Title
THE TERBIUM-IRON PHASE DIAGRAM

Permalink
https://escholarship.org/uc/item/9490n27c

Author
Dariel, M.P.

Publication Date
1975-06-01
THE TERBIUM-IRON PHASE DIAGRAM

M. P. Dariel, J. T. Holthuis, and M. R. Pickus

June 1975

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE TERBIUM-IRON PHASE DIAGRAM

M. P. Dariel,* J. T. Holthuis and M. R. Pickus

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering; University of California, Berkeley, California 94720

Summary

The terbium-iron phase diagram has been determined using metallographic, X-ray diffraction, differential thermal analysis, and electron microprobe techniques. The terminal solubilities of the two elements are extremely restricted, of the order of 0.1 at.% for Tb in Fe. A eutectic reaction takes place at 28 at.% Fe, 847°C. The four intermetallic compounds, TbFe₂, TbFe₃, Tb₆Fe₂₃, and Tb₂Fe₁₇ melt non-congruently at 1187, 1212, 1276, and 1312°C respectively. The Tb₂Fe₁₇ compound appears in the rhombohedral Th₂Zn₁₇ modification on the Tb-rich side and the hexagonal Th₂Ni₁₇ modification on the Fe-rich side of the stoichiometric composition.

* At leave from the Department of Material Engineering, Ben-Gurion University of the Negev, Beer-Sheva and the Nuclear Research Center Negev.
Introduction

The equilibrium phase diagrams of most rare-earth metal-iron binary systems have been reported in the literature.\(^1\)-\(^7\) Notable exceptions are the bivalent rare-earth metals Eu and Yb and trivalent Tb. Some terbium-iron intermetallic compounds and, in particular, the Laves phase TbFe\(_2\), possess exceptionally interesting properties such as giant magnetostriction\(^8\),\(^9\) and huge $\Delta E$ effect.\(^10\) These compounds are therefore considered as being potentially useful materials for various applications. In order to facilitate the development of technologically useful materials based on these compounds, we undertook the determination of the Tb-Fe phase diagram by means of standard metallographic, DTA, X-ray diffraction, and electron microprobe analysis techniques.

The presence of four intermetallic compounds, namely TbFe\(_2\), TbFe\(_3\), Tb\(_6\)Fe\(_{23}\), and Tb\(_2\)Fe\(_{17}\) has been previously reported.\(^11\) There is lack of agreement, however, concerning the existence of the Tb\(_6\)Fe\(_{23}\) compound. Kripyakevich et al.\(^12\) and Ray\(^11\) report its presence; whereas, according to Oesterreicher,\(^13\) Tb\(_6\)Fe\(_{23}\) was not found either in cast or in heat-treated alloys. Only by substituting some Al for Fe could it be prepared.\(^13\) On the other hand, it proved practically impossible to prevent the formation of Tb\(_6\)Fe\(_{23}\) in alloys prepared by powder metallurgical techniques.\(^14\) Contradictory reports have also been given concerning the structure-type of the Tb\(_2\)Fe\(_{17}\) compound.\(^13\),\(^15\) In the course of the present study efforts were made to clarify these issues.

Experimental Techniques

Alloy Preparation and Metallography

The alloys were prepared by arc melting 99.99\% pure iron and 99.9\% pure
terbium (Research Chemicals, Phoenix, Arizona), on a water-cooled copper hearth under a zirconium gettered argon atmosphere. Each alloy button, weighing 5-10 grams was turned over and remelted several times in order to ensure a good homogeneity.

For heat treatments up to 1100°C, the samples were wrapped in thin tantalum foils and sealed in evacuated quartz capsules. For higher temperature anneals, the quartz capsules were back-filled with a partial pressure of argon.

The metallographic preparation of the samples consisted in standard cold mounting, grinding and polishing techniques. The final polishing stage consisted of vibratory polishing with a Linde γ alumina water suspension. A 1% nital solution was used for etching the polished samples. A 3% ferric chloride solution was useful for revealing the grain structure of iron-rich compounds. Essentially, a similar, though particularly careful procedure was followed in order to reveal magnetic domain patterns detectable by the Kerr effect.

Thermal Analysis

The differential thermal analysis (DTA) runs were carried out on 5-7 gram samples in tantalum crucibles for rare-earth-rich alloys. Boron nitride or recrystallized alumina crucibles were used for the iron-rich samples. The temperatures were measured with suitably sheathed Pt-Pt 10 Rh thermocouples. A protective argon atmosphere was used. The argon in a closed circuit was purified by passing it over Ti chips at 850°C and through a liquid nitrogen trap.

X-Ray Diffraction and Electron Microprobe Analysis

For X-ray analysis a Pickart diffractometer was employed using Cu Kα.
radiation in conjunction with an X-ray monochromator. The diffraction patterns were indexed with the help of an X-ray powder diffraction pattern generating computer program. Lattice parameters were determined using Cohen's least-squares fit method. In several instances a MAC (Materials Analysis Company) electron microprobe was used for phase identification and for checking the terminal solubility of terbium in iron. Unfortunately, the relative closeness of the relevant Tb lines, Tb Lα, and Tb Lβ to the Fe lines Kα and Kβ, respectively, detracted from the accuracy of the solubility determinations.

Results and Discussion

On the basis of the DTA thermal arrests and the information provided by the X-ray and micrographic analyses, the phase diagram shown in Fig. 1 was constructed. The invariant temperatures of the eutectic and of the four peritectic reactions were determined from the thermal arrests appearing on the heating curves. The possible error for the eutectic temperature is ±3°C; for the peritectics, ±5°C.

Terminal Solid Solubilities

The solubility of iron in terbium is below the detection limit of the experimental techniques employed in this study. The addition of iron to terbium does not affect the temperature of the α(HCP) to β(BCC) transformation in terbium (1318 ± 2°C). From radioactive tracer diffusion studies, it has been recently inferred that a significant fraction of dissolved iron in the light rare-earth metals, Ce, Pr, and Nd is located on interstitial sites. It would be interesting to check in what way does the lanthanide contraction in the heavier rare-earth metals like terbium, affect that tendency.
The results of the DTA runs indicated that the temperature of the 
\( \alpha + \gamma \) phase transformation in iron is slightly increased, while that of 
the \( \gamma + \delta \) transition is decreased by terbium additions. This behavior 
is similar to that observed in all other rare-earth iron systems, with 
the exception of Er, for which there is conflicting evidence.\(^{5-6}\) The 
rare-earth metals, including terbium, act, therefore, as BCC stabilizers, 
with a severely limited solubility. The lattice parameter of a Tb saturated 
solid solution, quenched from 880°C is slightly increased to 2.8672±0.0002 Å, 
as compared to its value (2.8664 Å) in pure iron. Assuming a linear 
dependence of the lattice parameter on Tb concentration (Vegard's Law), 
the solubility limit would be 0.07±0.03 at.% Using electron microprobe 
measurements, a value of 0.1±0.05 at.% Tb was found, roughly agreeing with 
the lattice parameter measurements. No significant difference was observed 
for Tb-saturated solid solutions quenched from the \( \gamma \) temperature interval.

The Intermetallic Compounds

Similar to all other rare-earth iron binary systems from Gd onto Lu 
(with the exception of unknown Yb), four intermetallic compounds are 
present in the Tb-Fe system. Structural data concerning these compounds 
is given in Table I.

\( \text{TbFe}_2 \) and \( \text{TbFe}_3 \)

The eutectic temperature between Tb and the first iron-containing 
compound, \( \text{TbFe}_2 \), is situated at 28±0.5 at.% Fe and 847±3°C. The micro-
structure of a slowly (5°/min) cooled hypereutectic alloy (Fig. 2) reveals 
primary \( \text{TbFe}_2 \) dendrites, embedded in a Tb-\( \text{TbFe}_2 \) eutectic matrix. Dwight 
and Kimball\(^{17}\) have recently shown that the \( \text{TbFe}_2 \) compound is a rhombohedrally-
distorted Laves phase. The rhombohedral distortion although small \( \alpha = 59.6^\circ \), instead of \( 60^\circ \) for a regular cubic C-15 structure) is clearly apparent when checking the medium and high angle diffraction line profiles. The rhombohedral distortion is a direct result of the giant [111]-type magnetostriction present at room temperature in TbFe\(_2\).

The Laves phase TbFe\(_2\) melts non-congruently at 1187°C. In this respect it is interesting to note that with increasing atomic number of the rare earth component, \((R)\), the ratio of the atomic radii components \( r_{R}/r_{Fe} \) gets closer to the ideal Laves phase ratio, 1.225. This is reflected by the increasing stability of the RFe\(_2\) phases. Thus, from SmFe\(_2\) to HoFe\(_2\), these compounds melt non-congruently at increasingly higher temperatures. From ErFe\(_2\) to LuFe\(_2\) they melt congruently at temperatures above 1300°C. A similar trend is, by the way, also observed in the RCo\(_2\) series.

The minority phase, in the two-phase TbFe\(_2\)-TbFe\(_3\) region, appears in the form of elongated platelets (Fig. 3). Slowly cooled alloys in this two-phase region revealed the presence of a precipitation reaction taking place within the TbFe\(_2\) grains. In rapidly quenched samples no such precipitation could be detected. A definite orientation relationship is apparent between the iron-rich thin platelets, forming 120° angles among themselves, and the parent grains. The microstructure of a sample annealed for 2 hr at 1100°C, followed by an 8 hr long anneal at 700°C, is shown in Fig. 4. A phase boundary between a TbFe\(_3\) on the left side and a TbFe\(_2\) grain on the right, runs along the figure. Noteworthy is that no precipitation occurred in the TbFe\(_2\) grain, in regions adjacent to the grain boundary, presumably because the excess iron, instead of precipitating, diffused
during the low-temperature anneal towards the phase boundary. It follows that, similar to the Er-Fe system as observed by Meyer, TbFe$_2$ has a homogeneity range at elevated temperatures extending towards iron-rich compositions. This composition interval is schematically shown by dashed lines in Fig. 1. Efforts were made to confirm such a homogeneity range by comparing lattice parameters of alloys having compositions which bracket that of TbFe$_2$. No difference, within experimental errors, was observed. The experimental errors on the lattice parameters of the rhombohedrally-distorted compounds are, however, much larger than for an ordinary cubic Laves phase. Similar lattice parameter measurements on both sides of the stoichiometric TbFe$_3$ composition did not confirm Gilmore and Wang's reported homogeneity range for this compound.

Tb$_6$Fe$_{23}$

The X-ray patterns of arc-melted samples of composition ranging from 75-90 at.% Fe contained only the diffraction lines corresponding to the TbFe$_3$ and Tb$_2$Fe$_{17}$ phases. A lengthy anneal of 14 D at 1220°C of a 79.5 at.% Fe sample yielded, however, a nearly single phase Tb$_6$Fe$_{23}$ structure. The melting point of this compound, as shown by the thermal arrest on its heating curve, is situated at 1276°C. Noteworthy is that this sample did not contain any detectable Tb$_6$Fe$_{23}$ phase upon relatively rapid (20°/min.) cooling subsequent to its melting. It again required a lengthy high-temperature anneal in order to cause the reappearance of TbFe$_{23}$. Similar difficulty in the nucleation of this phase has been observed in the Dy-Fe$^2$ and Gd-Fe$^2$ systems. Earlier published phase diagrams of this latter system fail to make mention of the presence of Gd$_6$Fe$_{23}$. The lengthy anneals required at relatively elevated temperatures (>1100°C) would account
for the recent report that this phase is absent in the Tb-Fe system.\textsuperscript{13} In agreement with Oesterreicher's findings,\textsuperscript{13} we also observed that ternary additions, oxygen in our case, greatly enhance the rate of nucleation and growth of the Tb\textsubscript{6}Fe\textsubscript{23} phase. Very slow cooling at 1°/min through the 1400-1200°C temperature interval yielded a microstructure which did clearly show the peritectic nature of the compound formation, as shown in Fig. 5. The lattice parameters of Tb\textsubscript{6}Fe\textsubscript{23} are in good agreement with those previously reported by Ray.\textsuperscript{11}

Tb\textsubscript{2}Fe\textsubscript{17}

Contrary to the previous compound, Tb\textsubscript{2}Fe\textsubscript{17} single phase samples were easily obtained, even though both compounds melt non-congruently. This is illustrated in Fig. 6, for a 92 at.% Fe sample showing primary Fe dendrites surrounded by the Tb\textsubscript{2}Fe\textsubscript{17} matrix. Figure 7 shows the highly twinned microstructure of a 89.5 at.% Fe sample, corresponding to the stoichiometric Tb\textsubscript{2}Fe\textsubscript{17} composition.

Alloys of the rare-earth metals with approximately 89 at.% of transition metals Fe, Co, or Ni have been reported to possess either a hexagonal Th\textsubscript{2}Ni\textsubscript{17} or a rhombohedral Th\textsubscript{2}Zn\textsubscript{17}-type structure. Both structure types may be regarded as different stacking sequences of a basic structural layer related to the CaCu\textsubscript{5}-type structure. The occurrence of these various structure types has been discussed by Buschow\textsuperscript{15} and by Givord \textit{et al.}\textsuperscript{20} It appears that with decreasing rare-earth size, the ThNi\textsubscript{17}-type structure is favored. Thus, one finds the Th\textsubscript{2}Zn\textsubscript{17}-type for the light rare-earth elements Ce to Gd, while the ThNi\textsubscript{17}-type is present in Dy to Er-iron systems. The atomic size of Tb places it at the borderline between these two groups.
According to Buschow, the common room temperature modification of TbFe\(_{17}\) is the Th\(_2\)Zn\(_{17}\) structure type. The Th\(_2\)Ni\(_{17}\) type could be found only in splat cooled samples. Oesterreicher or the other hand, observed only the Th\(_2\)Ni\(_{17}\) type structure, both for the as cast and for samples given a prolonged anneal at relatively low (700 and 880°C) temperature.

Our results indicate that both the Th\(_2\)Zn\(_{17}\) and the Th\(_2\)Ni\(_{17}\) structure types are present in the Tb–Fe system. The rhombohedral Th\(_2\)Zn\(_{17}\) type was found in all samples having a composition on the Tb-rich side of the Tb\(_2\)Fe\(_{17}\) composition, while the Th\(_2\)Ni\(_{17}\) type was found on the iron-rich side. We believe that the strongly twinned structure shown in Fig. 7 represents a mixture of the two structure types. The hexagonal structure type was always and exclusively observed in iron-rich Tb\(_2\)Fe\(_{17}\) samples, irrespective of the annealing temperature (1200°C, 8 hr; 1000°C, 24 hr; 800°C, 72 hr). On the other hand, rapidly cooled Tb-rich samples yielded a mixture of the Th\(_2\)Zn\(_{17}\) and Th\(_2\)Ni\(_{17}\) structure types. A two hour anneal at 1200°C was sufficient, however, to result in a purely rhombohedral Th\(_2\)Zn\(_{17}\) type structure.

These findings seem in qualitative agreement with Givord et al. analysis of the 2:17 compounds. Both the Th\(_2\)Zn\(_{17}\) and the Th\(_2\)Ni\(_{17}\) variants are derived from the CaCu\(_5\) type structure by orderly substitution of a pair of transition metal atoms for each third rare-earth atom. The Th\(_2\)Ni\(_{17}\) hexagonal variant retains, however, some disorderly substitutions and is, therefore, more able to accommodate excess transition metal atoms and also tends to be more stable at elevated temperatures. Whether the two structure variants at room temperature are equilibrium structures having slightly different compositions, implying thereby a finite width in the region corresponding to the 2:17 phase, has not been ascertained in the present study.
Finally, we wish to mention that careful sample surface preparation reveals the magnetic domain pattern by use of the Kerr effect. In Fig. 8 the different domain width in three different terbium-iron intermetallic compounds is shown. This technique offers, potentially, a highly useful tool for studying some aspects of the exceptional magnetic anisotropy properties of the these compounds.

Acknowledgment:

We wish to thank G. Gordon, Jr., J. Jacobsen, and M. Malekzadeh for their helpful cooperation.

This work was supported by the U. S. Energy Research and Development Administration.
References

19. R. P. Elliott, "Constitution of Binary Alloys, First Supplement"

20. D. Givord, F. Givord, R. Lemaire, W. J. James, and J. S. Shan,
TABLE I

Structural Data for the Tb-Fe Intermetallic Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Symmetry</th>
<th>Space Group</th>
<th>Structure Type</th>
<th>Lattice Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbFe₂ (room temperature)</td>
<td>Rhombohedral</td>
<td>R₃m</td>
<td>Distorted MgCu₂</td>
<td>a = 5.1896 (a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 12.8214 (hex. axes)</td>
</tr>
<tr>
<td>TbFe₃</td>
<td>Rhombohedral</td>
<td>R₃m</td>
<td>PuNi₃</td>
<td>a = 5.139±0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 24.610±0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(hex. axes)</td>
</tr>
<tr>
<td>Tb₆Fe₂₃</td>
<td>Cubic</td>
<td>F₄m₃m</td>
<td>Th₆Mn₂₃</td>
<td>12.085±0.002</td>
</tr>
<tr>
<td>Tb₂Fe₁₇ (Tb-rich side)</td>
<td>Rhombohedral</td>
<td>R₃m</td>
<td>Th₂Zn₁₇</td>
<td>a = 8.504±0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 12.413±0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(hex. axes)</td>
</tr>
<tr>
<td>Tb₂Fe₁₇ (Fe-rich side)</td>
<td>Hexagonal</td>
<td>P₆₃/mmc</td>
<td>Th₂Ni₁₇</td>
<td>a = 8.472±0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 8.321±0.002</td>
</tr>
</tbody>
</table>

(a) Results taken from Ref. 17.
Figure Captions

Fig. 1. The Terbium-iron phase diagram.

Fig. 2. Hypereutectic 52. at.% Fe alloy. Primary TbFe₂ dendrites in a Tb-TbFe₂ eutectic matrix (x400).

Fig. 3. Primary elongated TbFe₃ platelets in a TbFe₂ matrix of a 68 at.% Fe alloy phase contrast at (x600).

Fig. 4. 68 at.% alloy, annealed for 2 hr at 1100°C and subsequently for 8 hr at 700°C. The TbFe₃ grain lies on the left, TbFe₂ on the right. Iron-rich plate-like precipitates are present in the TbFe₂ grain. Note their absence in the region adjacent to the phase boundary (x400).

Fig. 5. 79.5 at.% Fe alloy slowly (1°/min) cooled through the 1400-1200°C temperature range. Grain "a" is primary Tb₂Fe₁₇, surrounded by peritectically formed Tb₆Fe₂₃ (grains "e"). Final product of solidification TbFe₃ (grain "i") (x1000).

Fig. 6. 92 at.% Fe alloy. Primary Fe dendrites embedded in a Tb₂Fe₁₇ matrix (x100).

Fig. 7. Strongly twinned 89.5 at.% Fe sample, believed to represent a mixture of the two, Th₂Zn₁₇ and Th₂Ni₁₇ type structure variants of Tb₂Fe₁₇ (x400).

Fig. 8. Magnetic domain pattern of the same area as in Fig. 5, revealed through the Kerr effect, illustrating the different domain width in three different Tb-Fe intermetallic compounds. The arrow points to an area where reverse magnetization domain spikes appear (x1000).
XBB 755-3920

Fig. 6
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.