sectioned and a half was kept in the as-cast state. The samples were analysed in a scanning electron microscope with energy dispersive X-ray spectroscopy, and in an X-ray diffractometer to derive the microstructures and to determine the overall and phase compositions. Coring occurred in many samples, which was expected due to the wide composition range of the main solid solution in the system. The microstructures were not similar to any of the work of sixty years ago when the Co-Fe-Pd phase diagram was studied. Some of the phases were too fine to be analysed with EDS in the as-cast samples.

1. Introduction
Magnetic materials are essential in many industries, and there is a need to replace expensive rare earth metals with cheaper and more readily available metals. Historically, patents held by American and Japanese companies have been a barrier to entry into the magnet market. However, China’s establishment of research institutes in the 1950s and 1960s, and the expiry of the American and Japanese patents in the 1980s has enabled China to enter and dominate the magnet market. Currently, China has a monopoly on the magnet value chain, producing 90% of the world’s permanent magnets, and China also has most of the world’s rare earth resources.

There is potential to use Co-Fe-Pd rare earth-doped alloys for magnets, because FeCo is a soft magnetic material with high saturation magnetism and a high Curie temperature, due to the cobalt [1]. Palladium nano-particles have localized paramagnetism, with the potential to become magnetic, and so Pd can improve the magneto-crystalline anisotropy of FeCo. Thus, the Co-Fe-Pd system offers possible alternatives to the heavy and expensive rare-earth magnets, which are in current use.

The Fe-Co-Pd alloy has potential applications in biotechnology, electronics and green technologies. Magnetic thin films and nanostructures, which are magnetized perpendicular to their surfaces, are essential to many developing technologies, including spintronics devices [2] and patterned media [3, 4]. This maintained the thermal stability even as the device dimensions became increasingly nanoscale. Multilayers or superlattice structures consisting of alternating ferromagnetic and non-magnetic layers are highly suitable for these applications, due to their tunable perpendicular magnetic anisotropy (PMA) and saturation magnetization [5, 6].
By combining the soft magnetic properties of iron and the hard magnetic properties of cobalt and palladium, an optimal magnetic material could be developed. Fe-Co alloys have a B2 structure which makes them extremely brittle at room temperature [1]. The workability of these alloys can be improved by adding nickel or palladium, and palladium especially leads to a higher tensile strength and elongation at room temperature [1].

Apart from the mechanical properties [1] of the Fe-Co-Pd alloys and research on the magnetic shape memory properties [7, 8, 9], little work has been done on the ternary phase diagram [10-13]. The published phase diagram work is from four papers by a group in Russia [10-13] and these papers are contradictory, even sometimes within the same paper. Ragavhan [14] attempted to assess the system, and was unable to satisfactorily interpret it due to the contradictory data, and admitted that his interpretation was very speculative. His isothermal section at 25°C [14] is given in figure 1, and is much simpler than that of Grigorev and Kuprina [13].

![Figure 1. Co-Fe-Pd Isothermal section at ~25°C (at.%) [14].](image)

Since Co-Fe-Pd alloys are being studied to improve their magnetism [15], it is necessary to know the extent of the promising Co-Fe phases into the ternary system. There are problems with the phase diagram [14], and so this study was to identify the extents of those phases.

### Table 1. Nominal composition of samples.

| Alloy | Fe (at.%) | Co (at.%) | Pd (at.%) |
|-------|-----------|-----------|-----------|
| 1     | 60        | 30        | 10        |
| 2     | 15        | 30        | 75        |
| 3     | 30        | 30        | 40        |

2. **Experimental procedure**

The composition of the samples shown in table 1 were determined by choosing three-phase regions from the 25°C isothermal section of Raghavan [14], as well as compositions of interest for magnetic properties [15]. The alloys were prepared from 99.99% pure elemental powders of Fe, Co and Pd. The powders were weighed, mixed and cold compacted (to hold the components together prior to melting) and then melted in a button arc-furnace (BAF), according to standard preparation method PMD-SOP-O37. An argon atmosphere and a water-cooled copper hearth were used, together with a titanium oxygen-getter, which was melted before making each sample. The samples were cut using a Struers automatic cutting machine with an Accutom cutting wheel, mounted in a mounting press, ground and polished. Grinding and polishing were done using a Saphire 520 automatic machine. One half of each sample was studied in the as-cast condition. Once the samples were polished, they were removed from the polystyrene resin and X-ray diffraction (XRD) was conducted using a Bruker D2 Phaser and the Diffrac Plus EVA program with the 2018 database to analyse the data.

Due to the wide range of compositions of the samples (from 10-75 at.% Pd), different etching techniques were tried, and the best results for each sample was used. The first etch tried was using a
steel wire cathode and a solution of 90ml water and 10ml hydrochloric acid [16]. The second etch was immersion in a solution of distilled water (50 ml), hydrochloric acid (SG 1.19, 100 ml) and nitric acid (SG 1.4, 10ml) [16]. Once the samples were etched, they were analyzed on a Sigma Zeiss scanning electron microscope (SEM) using backscattered (BSE) and secondary electron (SE) modes. Once the microstructures were visible, EDX analyses were done to determine the composition of the different phases and the overall compositions of each sample.

3. Results

For Alloy 1 (Fe$_{60}$:Co$_{30}$:Pd$_{10}$ (at.%)), the low Pd content allowed a less aggressive etchant to be used: electric etching with a steel wire cathode in a solution of water and hydrochloric acid. The dendrites in figure 2a were due to coring from the fast cooling from arc-melting, given the lack of a definite interface between the dendritic and interdendritic regions, and they also had similar compositions, table 1. There was also a finer, darker phase visible, which was too small (<2 µm) to analyse accurately [17], without collecting X-rays from the surrounding phase. The XRD results (figure 3) showed that the major phase was $\gamma$ (fcc), and the minor phase was $\alpha$ (bcc).

Alloy 2 (Fe$_{15}$:Co$_{10}$:Pd$_{75}$ (at.%)) needed the most aggressive etchant method, 2, because of its high Pd content. The microstructure in figure 2b shows dendrites, and two-phase interdendritic regions, where the second phase was darker. Once again, the smallest phases were too fine to analyse accurately [17], resulting in similar compositions of the dendritic and interdendritic areas, table 2. The XRD pattern (figure 4) indicated FePd$_3$ and FePd.

![Figure 2. SEM-BSE images of as-cast a) Alloy1 Fe$_{60}$:Co$_{30}$:Pd$_{10}$ (at.%) showing dendrites (darker) and b) Alloy 2 Fe$_{15}$:Co$_{10}$:Pd$_{75}$ (at.%) showing gamma dendrites (lighter) and two phase interdendritic area (dark).](image)

![Figure 3. XRD pattern for Alloy 1 Fe$_{60}$:Co$_{30}$:Pd$_{10}$ (at.%), as-cast condition.](image)
Figure 4. XRD pattern for nominal Alloy 2 Fe$_{15}$:Co$_{10}$:Pd$_{75}$ (at.%), as-cast condition.

Figure 5 of Alloy 3 (Fe$_{30}$:Co$_{30}$:Pd$_{40}$ (at.%) shows a single phase, with pores filled with debris from grinding. The XRD pattern in figure 6 shows one major phase which matched two different compositions of $\gamma$, with wide peaks, indicating a cored phase.

Figure 5. SEM-BSE image of as-cast Alloy 3 Fe$_{30}$:Co$_{30}$:Pd$_{40}$ (at.%) showing a single phase with pores.

Figure 6. XRD pattern for nominal Fe$_{30}$:Co$_{30}$:Pd$_{40}$ (at.%), as-cast condition.
Table 2. SEM-EDS analyses of the sample overalls and the phases of different contrasts.

| Alloy | Overall | Dark: γ | Light: γ | Light: FePd | Dark: FePd |
|-------|---------|---------|---------|-------------|-----------|
| Fe 59.6 | 59.1±0.1 | 54.8±1.2 |
| Co 29.1 | 28.5±0.3 | 25.1±1.3 | -- | -- |
| Pd 11.3 | 12.4±0.3 | 20.1±2.5 |
| Fe 13.6 | 13.4±0.4 | 14.5±0.1 |
| Co 9.0 | -- | -- | 8.2±0.4 | 11.1±1.3 |
| Pd 77.4 | | | 78.4±0.5 | 74.4±1.2 |
| Fe 28.2 | 28.7±0.1 | 29.2±0.1 |
| Co 28.3 | 28.3±0.1 | 27.7±0.1 | -- | -- |
| Pd 43.5 | 43.0±0.1 | 43.1±0.1 |

4. Discussion

Due to the samples containing Pd, a high acceleration voltage (20kV) had to be used on the SEM in order to excite the Pd X-rays for EDS. Using a high kV causes the electron beam to spread out further [17], making the area for accurate EDS analysis larger (typically ≥2 microns), hence the samples with fine microstructures could not be accurately analysed in the SEM.

Given the very wide γ liquidus of the system and the few solid phases [10-14], it is not surprising that the alloys were cored. None of the microstructures found to date was similar to those of the previous workers [10-14], although the decomposition of Alloy 1 would be expected from the ~25°C isothermal section of Raghavan [14] because the alloy composition lies in a two-phase region. However, the phases found here were γ and α, whereas Raghavan [14] showed that the phases should be γ and α’ (Figure 1). Thus, Alloy 1 suggests a wider γ + α phase field than Raghavan [14]. Alloy 2 shows that the γ phase was more narrow than Raghavan [14] indicated (Figure 1). Conversely, Alloy 3, is a single-phase solid solution of γ, showed that this phase had a greater extent at this alloy composition than in Raghavan’s isothermal section [14], Figure 1.

There was a better agreement of the as-cast samples with the 25°C isothermal section of Raghavan [14] than with that of Kuprina and Grigorev [11]. Strictly, the as-cast samples of this work should not have been compared to the ~25°C isothermal sections of Kuprina and Grigorev [11] and Raghavan [14], but there was no other information available for comparison.

The coring in Alloy 1 was used to assess the validity of the two liquidus surfaces [11, 14] since the dendrites would form first, and the interdendritic area would form next, and the direction from the former to the latter should follow the slope of the liquidus surface. The deduced liquidus slope agreed with both of the liquidus surfaces [11, 14], so it was not possible to choose a better one. The XRD patterns showed very few peaks, making identification of the phases difficult.

5. Conclusions

Three alloys of different compositions were manufactured by arc melting and studied in the as-cast condition. Alloy 1 comprised γ and α, suggesting a wider γ + α phase field than Raghavan [14]. Alloy 2 showed that the γ phase was more narrow than Raghavan [14], whereas Alloy 3, a single-phase solid solution of γ, showed a greater extent than Raghavan’s isothermal section [14]. The results were in better agreement with Raghavan’s [14] isothermal section at ~25°C. The compositions of the cored microstructures of Alloy 1 agreed with both published liquidus surfaces.

References
[1] Matsuda M, Sago R, Akamine K, Tsurekawa S, Takashima K and Nishida M 2016 Enhancement of Ductility in Fe-Co Based Alloys by Substitution of Pd (in English) J. Alloys
Compd. 682 124-131

[2] Ravelosona M S, Katine D, Carey J A, Terris M J and Fullerton E E 2006 Current-induced magnetization reversal in nano-pillars with perpendicular anisotropy Nat. Mater. 5 210–215

[3] Todorovic M, Schultz S, Wong J and Scherer A 1999 Writing and reading of single magnetic domain per bit perpendicular patterned media Appl. Phys. Lett. 74 2516–2518

[4] Ding J and Adeyeye A O 2013 Binary ferromagnetic nano-structures: fabrication, static and dynamic properties Adv. Funct. Mater. 23 1684–1691

[5] Terris B D and Thomson T 2005 Nano fabricated and self-assembled magnetic structures as data storage media J. Phys. D 38 199–222

[6] Rippard W H, Deac A M, Pufall M R, Shaw J M, Keller M W, Russek S E, Bauerand G E and Serpico C 2010 Spin-transfer dynamics in spin valves with out-of-plane magnetized CoNi free layers Phys. Rev. B 81

[7] Koeda J, Nakamura Y, Fukuda T, Kakeshita T, Takeuchi T and Kishio K 2001 Trans. Mater. Res. Soc. (Japan) 26 215-217 as quoted by [18]

[8] Oshima R 1981 Scripta Metall. 15, 829-833 as quoted by [18]

[9] Kauffmann-Weiss S, Hamann S, Gruner M E, Buschbeck J, Ludwig A, Schultz L and Fähler S 2012 Understanding the Magnetic Shape Memory System Fe-Pd-X by Thin Film Experiments and First Principle Calculations Adv. Eng. Mater. 14 (8) 724-749

[10] Grigorev A T and Kuprina V V 1961 Order-Disorder Transformation in Alloys of Iron with Cobalt and Palladium (in Russian) Zh. Neorg. Khim. 6 (8) 1891-1898, English translation: J. Inorg. Chem. 6(8) 966-970

[11] Kuprina V V and Grigorev A T 1958 Investigation of Alloys of Fe-Co-Pd System. I. Fusibility Diagram of the Fe-Co-Pd System (in Russian) Zh. Neorg. Khim. 3 (12) 2736-2739

[12] Kuprina, V V and Grigorev AT 1959 Solid-State Transformations in Alloys of Iron with Cobalt and Palladium (in Russian) Zh. Neorg. Khim. 4 (7) 1606-1610 English translation: J. Inorg. Chem. 4 (7) 724-727

[13] Kuprina V V and Grigorev A T 1961 Polymorphic Transformation in Alloys of Iron with Cobalt and Palladium (in Russian) Izv. Vyss. Uchebn. Zaved. Khim., Khim. Tekhnol) 4 (1) 7-10

[14] Raghavan V 1992 The Co-Fe-Pd (Cobalt-Iron-Palladium) System (in English) Phase Diagrams of Ternary Iron Alloys (Indian Institut of Metals, Calcutta) 6 A, 623-627.

[15] Manyti H 2017 Personal communication

[16] Wing G 1996 A lexicon of metallographic etchants, MSc Thesis (University of the Witwatersrand South Africa)

[17] Goldstein G I, Newberry D E, Echlin P, Joy D C, Fiori C and Lifshin E 1981 Scanning Electron Microscopy and X-Ray Microanalysis (New York: Plenum Press) 56-59

[18] Tsuchiya K, Nojiri T, Ohtsuka H and Umemoto M 2003 Effect of Co and Ni on Martensitic Transformation and Magnetic Properties in Fe-Pd Ferromagnetic Shape Memory Alloys Mater. Trans. 44 (12) 2499-2502