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SYNTHESIS AND STRUCTURAL DETERMINATION OF INTERMETALLIC COMPOUNDS IN THE Fe-Ho SYSTEM

BY

GERALD JOHN ROE - 1942 -

A

THESIS

submitted to the faculty of the
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Approved by

Thomas O'Keefe (Adviser) W. J. James
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ABSTRACT

The intermediate phases in the holmium-iron system were investigated by means of X-ray diffraction and metallographic examination. The intermediate phases identified by X-ray diffraction data were $HoFe_2$, $HoFe_3$, $HoFe_5$, and Ho_2Fe_{17}.

A new intermediate phase, $HoFe_3$, was found. $HoFe_3$ was indexed as hexagonal with lattice parameters of $a = 5.084$ Å and $c = 24.45$ Å, and was thought to be of the space group $R\bar{3}m$.

$HoFe_2$ was formed by a peritectic reaction and its solidus was estimated to be between 1325°C and 1340°C. Ho_2Fe_{17} was suggested to be a congruent melting intermetallic compound with a melting point below 1340°C.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

A great deal of interest has recently been shown in the rare earth metals and their alloys. This interest has been accelerated by increased availability of high purity rare earth metals. Since the rare earth elements are very similar in physical, chemical and metallurgical properties, they are excellent examples to use in studies for improving existing alloying and magnetic structure theories.

In order to obtain more accurate information on the alloying and magnetic properties of these metals, many of their binary systems must be determined or more accurately described.

The purpose of this study was to investigate the intermediate phases in the holmium-iron system by means of X-ray diffraction, metallographic examination, and a comparison of X-ray diffraction data and metallographic results. The crystal structure and lattice parameters of the intermediate phases found were determined, and an estimation of the solidus of these phases was made by use of these techniques.

Due to the similar alloying characteristics of the rare earths, it was assumed that the general appearance of the unknown holmium-iron system was similar to other rare earth-iron binary systems.

II. REVIEW OF LITERATURE

An indication of the general appearance of the unknown Ho-Fe phase diagram can be obtained by studying known rare earth-iron binary phase diagrams. The Y-Fe(1) and Dy-Fe(2) phase diagrams, shown in Figures 1 and 2, were used as a guide to approximate the Ho-Fe system. One of the general characteristics found in all of the rare earth-iron binary systems was the presence of peritectic or incongruently melting intermediate compounds. The peritectic intermediate compound is very difficult to form in an equilibrium, as-cast condition.

The factors controlling the occurrence of intermediate compounds in rare earth-transition metal binary systems has been studied by various investigators. The most common intermediate phase found in these systems is the Laves phase (C 14), which has the cubic $MgCu_2$ - type structure. The notation used here is AB_2 where A refers to the lanthanon and B to the transition metal. There are approximately 250 known Laves phases and the rare earth Laves phases comprise about 60 percent of this total(3).

Both the size of the alloying atoms and the electron concentration determine the existence or non-existence of a Laves phase. Dwight(4) has shown that ratios of the Goldschmidt radii (R_A/R_B) ranged from 1.05 to 1.68 in a study of 164 Laves phases. Using the Goldschmidt radii given by Dwight(5), R_{Ho}/R_{Fe} has a value of 1.37. An arbitrary

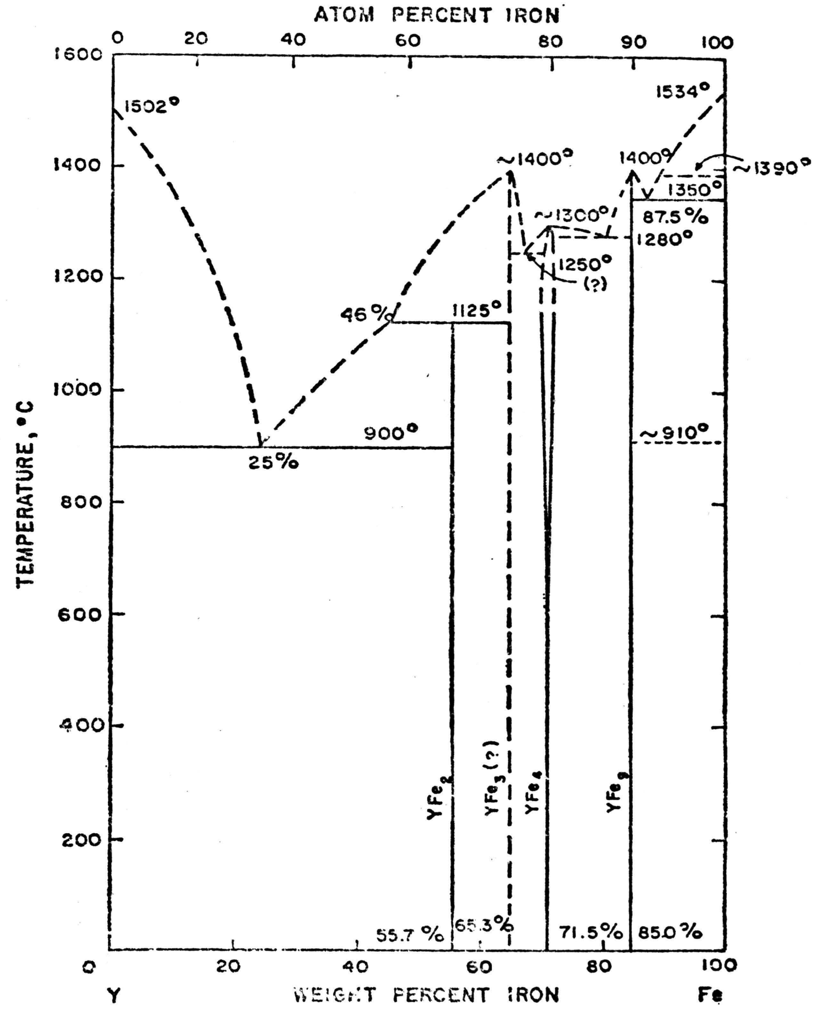


Figure 1. Yittrium-Iron Phase Diagram.

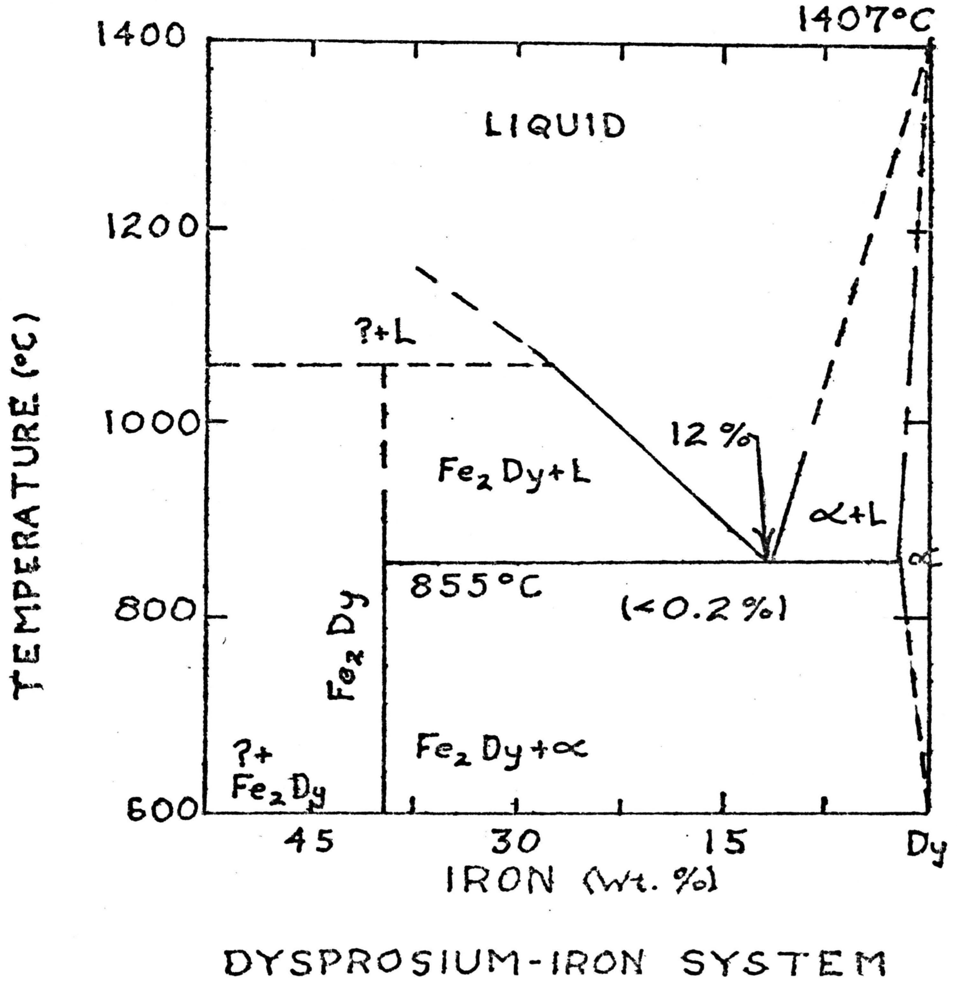


Figure 2. Dysprosium-Iron Phase Diagram.

assignment of valency is sometimes required to make the electron/atom ratio fall into ranges of 1.38 to 1.8 and 2.32 to 2.8(6,7).

Cromer and Larson(8) have shown that the AB_5-$CaZn_5$ type structure, AB_3-$CeNi_3$ and $PuNi_3$ types, and the AB_2 Laves phases (C14, C15, and C36) are all related. If additional A atoms are substituted into the B positions of the AB_5 structure and certain layers are shifted, a series of stoichiometries from AB_5 through AB_4, A_5B_{19}, A_2B_7 and AB_3 to AB_2 can be obtained. For example, the AB_3-$PuNi_3$ type structure can be shown as a combination of the AB_2-$MgCu_2$ type and AB_5-$CaZn_5$ type structures.

The first reported work on the Ho-Fe system was by Nassau(9). Levitation melting was used for sample preparation, and the existence of two intermediate phases was reported. A single phase $HoFe_2$ alloy was prepared with a cubic Laves phase (C15) lattice parameter of a = 7.28 Å. From a multiphase alloy of $HoFe_5$ stoichiometry, hexagonal lattice parameters of a = 4.86 Å and c = 4.10 Å were reported for the $HoFe_5$ intermediate compound. $HoFe_5$ had a $CaZn_5$ type structure. Other phases reported present in the multiphase alloy were $HoFe_2$ and possibly iron. Melts prepared by Nassau that were of a higher weight percent holmium than $HoFe_2$ showed only Ho and $HoFe_2$ phases present in the diffraction patterns.

In a study of rare earth compounds with the $MgCu_2$ structure, Wernick and Geller(10) reported the lattice parameter of $HoFe_2$ as $a = 7.300 \pm 5$ Å. Their samples were prepared by induction melting in an argon atmosphere.

Kripjakevich and Frankenich(11) have reported the possible existence of a cubic intermediate phase Ho_6Fe_{23} with $a = 12.04$ Å.

In a study of intermediate phases which occur in the transition metal-rich portions of the rare earth-transition metal binary systems, A. E. Ray(12) found the Ho_2Fe_{17} phase in the holmium-iron system. Ho_2Fe_{17} had the hexagonal Th_2Ni_{17} structural arrangement with lattice constants $a = 8.460$ Å, $c = 8.278$ Å for an alloy annealed and quenched from 1100°C. The X-ray patterns also indicated the possibility of a high temperature modification of rhombohedral Th_2Zn_{17}. Alloys were prepared by arc melting. Metallographic procedures consisted of a rough grinding on silicon carbide papers, lapping with graded Al_2O_3 abrasives, and etching with 1% Nital solution. It was indicated that the above metallography procedure did not work very well for the Ho-Fe alloys.

A summary of the metallographic techniques used on rare earth metals and their alloys was given by Spedding and Daane(13). Of the different etches mentioned, the 1 to 5% Nital etch given in this summary was used in many rare earth-transition metal phase diagram investigations. Peterson and Hopkins(14) have developed a successful electropolishing technique which consists of an electrolyte of 1% perchloric acid in methanol, maintained at -76°C by a bath of dry ice and acetone.

The data obtained by Lemaire(15) on $HoCo_3$ was referred to in an attempt to index the X-ray pattern obtained from an alloy of $HoFe_3$ stoichiometry in this investigation. In his investigation of the Ho-Co system, Lemaire found the intermediate phase $HoCo_3$. $HoCo_3$ had the $PuNi_3$ rhombohedral structural arrangement with a space group of $R\overline{3}m$. This rhombohedral structure when indexed as hexagonal had lattice constants of $a = 4.992$ Å and $c = 24.30$ Å.

III. EXPERIMENTAL PROCEDURE

A. Materials Used.

1. Holmium. The metal was obtained from the Michigan Chemical Corporation, Saint Louis, Michigan in bar form and had a purity of 99+%. All alloy samples were prepared in a dry bag under an argon atmosphere to prevent oxidation of the holmium.

2. Iron. The iron was supplied by the United States Steel Corporation, Research Laboratory, Monroeville, Pennsylvania, and had a purity of 99.9+%. The composition in weight percent is as follows:

C - 0.005
Mn - >0.01
P - 0.005
S - 0.010
N - 0.001
Pb - Res.
Fe - Balance

B. Preparation of Alloys.

All alloys in Table I were induction-melted using dry, high purity argon as the atmosphere. The proper amounts of holmium and iron to give the desired alloy stoichiometry were weighed on an analytical balance to ± 0.0007 grams and placed in Morganite recrystallized alumina crucibles. The pieces of iron and holmium were approximately 10 mm by 10 mm, a size appropriate to the size of the crucible. It was found that by placing the holmium on top of the iron a more homogeneous melt resulted. Incomplete mixing occurred when iron was placed on top of the holmium. The

TABLE I

Alloys Prepared By Induction Melting

Stoichiometry of Alloy	Weight % Ho	Atomic % Ho	Weight of Sample (gms.)
Ho_5Fe_3	83.09	62.50	4.2482
$HoFe_2$	59.62	33.33	7.5525
$HoFe_2$	59.62	33.33	11.6167
$HoFe_2$	59.62	33.33	11.1172
$HoFe_2$	59.62	33.33	16.2956
$HoFe_2$	59.62	33.33	15.4768
$HoFe_2$	59.62	33.33	16.9223
$HoFe_2$	59.62	33.33	9.3606
$HoFe_2$	59.62	33.33	13.0270
$HoFe_3$	49.61	25.00	5.4432
$HoFe_3$	49.61	25.00	15.8133
$HoFe_3$	49.61	25.00	9.1654
$HoFe_3$	49.61	25.00	10.9986
$HoFe_3$	49.61	25.00	10.5437
Ho_2Fe_7	45.76	22.22	5.1610
$HoFe_5$	37.13	16.67	14.1678
$HoFe_5$	37.13	16.67	11.4956
$HoFe_5$	37.13	16.67	13.1484
$HoFe_6$	32.98	14.29	5.8917
Ho_2Fe_{17}	25.78	10.53	25.9693
Ho_2Fe_{17}	25.78	10.53	16.2980

18 mm diameter crucibles were inserted into the melting chamber and the system was flushed with argon for at least one hour before heating was started. Subsequent heating, melting, and cooling of the samples was carried out under a positive pressure of argon.

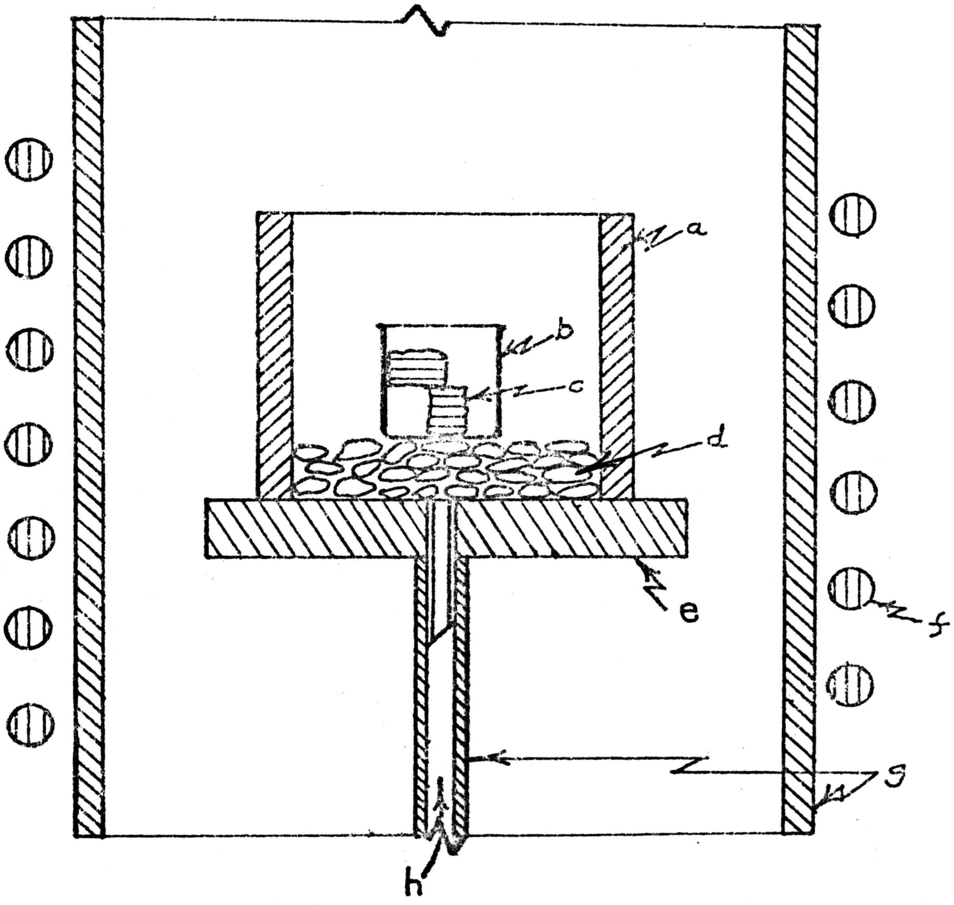
The general appearance of the induction melting apparatus is shown in Figure 3. The melting chamber consisted of a Vycor tube 5 cm in diameter by 70 cm in length with $\frac{55}{50}$ ground glass fittings. Figure 4 shows the details of the sample holder and heat shield.

The samples were melted and held at approximately 1600°C for three to five minutes. The furnace was then turned off and the sample allowed to cool slowly (approximately one hour) to room temperature. All high temperature measurements were made with an optical pyrometer.

In addition to induction melting, two samples of $HoFe_2$ stoichiometry were prepared in an arc furnace at the U. S. Bureau of Mines, Rolla, Missouri. The arc-melted samples were made to determine what effect a rapid solidification rate had on the formation of equilibrium structures. The arc melted samples were also compared with the induction-melted samples to check on the impurity pickup from alumina crucibles used in induction heating.

Since most of the as-cast alloys were in a non-equilibrium condition, subsequent heat treatments were tried. Various furnaces were utilized with heat-treating temperatures ranging from 900°C to 1400°C. Atmospheres

Figure 3. Induction Melting Apparatus



a) morganite heat shield

b) recrystallized alumina crucible

c) Ho-Fe charge

d) MgO pieces

e) lavite pedestal

f) induction coil

g) Vycor tubing

h) Argon

Figure 4. Melting Chamber

used in these furnaces ranged from a partial vacuum to a positive pressure of argon. The most successful results were obtained with a positive pressure of argon and temperatures between 1200°C and 1340°C. Holding time at these temperatures ranged from 24 to 72 hours.

C. X-ray Diffraction Procedure.

Particles from various sections of each alloy ingot were collected, and crushed for use as X-ray diffraction samples. This was done in order to get a sample of representative composition for each alloy. The powder was then screened through a 325 mesh screen.

The minus 325 mesh powder was mounted on a lithium-boron glass fiber which had been coated with a thin uniform layer of oil. The best portion of the mounted sample was aligned and centered in the camera.

The film was loaded into the powder camera in an asymmetric position. By use of the asymmetric diffraction technique the front and back reflection angles, as well as the circumference of the film cylinder, can be determined. Filtered iron radiation was used with an exposure time of two hours. A comparator, with an accuracy of $\pm$ 0.05 degrees, was used to measure the diffracted lines.

With the θ values determined, the X-ray patterns were indexed according to their crystal structure by analytical indexing methods(16). For indexing a hexagonal structure, the general equation $\sin^2\theta = A(h^2 + hk + k^2) + Cl^2$, where

$A = \lambda^2/3a^2$ and $C = \lambda^2/4c^2$, was applied. By combining the equation $\lambda = 2d\sin\theta$ and $d = a_o/\sqrt{h^2 + k^2 + l^2}$, the general equation $a_o = \lambda\sqrt{h^2 + k^2 + l^2}/2\sin\theta$ was obtained and used in indexing cubic structures.

D. Metallography

Since the intermetallic phases in the Ho-Fe system are very brittle and moderately attacked under atmospheric conditions, difficulties were encountered in polishing these alloys. Smearing of the metal surface on the polishing wheel frequently occurred and distilled water in the abrasive solution attacked the majority of the alloys prepared.

All samples were mounted in a cold mounting material. In order to obtain a flat surface, the sample was rough sanded on a belt sander followed by kerosene lapping on 0, 2/0, 3/0, and 4/0 emery polishing paper. The final surface was prepared on a kitten ear polishing cloth, using 0.3 and 0.1 micron alumina polishing powder in methyl alcohol. Methyl alcohol did not attack the metal surface to the degree exhibited when distilled water was used.

Ferric chloride and 3% Nital were used as etching reagents on the metallographic samples. Ferric chloride was used to give a greater contrast between two different phases, but had a tendency to mask finer structural details. On the other hand, Nital revealed fine details, but sometimes showed very little contrast between different phases in the same sample.

IV. EXPERIMENTAL RESULTS

A. X-ray Diffraction Data.

The results of the X-ray data were tabulated in Tables II through IX. Three X-ray films were obtained which showed only one phase to be present, and these were of the stoichiometry $HoFe_2$, $HoFe_3$ and Ho_2Fe_{17}. For the $HoFe_2$ and $HoFe_3$ single phase samples, the observed as well as the calculated $\sin^2\Theta$ values of all lines measured are given. For a given intermediate phase, the calculated $\sin^2\Theta$ values were obtained by using the known or calculated lattice parameters and a corresponding space group in a computer program. This computer program generated the theoretical $\sin^2\Theta$ values and intensities for planes which should ideally be observed for the given lattice parameters and space group. The observed Ho_2Fe_{17} $\sin^2\Theta$ values were compared with the X-ray data obtained from Dr. Alden E. Ray(12).

Individual $\sin^2\Theta$ values in multiphase X-ray films have the diffracting plane and corresponding phase given. Very strong, strong, medium and weak, abbreviated VS, S, M, and W respectively, were used to approximate relative intensities of all observed lines on the X-ray patterns.

In addition to the data given in the tables, other X-ray data were obtained on various heat-treated samples. A sample of stoichiometric $HoFe_2$ heat-treated at 1290°C for 31 hours showed the $HoFe_3$, (107) plane, present but of weaker intensity than in the as-cast alloy. Another

TABLE II

Front Reflection $\sin^2\theta$ Values of As-Cast 83.09 Weight % (62.5 At. %) Ho Alloy

Observed $\sin^2\theta$	h k l	Phase	Observed Intensity
.0532	1 1 1	$HoFe_2$	W
.0978	1 0 0	Ho	M
.1181	0 0 2	Ho	W
.1285	1 0 1	Ho	VS
.1415	2 2 0	$HoFe_2$	M
.1946	3 1 1	$HoFe_2$	S
.2160	1 0 2	Ho	W
.3014	1 1 0	Ho	W
.3650	1 0 3	Ho	W
.4134	1 1 2	Ho	M
.4233	2 0 1	Ho	S
.4233	4 2 2	$HoFe_2$	S
.4751	5 1 1	$HoFe_2$	W
.4751	3 3 3	$HoFe_2$	W
.5641	4 4 0	$HoFe_2$	W

TABLE III

$\text{Sin}^2\theta$ Values of As-Cast $HoFe_2$ Alloy

Observed $\text{Sin}^2\theta$	h k l	Phase	Observed Intensity
.0531	1 1 1	$HoFe_2$	M
.1258	1 0 7	$HoFe_3$	S
.1414	2 2 0	$HoFe_2$	M
.1945	3 1 1	$HoFe_2$	VS
.2121	2 2 2	$HoFe_2$	M
.3345	3 3 1	$HoFe_2$	W
.3540	2 1 3	$HoFe_3$	W
.4225	4 2 2	$HoFe_2$	M
.4751	5 1 1	$HoFe_2$	M
.4751	3 3 3	$HoFe_2$	M
.5632	4 4 0	$HoFe_2$	M
.6159	3 5 1	$HoFe_2$	W
.6159	5 3 1	$HoFe_2$	W
.7045	2 6 0	$HoFe_2$	M
.7045	6 2 0	$HoFe_2$	M
.7573	5 3 3	$HoFe_2$	M
.7746	6 2 2	$HoFe_2$	W
.8213	2 0 20	$HoFe_3$	W
.8979	5 5 1	$HoFe_2$	W
.8979	7 1 1	$HoFe_2$	W
.9859	4 6 2	$HoFe_2$	S
.9859	6 4 2	$HoFe_2$	S

TABLE IV

$\mathrm{Sin}^2\theta$ Values of $HoFe_2$, Single Phase X-ray, Heat Treated at 1325°C for 24 Hours

Observed $\sin^2\theta$	Calculated $\sin^2\theta$	hkl	Observed Intensity	Calculated Intensity
.0531	.0528	111	M	M
.1416	.1409	220	S	S
.1946	.1937	311	VS	VS
.2122	.2113	222	M	M
.3345	.3345	331	W	W
.4225	.4226	422	M	M
.4751	.4754	511	M	M
.4751	.4754	333	M	W
.5630	.5634	440	M	M
.6159	.6162	351	W	W
.6159	.6162	531	W	W
.7045	.7043	260	M	M
.7045	.7043	620	M	M
.7563	.7571	533	M	M
.7738	.7747	622	W	W
.8979	.8979	551	W	W
.8979	.8979	711	W	W
.9859	.9860	462	VS	VS
.9859	.9860	642	VS	VS

TABLE V

$Sin^2\Theta$ Values of As-Cast $HoFe_3$, Single Phase X-Ray

Observed $Sin^2\Theta$	Calculated $Sin^2\Theta$	h k l	Observed Intensity	Calculated Intensity
.1259	.1253	1 0 7	S	S
.1450	.1452	1 1 0	S	S
.1495		1 1 1	M	
.1953		2 0 1	M	
.2005	.1999	2 0 2	M	W
.3541		2 1 3	M	
.4151	.4157	2 1 7	M	M
.4356	.4356	3 0 0	W	W
.4493	.4497	3 0 3	W	W
.4920	.4921	3 0 6	M	M
.4956	.4958	2 110	M	W
.5808	.5808	2 2 0	M	M
.6471	.6472	2 017	W	W
.7995	.7995	4 0 4	W	W
.8068	.8068	2 212	W	W
.8213	.8214	2 020	M	W

TABLE VI

Sin$^2\Theta$ Values of As-Cast 45.76 Weight % (22.2 At. %) Ho Alloy

Observed Sin$^2\Theta$	h k l	Phase	Observed Intensity
.0526	1 0 0	$HoFe_5$	W
.1254	1 0 7	$HoFe_3$	S
.1448	1 1 0	$HoFe_3$	S
.1488	1 1 1	$HoFe_3$	M
.1570	1 1 0	$HoFe_5$	W
.1758			M
.1952	2 0 1	$HoFe_3$	M
.2006	2 0 2	$HoFe_3$	M
.2335	0 0 2	$HoFe_5$	W
.3546	2 1 3	$HoFe_3$	M
.4149	2 1 7	$HoFe_3$	M
.4359	3 0 0	$HoFe_3$	W
.4688	3 0 0	$HoFe_5$	W
.4918	3 0 6	$HoFe_3$	M
.4958	2 110	$HoFe_3$	M
.5276	3 0 1	$HoFe_5$	W
.5802	2 2 0	$HoFe_3$	M
.6469	2 017	$HoFe_3$	W
.8065	2 212	$HoFe_3$	M

TABLE VII

Front Reflection $\mathrm{Sin}^2\Theta$ Values of As-Cast $HoFe_5$ Alloy

Observed $\mathrm{Sin}^2\Theta$	hkl	Phase	Observed Intensity
.0526	100	$HoFe_5$	W
.0787			M
.1081	112	Ho_2Fe_{17}	M
.1081	101	$HoFe_5$	M
.1250	107	$HoFe_3$	M
.1571	110	$HoFe_5$	S
.1762			S
.1936	023	Ho_2Fe_{17}	W
.2118	200	$HoFe_5$	VS
.2118	032	Ho_2Fe_{17}	VS
.2135	111	$HoFe_5$	VS
.2335	002	$HoFe_5$	W
.2662	201	$HoFe_5$	W
.3313			M
.3827	112	$HoFe_5$	M
.4356	202	$HoFe_5$	M
.4691	300	$HoFe_5$	M
.4910	306	$HoFe_3$	M
.5274	301	$HoFe_5$	W

TABLE VIII

Front Reflection $\sin^2\theta$ Values of As-Cast 32.98 Wt. % (14.3 At. %) Ho Alloy

Observed $\sin^2\theta$	hkl	Phase	Observed Intensity
.0524	100	$HoFe_5$	W
.0787			M
.1071	112	Ho_2Fe_{17}	M
.1249	107	$HoFe_3$	M
.1571	110	$HoFe_5$	M
.1571	030	H_2Fe_{17}	M
.1760			S
.1936	023	Ho_2Fe_{17}	W
.2117	200	$HoFe_5$	VS
.2117	032	Ho_2Fe_{17}	VS
.2194	004	Ho_2Fe_{17}	W
.2335	002	$HoFe_5$	M
.2457	123	Ho_2Fe_{17}	W
.2662	201	$HoFe_5$	W
.2775	102	$HoFe_5$	W
.3308			M
.3829	112	$HoFe_5$	M
.4354	202	$HoFe_5$	M
.4688	300	$HoFe_5$	M
.4918	306	$HoFe_3$	W
.5279	301	$HoFe_5$	W

TABLE IX

$\mathrm{Sin}^2\Theta$ Values of As-Cast Ho_2Fe_{17}, Single Phase X-ray

Observed $\mathrm{Sin}^2\Theta$	A.E. Ray(12) $\mathrm{Sin}^2\Theta$	hkl	Observed Intensity	A.E. Ray(12) Intensity
.0845	.0841	021	W	W
.1080	.1075	112	S	S
.1365	.1365	121	W	W
.1578	.1576	030	S	S
.1935	.1932	023	M	M
.2128	.2121	032	VS	VS
.2193	.2193	004	W	M
.2470	.2467	123	W	M
.2704	.2715	114	W	W
.3507	.3507	133	W	W
.4208	.4210	142	S	S
.4278	.4282	224	S	S
.4567	.4566	233	W	W
.4754	.4729	330	W	W
.5257	.5253	332	M	S
.6117	.6111	243	W	W
.6270	.6275	060	M	S
.6481	.6483	036	M	S
.7424	.7429	153	M	W

sample of the same stoichiometry heat-treated at 1340°C for 8 hours showed the $HoFe_3$, (107) plane, with a greater relative intensity than was present in the as-cast $HoFe_2$ alloy.

An indication of the $HoFe_5$, (110) plane, was visible on the X-ray pattern of $HoFe_3$ heat-treated at 1270°C for 21 hours. A Ho_2Fe_{17} sample heat-treated at 1340°C for 8 hours showed an X-ray pattern that had the iron, (110) plane, present.

B. Microstructure Studies.

Microstructure studies were made to supplement the X-ray diffraction data. With the exception of 83.09 weight % Ho alloy, metallographic results were obtained on all as-cast and heat treated alloys. The 83.09 weight % Ho alloy, Ho and $HoFe_2$ combined, oxidized too rapidly during polishing to allow visual examination.

In the early stages of this investigation a rough polish was performed on heat-treated samples to see if any structure change had taken place. It was possible by means of this technique to estimate heat-treating temperatures and holding times needed to obtain a homogeneous structure. In all multiphase alloys temperatures above 1100°C with a holding time greater than 24 hours were needed to obtain a homogeneous structure.

Shrinkage porosity was found in all the alloys prepared. Ho_2Fe_{17} alloys had the smallest amount of shrinkage porosity and the largest centralized shrinkage cavity. Because Ho_2Fe_{17} had a small amount of shrinkage porosity present and did not tend to oxidize as rapidly as the other alloys, metallography was less difficult on this alloy.

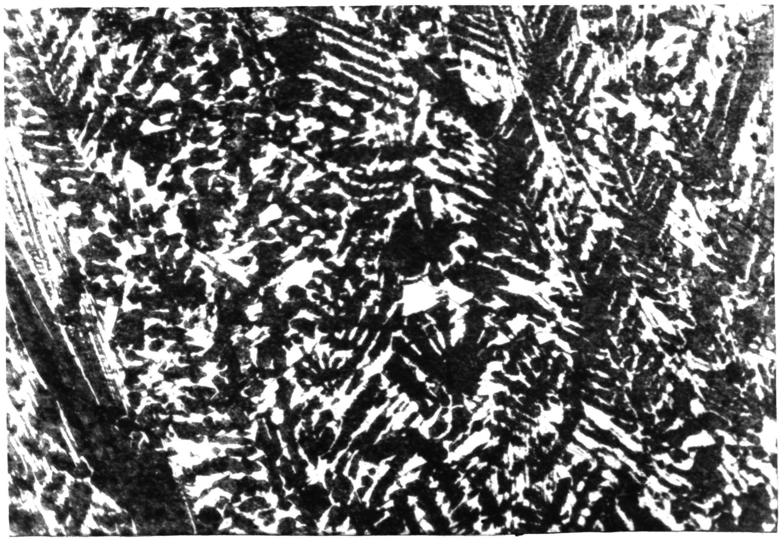


Figure 5. As-Cast, Arc Melted, 59.6 Wt.% (33.3 At.%) Ho Alloy. 5% Ferric Chloride Etch. 133X. Phases Identified: $HoFe_2$, $HoFe_3$.

Figure 6. Annealed 1100°C, 33 hrs., 59.6 Wt.% (33.3 At.%) Ho Alloy. 5% Ferric Chloride Etch. 133X. Phases Identified: $HoFe_2$, $HoFe_3$.

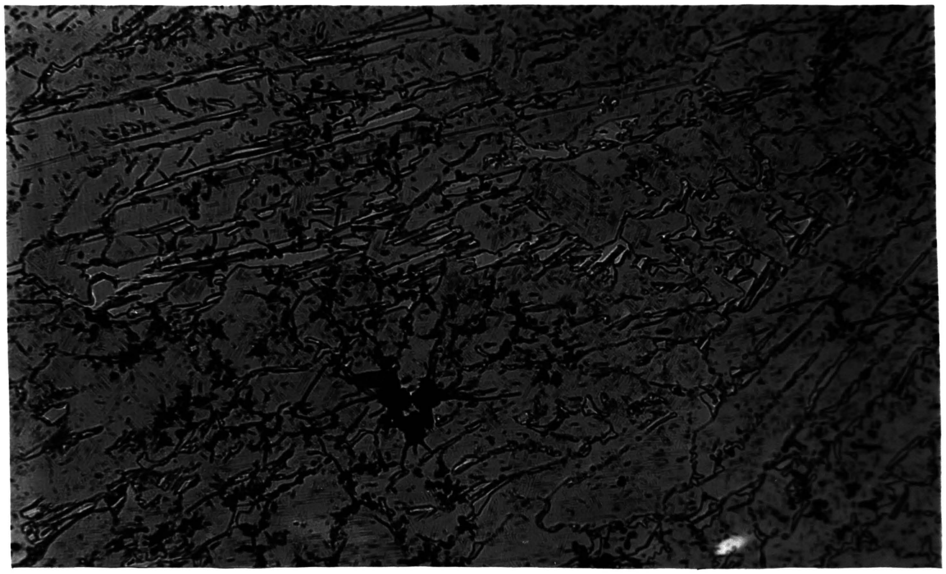


Figure 7. As-Cast, Induction Melted, 59.6 Wt.% (33.3 At.%) Ho Alloy. 3% Nital Etch. 200X. Phases Identified: $HoFe_2$, $HoFe_3$.

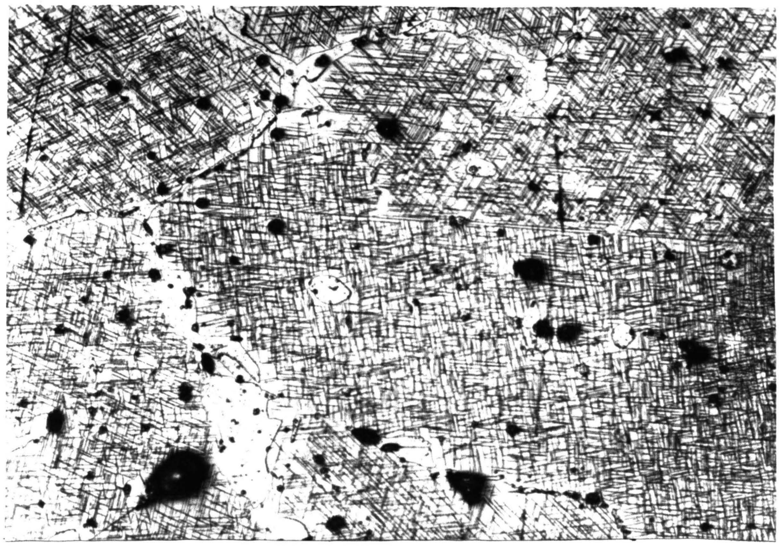


Figure 8. Annealed 1325°C, 24 hrs., 59.6 Wt.% (33.3 At.%) Ho Alloy. 3% Nital Etch. 133X. Phases Identified: $HoFe_2$

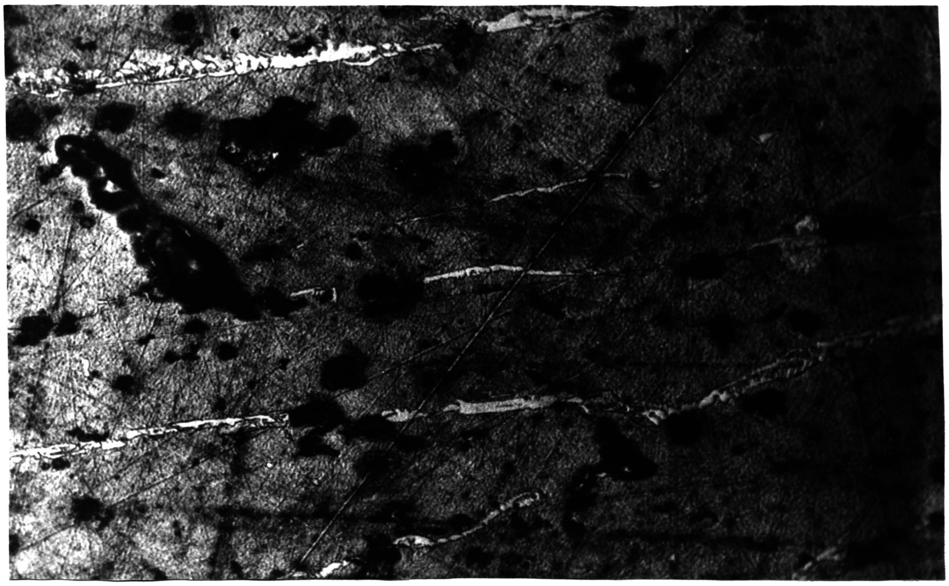


Figure 9. As-Cast, Induction Melted, 49.6 Wt.% (25.0 At.%) Ho Alloy. 5% Ferric Chloride Etch. 200X. Phases Identified: $HoFe_3$

Figure 10. As-Cast, Induction Melted, 45.8 Wt.% (22.2 At.%) Ho Alloy. 5% Ferric Chloride Etch. 200X. Phases Identified: $HoFe_3$, $HoFe_5$.

Figure 11. As-Cast, Induction Melted, 37.1 Wt.% (16.7 At.%) Ho Alloy. 3% Nital Etch. 200X. Phases Identified: $HoFe_3$, $HoFe_5$, Ho_2Fe_{17}.

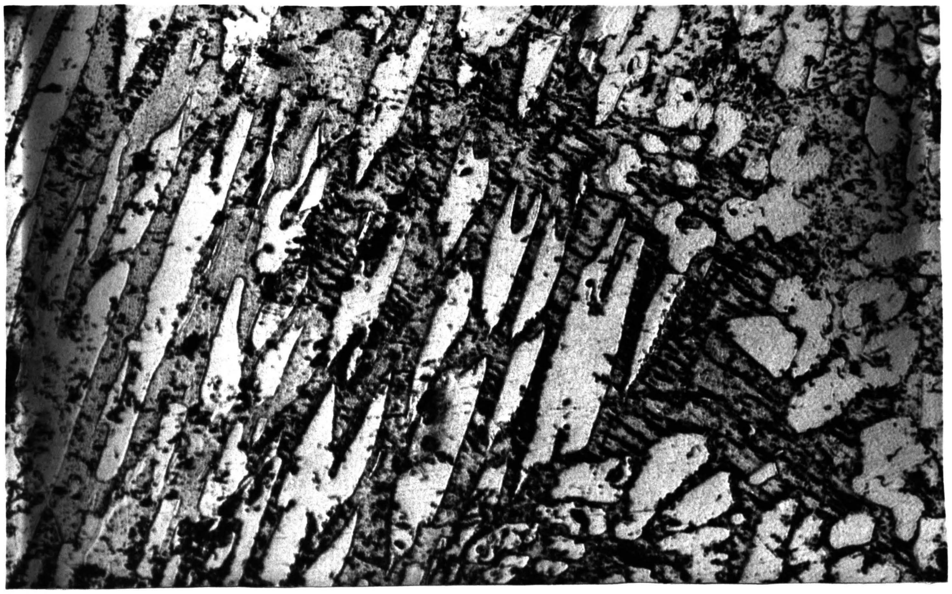


Figure 12. As-Cast, Induction Melted, 33.0 Wt.% (14.3 At.%) Ho Alloy. 3% Nital Etch. 200X. Phases Identified: $HoFe_3$, $HoFe_5$, Ho_2Fe_{17}.

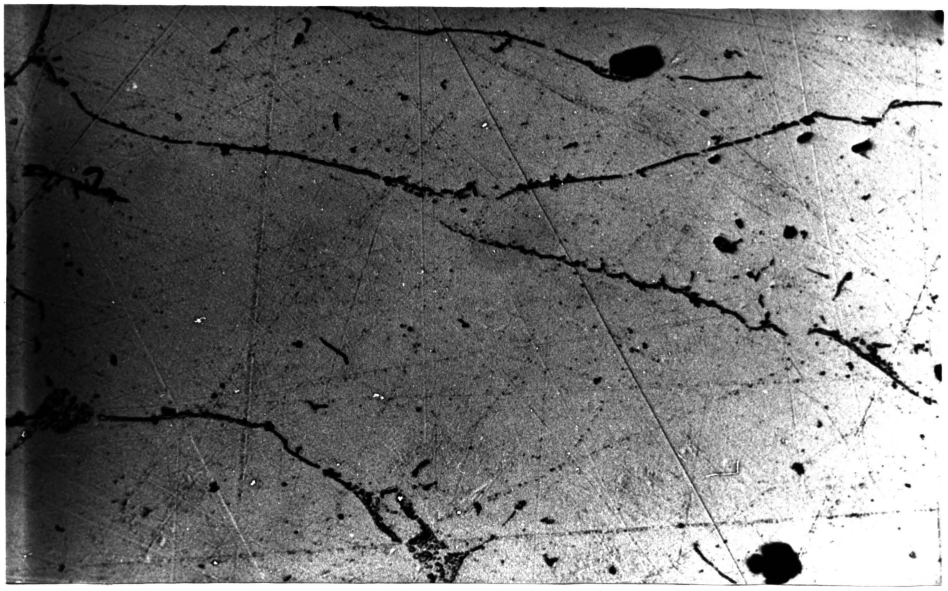


Figure 13. As-Cast, Induction Melted, 25.8 Wt.% (10.5 At.%) Ho Alloy. 3% Nital Etch. 200X. Phases Identified: Ho_2Fe_{17}.

V. DISCUSSION

All as-cast $HoFe_2$ samples produced in an induction furnace showed at least two phases in the microstructure and had the general appearance of Figure 7. The presence of more than one phase in the $HoFe_2$ microstructure was considered to be evidence of an incomplete peritectic reaction. The X-ray studies of these melts showed the diffraction pattern of $HoFe_2$ plus lines which were not produced by Ho, $HoFe_2$, or $HoFe_5$.

Arc melting was performed to determine if a rapid solidification rate could produce an equilibrium, as-cast, $HoFe_2$ structure. During arc melting the top of the $HoFe_2$ button was molten while the bottom portion of the button, which was in contact with a water cooled copper hearth, remained solid. This arc melting technique produced a dendritic structure (see Figure 5) that was felt to be farther from equilibrium than the as-cast induction melts.

Heat treatments were performed after all attempts to produce an as-cast equilibrium $HoFe_2$ alloy failed. Heat treatments at temperatures of 1100°C or lower on $HoFe_2$ alloys showed little change in the microstructure when compared with as-cast samples. In Figures 5 and 6 the same area is shown before and after heat treatment. By review of the X-ray data of heat treated $HoFe_2$ alloys, the solidus of $HoFe_2$ appeared to be between 1325°C and 1340°C.

A single phase X-ray pattern with a corresponding microstructure showing only a small amount of other phases present in the grain boundaries was obtained from a sample held at 1325°C for 24 hours. It should be noted that the 1325°C heat-treated sample gave an X-ray pattern showing only one phase present while the corresponding microstructure was multiphase. The fine lines in the $HoFe_2$ grains, (Figure 8) are possibly twins produced during polishing of the sample or a Widmannstätten precipitate.

The lattice constants calculated from the single phase $HoFe_2$ X-ray pattern were in agreement with both Nassau(9) and Wernick and Geller(10). For the (311) plane in the front reflection the lattice constant calculated was a = 7.282 Å, while for the (533) plane in the back reflection, a = 7.303 Å. The value of Wernick and Geller, a = 7.300±5 Å, was more accurate since it was calculated from a plane in the back reflection region.

Melts were made on both sides of the $HoFe_2$ stoichiometry to determine the phase corresponding to the lines observed at $\sin^2\theta$ = .1258 and .3540 in the $HoFe_2$ as-cast X-ray pattern. No intermediate phases were found between $HoFe_2$ and Ho. The microstructure of the as-cast $HoFe_3$ alloy approached the appearance of a single phase alloy. The X-ray pattern of the $HoFe_3$ alloy was then indexed as hexagonal with lattice parameters of a = 5.084 Å and c = 24.45 Å. Because of the relatively good agreement between calculated and observed planes, $HoFe_3$ was thought to be of the same space group, $R\overline{3}m$, as $HoCo_3$. The X-ray studies of $HoFe_3$ showed the solidus to probably be below 1270°C.

A definite determination of the phases present between $HoFe_3$ and Ho_2Fe_{17} stoichiometry was not possible. From the X-ray patterns of alloys between these two stoichiometries $HoFe_5$ was indexed, but a single phase metallographic or X-ray sample was not obtained for the $HoFe_5$ stoichiometry. These specimens were highly brittle, and macro- and micro-cracking frequently occurred during grinding and polishing procedures. Heat treatments at temperatures of 1100°C or lower on these alloys produced little change in the as-cast microstructure. Holding temperatures above 1330°C caused melting of these alloys. Many of these samples were lost during heat treatment due to oxidation, resulting from the system not being completely tight.

The X-ray patterns of 45.76 weight % Ho, $HoFe_5$ (37.13 weight % Ho), and 32.98 weight % Ho alloys had lines present which could not be indexed with the known lattice parameters of $HoFe_3$, $HoFe_5$ and Ho_2Fe_{17}. It is possible that these lines not indexed ($\sin^2\theta$ = .0787, .1762, and .3313) could be due to a high temperature modification of the $HoFe_5$ structure or the Ho_6Fe_{23}(11) intermediate compound. If these $\sin^2\theta$ values are indexed as Ho_6Fe_{23}, they correspond respectively to the (222), (333), and (551) planes. The diffraction pattern of $HoFe_2$ was not found in the $HoFe_5$ as-cast X-ray pattern as reported by Nassau(9).

Metallography of the $HoFe_5$ and 32.98 weight % Ho alloys showed a cored structure, (Figures 11 and 12). This structure was thought to be caused by an incomplete peritectic reaction. The light, primary phase is Ho_2Fe_{17} and the surrounding matrix is composed of $HoFe_3$ and $HoFe_5$.

Ho_2Fe_{17} was thought to be a congruent melting intermetallic compound. The ease with which a single phase alloy was produced in an as-cast condition and the large centralized shrinkage voids found in Ho_2Fe_{17} ingots was evidence of a congruent melting compound.

VI. CONCLUSIONS

1. Induction melting and subsequent slow solidification rate produced as-cast alloys which were closer to equilibrium than arc melted alloys. The rapid solidification rate of the arc melted alloys produced a dendritic, as-cast structure.

2. Metallography on a heat-treated $HoFe_2$ stoichiometric alloy showed a multiphase microstructure, while the corresponding X-ray pattern showed only a single phase present. The lattice parameter calculated from this X-ray pattern was in agreement with the literature. This alloy stressed the importance of microstructure studies supplementing the X-ray diffraction data.

3. The solidus of $HoFe_2$ was estimated to be between 1325°C and 1340°C.

4. In all multiphase as-cast alloys, temperatures above 1100°C with a holding time of at least 24 hours were needed to obtain any microstructure change.

5. A new intermediate phase, $HoFe_3$, was found. $HoFe_3$ was indexed as hexagonal (possibly $R\bar{3}m$) with lattice parameters of $a = 5.084$ Å and $c = 24.45$ Å.

6. Ho_2Fe_{17} was suggested to be a congruent melting intermetallic compound with a melting point below 1340°C.

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APPENDIX

Computation of $HoFe_2$

Data Calculated for a Cubic Structure with

a = 7.30000 Å, WL = 1.93728 Å.

h k l	$Sin^2\theta$	θ(degrees)	Intensity
1 1 1	.05282	13.29	192.6
2 0 0	.07043	15.39	0.0
2 2 0	.14085	22.04	706.2
3 1 1	.19367	26.11	1000.0
2 2 2	.21128	27.36	132.0
4 0 0	.28171	32.06	10.5
3 3 1	.33453	35.34	48.0
4 2 0	.35213	36.40	0.0
2 4 0	.35213	36.40	0.0
4 2 2	.42256	40.55	267.8
5 1 1	.47538	43.59	253.3
3 3 3	.47538	43.59	84.4
4 4 0	.56342	48.64	277.1
3 5 1	.61624	51.72	28.5
5 3 1	.61624	51.72	28.5
4 4 2	.63384	52.76	0.0
6 0 0	.63384	52.76	0.0
2 6 0	.70427	57.06	100.4
6 2 0	.70427	57.06	100.4
5 3 3	.75709	60.47	224.0
6 2 2	.77470	61.66	87.0
4 4 4	.84512	66.82	12.8
5 5 1	.89794	71.37	52.5
7 1 1	.89794	71.37	52.5
4 6 0	.91555	73.11	0.0
6 4 0	.91555	73.11	0.0
4 6 2	.98598	83.20	901.6
6 4 2	.98598	83.20	901.6

Computation of $HoFe_3$

Data Calculated for a Hexagonal Structure with

A = 5.08400 Å, c = 24.4500 Å, WL = 1.93728 Å

h	k	l	$Sin^2\theta$	θ(degrees)	Intensity
1	0	1	.04997	12.92	185.0
0	0	6	.05650	13.75	30.3
1	0	4	.07351	15.73	52.9
1	0	7	.12531	20.73	454.0
1	1	0	.14520	22.40	265.9
2	0	2	.19988	26.56	64.5
1	1	6	.20170	26.69	442.1
1	0	10	.20535	26.95	22.5
0	0	12	.22601	28.39	49.1
2	0	5	.23284	28.85	86.0
2	0	8	.29405	32.84	34.4
1	0	13	.31365	34.06	10.5
2	1	1	.34037	35.69	19.7
2	1	4	.36392	37.10	2.8
1	1	12	.37121	37.54	5.3
2	0	11	.38352	38.26	0.1
2	1	7	.41571	40.15	173.0
3	0	0	.43561	41.30	50.1
3	0	3	.44973	42.12	2.1
1	0	16	.45020	42.14	8.4
3	0	6	.49211	44.55	115.3
2	1	10	.49576	44.76	22.7
2	0	14	.50123	45.07	116.9
0	0	18	.50852	45.49	4.7
3	0	9	.56274	48.60	8.2
2	2	0	.58081	49.65	124.3
2	1	13	.60405	51.01	6.5
1	0	19	.61500	51.65	0.0
3	1	2	.63549	52.86	2.5
2	2	6	.63731	52.97	9.3
2	0	17	.64719	53.56	55.9
1	1	18	.65373	53.95	3.6
3	0	12	.66162	54.43	31.1
3	1	5	.66845	54.84	1.1
3	1	8	.72966	58.67	93.3
2	1	16	.74060	59.38	24.2
4	0	1	.77598	61.75	79.8
3	0	15	.78875	62.64	60.7
4	0	4	.79952	63.40	21.7
2	2	12	.80682	63.93	88.3
1	0	22	.80805	64.02	47.0
3	1	11	.81912	64.83	67.0
2	0	20	.82141	65.00	9.8

Computation of $HoFe_3$ (Cont'd)

4 0 7	.85132	67.32	5.2
0 0 24	.90404	71.95	10.6
2 1 19	.90540	72.09	1.5
3 2 1	.92118	73.70	35.1
4 0 10	.93136	74.81	0.1
3 1 14	.93684	75.44	231.7
3 0 18	.94413	76.33	7.3
3 2 4	.94473	76.40	14.3
3 2 7	.99652	86.62	1000.0

Computation of Ho_6Fe_{23}

Data Calculated for a Cubic Structure with

a = 12.0400 Å, WL = 1.93728 Å

h	k	l	$Sin^2\Theta$	Θ(degrees)	Intensity
1	1	1	.01942	8.01	2.0
2	0	0	.02589	9.26	3.5
2	2	0	.05178	13.15	11.1
3	1	1	.07120	15.48	26.2
2	2	2	.07767	16.18	364.6
4	0	0	.10356	18.77	238.2
3	3	1	.12298	20.53	350.3
4	2	0	.12945	21.09	38.3
4	2	2	.15534	23.21	349.2
5	1	1	.17476	24.71	580.1
3	3	3	.17476	24.71	439.1
4	4	0	.20712	27.07	1000.0
5	3	1	.22654	28.42	82.2
4	4	2	.23301	28.86	4.9
6	0	0	.23301	28.86	205.5
6	2	0	.25890	30.59	18.1
5	3	3	.27832	31.84	57.7
6	2	2	.28479	32.25	1.3
4	4	4	.31068	33.88	16.3
5	5	1	.33010	35.07	142.6
7	1	1	.33010	35.07	35.4
6	4	0	.33657	35.46	75.4
6	4	2	.36246	37.02	4.6
5	5	3	.38188	38.17	35.7
7	3	1	.38188	38.17	117.3
8	0	0	.41424	40.06	59.3
7	3	3	.43366	41.19	266.5
8	2	0	.44013	41.56	0.0
6	4	4	.44013	41.56	16.1
6	6	0	.46602	43.05	90.1
8	2	2	.46602	43.05	255.0
7	5	1	.48544	44.17	20.8
5	5	5	.48544	44.17	138.4
6	6	2	.49191	44.54	0.0
8	4	0	.51780	46.02	17.4
7	5	3	.53722	47.13	60.8
9	1	1	.53722	47.13	0.1
8	4	2	.54369	47.51	125.7
6	6	4	.56958	49.00	4.4
9	3	1	.58900	50.13	18.3
8	4	4	.62136	52.02	146.9
9	3	3	.64078	53.18	149.5

Computation of Ho_6Fe_{23} (Cont'd)

7 7 1	.64078	53.18	96.2
7 5 5	.64078	53.18	3.1
100 0	.64725	53.56	67.6
8 6 0	.64725	53.56	23.3
102 0	.67314	55.13	21.3
8 6 2	.67314	55.13	29.7
9 5 1	.69256	56.33	154.8
7 7 3	.69256	56.33	116.2
102 2	.69903	56.73	5.9
6 6 6	.69903	56.73	59.4
9 5 3	.74434	59.63	61.2
8 6 4	.75081	60.05	0.0
104 0	.75081	60.05	96.8

Computation of $HoFe_5$

Data Calculated for a Hexagonal Structure with
a = 4.86000 Å, c = 4.10000 Å, WL = 1.93728 Å

h	k	l	$Sin^2\theta$	θ(degrees)	Intensity
1	0	0	.05297	13.31	52.5
0	0	1	.05582	13.67	101.3
1	0	1	.10878	19.26	646.4
1	1	0	.15890	23.49	345.1
2	0	0	.21186	27.41	351.0
1	1	1	.21471	27.60	1000.0
0	0	2	.22326	28.20	281.7
2	0	1	.26768	31.16	25.3
1	0	2	.27623	31.71	15.1
2	1	0	.37076	37.51	10.3
1	1	2	.38216	38.18	175.1
2	1	1	.42656	40.78	167.7
2	0	2	.43512	41.27	229.7
3	0	0	.47669	43.66	65.6
0	0	3	.50234	45.13	5.1
3	0	1	.53250	46.86	265.8
1	0	3	.55531	48.18	64.4
2	1	2	.59402	50.42	14.1
2	2	0	.63558	52.87	216.8
1	1	3	.66124	54.41	244.9
3	1	0	.68855	56.08	7.4
2	2	1	.69140	56.25	28.4
3	0	2	.69995	56.79	111.8
2	0	3	.71420	57.68	6.2
3	1	1	.74436	59.63	133.4
4	0	0	.84744	67.01	114.4
2	2	2	.85885	67.93	600.1
2	1	3	.87310	69.13	185.0
0	0	4	.89305	70.91	114.9
4	0	1	.90326	71.88	8.9
3	1	2	.91181	72.72	28.3
1	0	4	.94602	76.57	18.4
3	0	3	.97903	81.67	896.3

VITA

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