JOURNAL OF MATERIALS SCIENCE 13 (1978) 499–504

The ordered phase fields of the iron-nickel-platinum equilibrium diagram

G. T. STEVENS*, M. HATHERLY, J. S. BOWLES
School of Metallurgy, The University of New South Wales, Kensington, NSW 2033, Australia

The approximate limits of the ordered phases in the Fe–Ni–Pt system at 600° C are established; some results are also given for high nickel alloys at 475° C. Continuous solid solutions form between FePt and NiPt and between Fe_3Pt and Ni_3Pt at temperatures below the relevant critical temperatures, but not between $FeNi_3$ and Ni_3Pt. Ordering of the iron and nickel atoms was not detected in the ternary alloy $Fe_{25}Ni_{25}Pt_{50}$ but two tetragonal phases were found in the alloys containing about 60 at. % Pt. The lattice parameters of alloys heat-treated at these temperatures are given.

1. Introduction

The three binary systems formed from the elements iron, nickel and platinum have a number of ordered phases with either the Ll_2 cubic structure (Fe_3Pt, Ni_3Pt, $FePt_3$, $FeNi_3$) or the Ll_0 tetragonal structure (FePt, NiPt) [1]. A tetragonal superlattice has also been reported [2] in neutron irradiated FeNi. In a study of the formation of tetragonal superlattices [3] information was obtained about the extent of the tetragonal phase field in the ternary system Fe–Ni–Pt and the variation of lattice parameters and axial ratios within it. Since very little information is available concerning this ternary system [4–6], alloys with compositions outside the tetragonal phase field were also studied and were used to determine qualitatively the form of the 600° C isothermal section of the ternary equilibrium diagram.

2. Experimental

The alloys were prepared, either by vacuum induction melting of argon arc melting, from Johnson Matthey "Specpure" or "High Purity" iron and nickel and Matthey Garrett platinum. The compositions of the ternary alloys are shown in Table I. Typical levels of impurity revealed by spectrographic analysis were silicon 0.020, calcium 0.0008, chromium 0.006 and copper 0.005 at. %.

The specimens were homogenized at temperatures between 1000 and 1200° C for periods of 60 to 160 h and were then either quenched directly to the ordering temperature or reheated after quenching in water. The minimum ordering time for specimens ordered at 600° C was one week; three specimens were ordered at 475° C for 6 months. After ordering, the specimens were quenched in water.

The lattice parameters of the various phases in the ternary alloys and in some significant binary alloys were determined using an 11.483 cm diameter X-ray powder camera, and filtered cobalt radiation; the calculations incorporated a Hess least-squares refinement [7].

For optical metallography, platinum-rich high-iron alloys were etched in aqua regia and platinum-rich low-iron alloys were prepared by an a.c. polish and etch technique [8]. Considerable difficulty was encountered in the etching of alloys containing smaller amounts of platinum ($\simeq$30%) and a completely satisfactory procedure was not found.

3. Results and discussion

The phases present in the ternary alloys studied, and their lattice parameters, are shown in Table I. These results, together with the data available for

---

*Present address: Australian Atomic Energy Commission, Sutherland, NSW 2232, Australia.

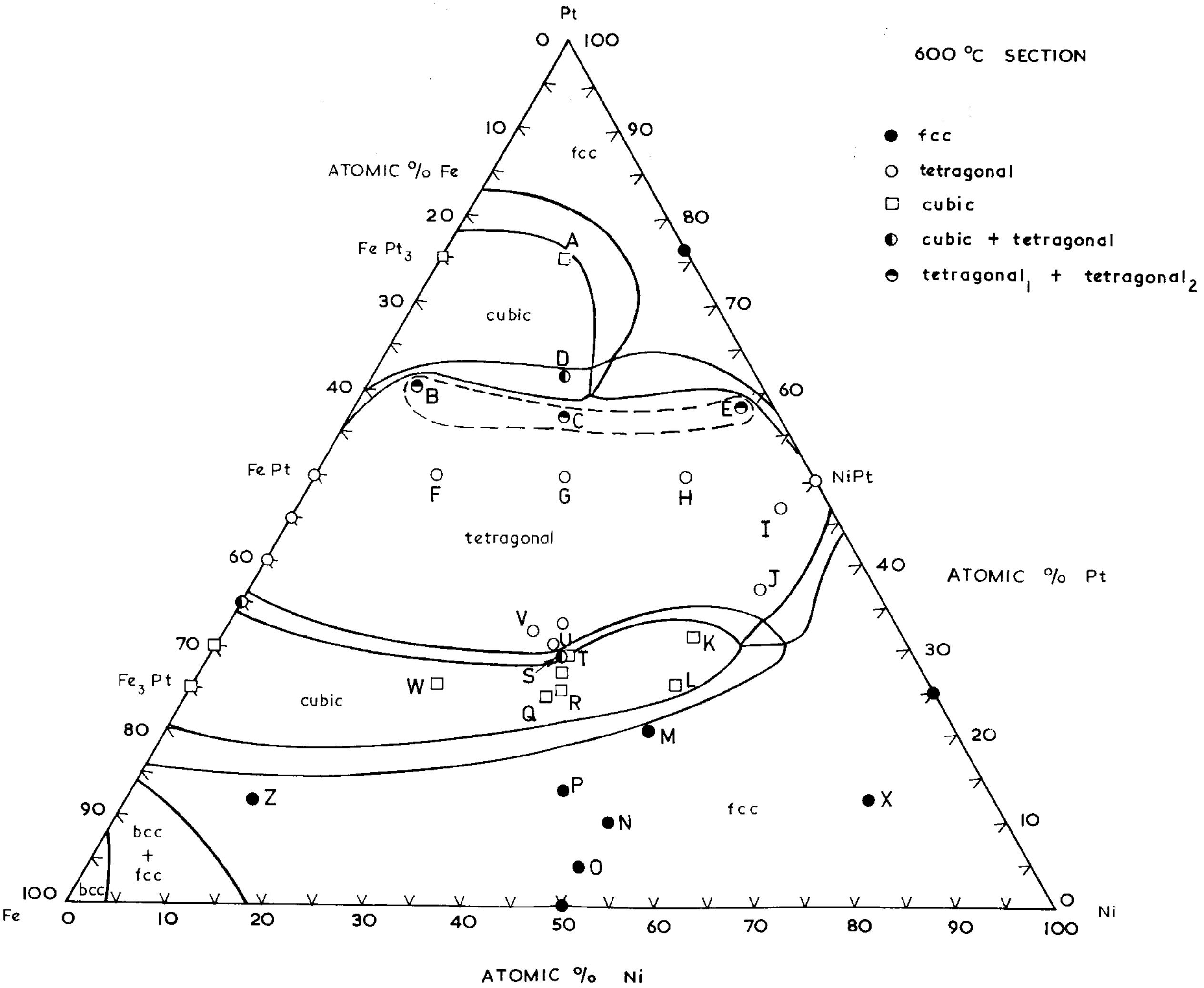


Figure 1 The 600° C isothermal section of the Fe–Ni–Pt equilibrium diagram.

TABLE I Structure and lattice parameters of alloys annealed at 600° C and 475° C.
(Cobalt radiation; Co$K\alpha_1$ 1.78892 Å, Co$K\alpha_2$ 1.79278 Å, Co$K\alpha$ 1.79021 Å.)

Alloy	Composition* (at. %)		Structure	Lattice parameters‡ (Å)		*c*/*a*
	Fe	Ni		*a*	*c*	
A	†12.5	12.5	cubic	3.839		
B	34.8	4.9	tet_1	3.864 (0.002)	3.737 (0.006)	0.967
			tet_2	3.862 (0.001)	3.773 (0.005)	0.977
C	21.7	21.6	tet_1	3.85	3.68	0.956
			tet_2	3.85	3.73	0.967
D	19.5	19.2	cubic	3.8112 (0.0002)		
			tet	3.83	3.79	0.990
E	3.1	39.0	tet_1	3.837 (0.001)	3.651 (0.004)	0.952
			tet_2	3.835 (0.002)	3.693 (0.005)	0.963
F	38.1	12.1	tet	3.840 (0.002)	3.676 (0.002)	0.957
G	†25	25	tet	3.837	3.656	0.953
H	†12.5	37.5	tet	3.829	3.621	0.946
I	4.7	48.8	tet	3.799 (0.001)	3.612 (0.002)	0.951
J	11.2	51.8	tet	3.775 (0.001)	3.636 (0.002)	0.963
K	20.8	47.9	cubic	3.6960 (0.0002)		
L	25.4	48.8	cubic	3.6783 (0.0003)		
M	30.7	48.7	fcc	3.6627 (0.0002)		
N	†40	50	fcc	3.627		
O	†45	50	fcc	3.608		
P	43.1	43.4	fcc	3.6332 (0.0002)		
Q	39.5	36.2	cubic	3.6958 (0.0005)		
R	†37.5	37.5	cubic	3.693		
S	35.4	35.6	tet	3.740 (0.001)	3.677 (0.001)	0.983
			cubic	3.72		
T	34.7	35.9	cubic	3.7097 (0.0003)		
U	35.6	33.9	tet	3.731 (0.001)	3.685 (0.003)	0.988
V	37.0	30.9	tet	3.753 (0.001)	3.675 (0.002)	0.979
W	49.9	24.6	cubic	3.7111 (0.0003)		
X	†12.5	75	fcc	3.604	(475° C)	
Y	23.9	76.1	cubic	3.5520 (0.0003)	(475° C)	
Z	†75	12.5	fcc	3.663		

*Remainder platinum
†Nominal composition only – alloy not analysed
‡Figures in parenthesis are standard deviations.

the binary systems [1, 9, 10] indicate that the isothermal sections at 600 and 475° C have approximately the forms shown in Figs. 1 and 2. At 600° C, a continuous Ll_0 tetragonal phase field exists between FePt and NiPt. The limits shown for this phase on the nickel–platinum side of the diagram are those determined by Esch and Schneider [11] who reported an ordering temperature of 645° C for NiPt. Much narrower limits would be expected if the ordering temperature were 603° C as reported by Woolly and Bates [12] but in the present work the ordered tetragonal phase was detected in NiPt held at 630° C for 240 h (Fig. 3), supporting the results of Esch and Schneider.

Extensive replacement of iron atoms by nickel can occur in both of the cubic Ll_2 phases $FePt_3$

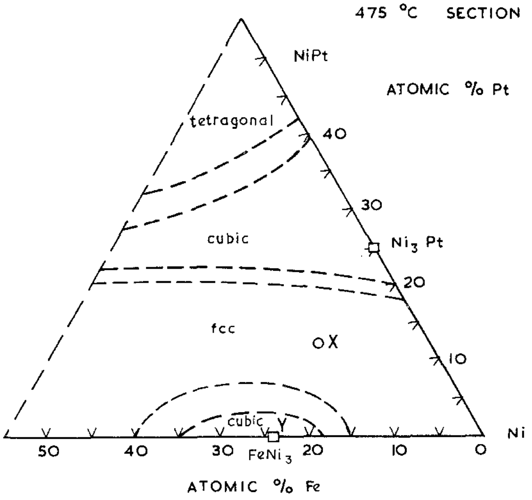


Figure 2 The Ni-rich corner of the 475° C isothermal section of the Fe–Ni–Pt diagram.

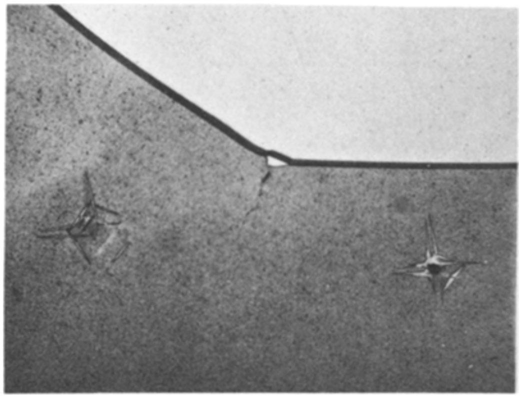
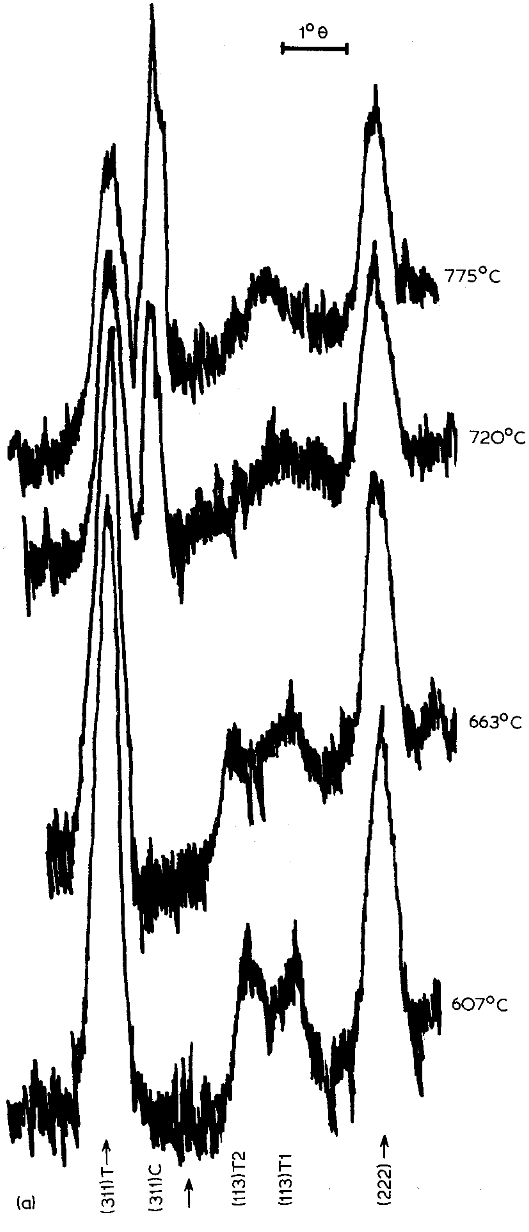


Figure 3 Microstructure of the 50 at.% Ni, 50 at.% Pt alloy cooled from 1000° C to 630° C and held for 240 h, showing lenticular precipitates and a grain boundary precipitate of the ordered NiPt. (500 X, etched.)

and Fe_3Pt. However, these phase fields cannot extend to the platinum–nickel side of the diagram because no superlattice forms at $NiPt_3$, and the Ni_3Pt superlattice is not stable at 600° C. At this temperature there are no ordered phases in the iron–nickel system. At 475° C the Ni_3Pt superlattice is stable and the ordered cubic phase field extends from Fe_3Pt to Ni_3Pt. The superlattice Ni_3Fe is also stable at this temperature but the disorder observed in the alloy, Fe 12.5%, Ni 75%, Pt 12.5%, shows that a continuous series of superlattices does not exist between Ni_3Fe and Ni_3Pt.



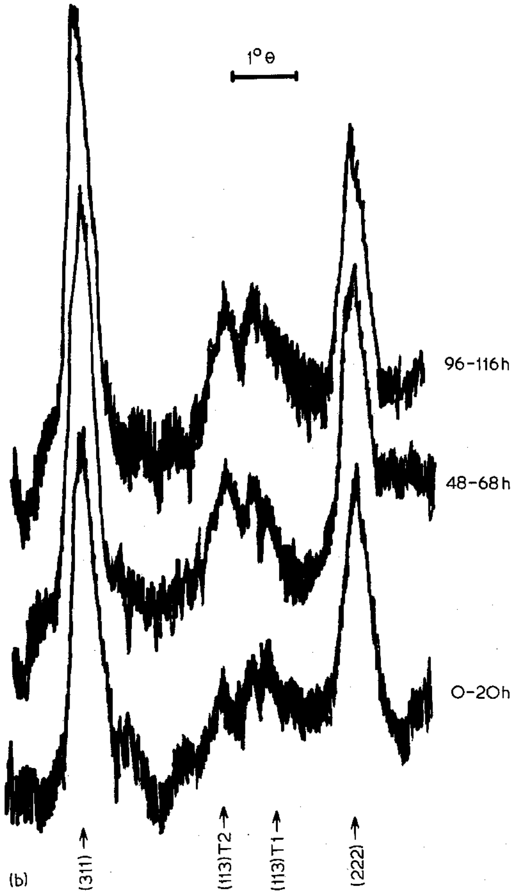


Figure 4 Microdensitometer traces of high temperature X-ray diffraction patterns from alloy E, Fe 3.1%, Ni 39.0%; (a) after annealing at progressively higher temperatures, (b) after cooling to 607° C and exposing at that temperature for the time interval shown.

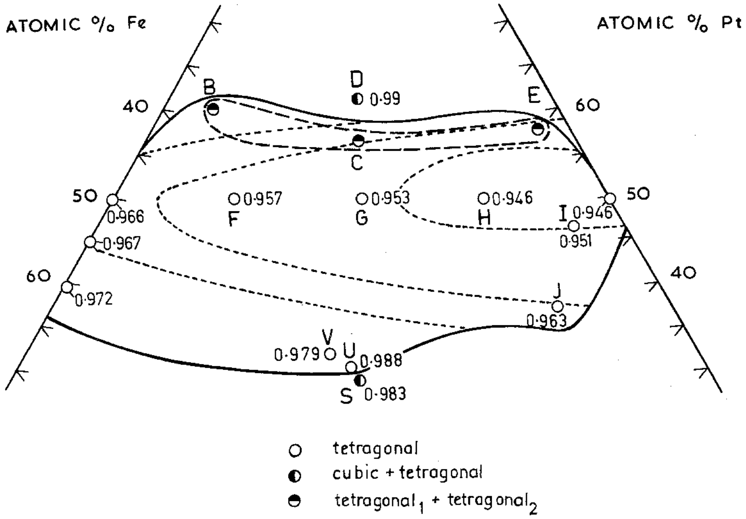


Figure 5 Approximate axial ratio contours for the 600° C isothermal section.

The platinum atoms evidently play the dominant role in determining the nature of the ordering in the ternary alloys. This dominance of the platinum atoms is also indicated by the asymmetry of the tetragonal phase field which, for alloys containing less than 50 at. % Pt, extends as far as the composition FeNiPt. For platinum concentrations greater than 50 at.%, it is no longer possible for platinum atoms to avoid having platinum nearest neighbours in neighbouring (0 0 1) planes and the ordered tetragonal structure rapidly becomes unstable.

Alloys B, C and E, containing respectively 60.3%, 56.7%, and 57.9%, platinum behaved in an unexpected fashion. The diffraction patterns showed splitting of the 0 0 2, 0 2 2, 1 1 3, etc. lines of the tetragonal pattern and were consistent with the presence of two tetragonal ordered phases. For alloy C (Fe 21.7%, Ni 21.6%) the lines were diffuse and the determinations of the individual lattice parameters were of limited accuracy, but for the other two alloys the splitting was clearly defined and accurate measurements of the lattice parameters were obtained. These diffraction patterns could not be accounted for in terms of a single orthorhombic structure. Heat treatment in a high temperature diffraction camera confirmed that these structures had not formed during cooling to room temperature. As shown in Fig. 4, heating to 775° C resulted in the development of a cubic (presumably disordered) phase. On cooling to 607° C the two tetragonal phases could be detected after 20 h and the splitting of the lines was clearly resolved after 68 h.

If these are equilibrium structures the existence of a miscibility gap in the tetragonal phase field, as shown in Fig. 1 by a dotted phase boundary, is implied. The approximate direction of the tie lines in such a miscibility gap can be deduced from the axial ratio contours shown in Fig. 5. The axial ratio of the tetragonal phase has minimum values for alloys containing 50 at.% platinum and, because the axial ratio is smaller in NiPt than in FePt, the contours take the form of c-shaped curves, concave to the Ni–Pt side of the diagram. Although the data are limited it is evident, from specimens B and E containing two tetragonal phases, that the $c/a = 0.977$ and 0.967 contours must lie above and below 60% Pt, 5% Ni respectively and the $c/a = 0.963$ and 0.952 contours must lie above and below 58% Pt, 3% Fe respectively. These requirements determine the approximate locations of the contours and indicate tie lines approximately at right angles to the Fe–Ni side of the diagram.

It seems unlikely however, that an ordered phase field could contain a miscibility gap and the structures containing two tetragonal phases are more likely to be non-equilibrium structures. One possibility is that a platinum depleted, ordered tetragonal phase is produced on cooling through the cubic plus tetragonal two-phase field and the remaining platinum enriched cubic phase orders and becomes tetragonal at lower temperatures without change of composition. Even if quenching prevents transformation during cooling to 607° C, competing modes of ordering at this temperature could produce a similar effect. Ordered regions produced by nucleation and growth would be expected to have a smaller concentration of platinum and be more tetragonal than ordered material formed from a "continuous" reaction. The diffraction patterns in Fig. 4 are consistent with the disappearance on heating of the less tetragonal phase (phase of higher platinum concentration) and its reappearance on ordering at 607° C.

The extremely high magnetic hardness of ordered cobalt–platinum alloys is usually attributed to the presence of very small, suitably oriented particles of the ordered tetragonal phase [13]. The ability to produce similar structures in ternary iron–nickel–platinum alloys over a wide range of electron concentration provides an opportunity to test this theory and could lead to the discovery in this system of alloys with similar properties.

References

1. M. HANSEN, "Constitution of binary alloys", (McGraw-Hill, New York, 1958).
2. J. PAULEVE *J. Phys. Rad.* **23** (1962) 841.
3. G. T. STEVENS, PhD Thesis, University of New South Wales (1970).
4. A. KUSSMANN and K. JESSEN, *Arch. Eisenhuettenwes.* **29** (1958) 585.
5. W. GUERTLER, "Herausgegeben von Konstitution der ternaren metallishen systeme" W. Guertler, Berlin, 1957).
6. S. SHIMIZU and E. HASHIMOTO, *J. Japan Inst. Metals.* **35** (1971) 902.
7. J. B. HESS, *Acta Cryst.* 4 (1951) 209.
8. C. J. SMITHELLS, "Metals reference book" 2nd edition, Vol. 1 (Butterworth, London, 1955).
9. M. SANDERSEN, *Russ. J. Phys. Chem.* **37** (1963) 1330.
10. J. CRANGLE and J. A. SHAW, *Phil. Mag.* 7 (1962) 207.
11. U. ESCH and A. SCHNEIDER. *Z. Elektrochem* **50** (1944) 268.
12. J. C. WOOLLEY and B. BATES, *J. Less-common Met.* **2** (1960) 11.
13. H. N. SOUTHWORTH, *Platinum Metals Review* **14** (1970) 28.

Received 31 March and accepted 22 June 1977.