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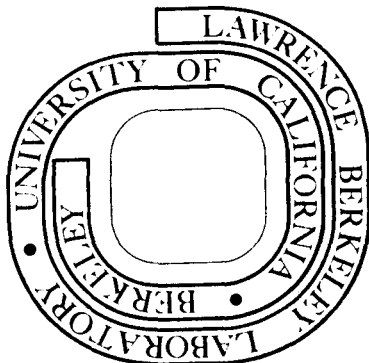
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OXYGEN STABILIZED RARE-EARTH IRON INTERMETALLIC COMPOUNDS*

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ABSTRACT

A new, oxygen-stabilized intermetallic compound was identified in sintered, pre-alloyed rare-earth iron powder samples. Its composition corresponds to formula $R_{12}Fe_{32}O_2$ and its crystal structure belongs to space group $\underline{Im3m}$. The presence of these compounds has been observed, so far, in several R-Fe-O systems, with R = Gd, Tb, Dy, Ho, Er and Y.

INTRODUCTION

Rare-earth iron intermetallics and in particular the RFe_2 (R = rare-earth metal) Laves phase compounds possess interesting properties such as huge magnetostriction, a strong dependence of the Young modulus on an applied field (ΔE effect) and high magnetocrystalline anisotropy. Similar to the RCo_5 -type permanent magnet materials, the R-Fe intermetallic compounds are extremely brittle. Powder metallurgical techniques seemed therefore appropriate for preparing suitably sized and shaped specimens. In the course of the characterization of the sintered powder compacts, the presence of a previously unreported compound was encountered. This compound was subsequently identified, synthesized and its crystal structure determined. It represents the first reported case of a rare-earth transition metal, oxygen stabilized compound with apparently metallic properties.

COMPOUND PREPARATION

A series of binary RFe_2 and ternary $R_{1-x}^1R_x^2Fe_2$ alloys, was prepared by arc-melting on a water cooled copper hearth under a Zr gettered argon atmosphere. After a 48h long homogeneization anneal at 1000°C in evacuated quartz capsules, the alloys were pulverized by ball milling under toluene in a planetary ball mill. The 40-50 μ particule size powder was rinsed and dried in an argon-containing glove box. Rubber tubing, 1" long, was manually filled with powder and isostatically compressed at 75,000 psi. The cold pressed samples were wrapped in Ta foils and sintered in a dynamic vacuum furnace. The temperature was increased stepwise, each 100 C to 1100 C. Each temperature increase resulted in an abrupt pressure increase in the system, due to the sample degassing. The samples were maintained for approximately 6 h at the highest temperature in a vacuum of 2×10^{-6} torr. The sintered products were

examined by optical microscopy and electron probe microanalysis. Powder diffraction patterns were taken using a Picker diffractometer with an X-ray monochromator.

In several instances the X-ray diffraction patterns included a series of lines which could not be attributed to any of the well known R-Fe intermetallics or to other compounds (e.g. oxides, nitrides), which could have been formed presumably, as a result of atmospheric contamination of the high specific surface powder.

In an effort to identify the unknown compound, which will hereafter be referred to as the β -compound, a series of Dy-Fe alloys was prepared in the 60-80 at. % Fe range, at 2 at. % increments. These alloys were submitted to the various powder preparation and sintering stages as described above. The alloy corresponding to approximately 72 at. % Fe yielded a nearly single β -phase diffraction pattern, which was subsequently used for the structure determination, with a few additional low intensity lines due to some residual DyFe_2 phase.

STRUCTURE DETERMINATION

The diffraction pattern of the single phase alloy was successfully indexed on the basis of a body-centered-cubic unit cell with a 8.91\AA lattice parameter (Table I). A literature search revealed that the only known crystal structures commensurate with that symmetry, lattice parameter and composition ratio of the 2 components were those of the binary compound Ca_3Ag_8 ¹ and the similar ternaries $\text{R}_3\text{Ni}_6\text{Si}_2$ ².

In order to ascertain the crystal structure of the β -compound, its experimental diffraction pattern was compared to computer generated ones. The computer program used as input the assumed space group, the atom position coordinates and the lattice constants. It computed the diffraction line positions and intensities. The intensities of the individual reflections were calculated according to $I = p|F|^2LP$, with p the multiplicity, $|F|^2$ the structure factor and LP the combined Lorentz-Polarization factor, corrected for the presence of the X-ray monochromator.

Good agreement between the experimental and the computer results was obtained by assuming for the β -compounds a component ratio corresponding to the formula Dy_3Fe_8 and the space group $\text{Im}\bar{3}\text{m}$ (Int. Tab. No. 229), with 4 formula units per unit cell. No such compounds however, have ever been reported in binary R-Fe systems and it seemed unlikely, that they should have been overlooked. It was assumed therefore, that the β -compounds had been stabilized by the presence of a ternary component. Chemical analysis of the single phase Dy-Fe β -compound revealed the presence of 0.94 w.% O, 0.05 w.% C and 0.09 w.% N. Crystal structure considerations, as well as the results of the chemical analysis suggest that the actual formula of the

β -compound should be $\text{Dy}_{12}\text{Fe}_{32}\text{O}_2$, space group $\text{Im}\bar{3}\text{m}$, with the atoms distributed on the following sites: (Fig. 1).

2 O in a
 12 Dy in e ($x = 0.28$)
 8 Fe_I in c
 24 Fe_{II} in h ($x = 0.667$)

The atomic position parameters for sites e and h were determined by trial and error, observing the best fit between the experimental and computed diffraction patterns (reliability factor 0.15). The positions assigned to the oxygen atoms are tentative only, since the X-ray spectra are insufficiently sensitive to the presence of the light atoms.

Efforts were made to determine the occurrence of the β -compounds in other than Dy, R-Fe systems. Single phase samples were successfully prepared for R = Gd and Ho. The presence of the β -compound was observed, though not as a single phase, for R = Tb, Er and Y, the additional phases being RFe_3 , R_6Fe_{23} intermetallics and some cubic R_2O_3 sesquioxides and RN nitrides. No trials have been made, so far, for preparing light rare-earth containing β -compounds. The lattice parameters of the β -compounds that have been observed, are shown in Table II.

The spatial arrangement of the atoms in the β -compound structure can be viewed as a network of Fe_{II} atoms located on pairs of parallel $\{110\}$ planes. The two planes of each pair are interconnected at regular intervals by the Fe_I atoms (Fig. 2). This network leaves empty spaces around the (0,0,0) and (1/2,1/2,1/2) positions, which are filled by regular R octahedra with an oxygen atom at their center. The molar volume of the β -compound is reduced by 11% with respect to that of its constituents, this figure being very similar to that in the RFe_2 Laves compounds.

DISCUSSION

Metalloid stabilized intermetallic compounds have been observed in intra-transition metal systems. Notable examples are the Ti_2Ni type phases, a large number of which are oxygen stabilized derivatives of nonoccurring binary phases. The effect of oxygen is to multiply by a factor of three the number of binary combinations for which the Ti_2Ni structure is stable.³ In the Ti_2Ni type phases, oxygen has a variable solubility, in the β -compounds this point has not been verified. The $\text{T}_3^1\text{T}_3^2\text{O}$ and $\text{T}_3^1\text{T}_3^2\text{C}$ phases^{4,5} ($\text{T}^1, \text{T}^2 =$ transition metals) are further examples of metalloid stabilized compounds which have no binary counterparts. Similar nitrogen or carbon stabilized compounds involving rare-earth metals with Group III-A and IV-A metals (Al, Ga, In, Tl, Sn and Pb) have been reported⁶.

No report has yet been made, to the best of the authors' knowledge, of oxygen stabilized rare-earth transition metal intermetallic compounds.

Ternary rare-earth, transition metal, oxygen systems have been subject to many investigations. The best known ternary compounds are the rare-earth iron garnets ($R_3Fe_5O_{12}$) and orthoferrites ($RFeO_3$). Both series have a relatively high oxygen concentration and are non-metallic. The β -compounds have a low oxygen concentration and a metallic luster. It is not clear at present whether they are thermodynamically stable, or only metastable, with respect to their decomposition into a rare-earth oxide (presumably R_2O_3) and a binary R-Fe intermetallic. If the latter were the case, it would account for the β -compounds not having been observed in previous investigations. In the course of ternary R-Fe-O system studies, oxygen is usually introduced in the form of rare-earth sesquioxides. It is not implausible that the high stability of these oxides would prevent their partial reduction to form a β -compound. In the present case, the method of preparation was different, in that high specific area pre-alloyed R-Fe compound powder was exposed to a low oxygen pressure at elevated temperatures.

Preliminary measurements below room temperature, using a VSM indicate that the Dy-based β -compound orders magnetically at 265 ± 5 K (Fig. 3). The residual magnetization after the abrupt decrease at 260 K is probably due to the presence of the minority $DyFe_2$ phase. Assuming a De Gennes like dependence of the magnetic ordering temperature on J of the rare-earth component, similar to that followed by the RFe_2 and RCo_2 compounds, the Tb and Gd-based β -compounds might, in principle, be still ordered at room temperature. The value of the magnetization at 4.2 K suggests that the magnetic moments of Dy and Fe are aligned antiferromagnetically. The crystal structure of the β -compounds being different from either that of R-Fe intermetallic compounds (RFe_2 , RFe_3 , R_6Fe_{23} , R_2Fe_{17}) or other high oxygen content compounds (orthoferrites, garnets), new magnetic structures can be expected. Both the intermetallics and the oxygen containing compounds possess highly interesting properties, many of which have found practical application. Magnetometric and Mossbauer effect studies of the β -compounds are being initiated with the purpose of determining some of their interesting and, perhaps useful, properties.

REFERENCES

- * This work was supported by the U.S. Energy Research and Development Administration.
- † On leave from the Nuclear Research Center-Negev and the Department of Materials Engineering, Ben-Gurion University, Beer-Sheva, Israel.
- 1. L. D. Calvert and C. Rand, *Acta Crystallogr.* 17, 1175 (1969).
- 2. E. L. Hladyschewsky, P. L. Krypiakewytsch and O. L. Bodak, *Z. Anorg. Allg. Chemie* 344, 95 (1966).
- 3. M. V. Nevitt, *Electronic Structure and Alloy Chemistry of the Transition Elements*, Ed. by P. A. Beck, Interscience, New York, (1963), p. 127.
- 4. N. Schönberg, *Acta Chem. Scand.* 8, 932 (1954).
- 5. K. Kuo, *Acta Met.* 1, 301 (1953).
- 6. H. Nowotny, *Seventh Rare-Earth Research Conference*, Coronado, California, 1968, p. 309.

Table I. OBSERVED* d-VALUES OF THE Dy-BASED β -compound ($Dy_{12}Fe_{32}O_{2}$)

h k l	d	I	h k l	d	I	h k l	d	I
1 1 2	3.622	11	5 1 0	1.739	6	4 4 4	1.2797	12
2 2 0	3.162	4	5 2 1	1.6187	16	7 1 0	1.2539	4
3 1 0	2.805	30	4 4 0	1.5666	20	7 2 1	1.2064	21
2 2 2	2.561	51	5 3 0	1.5203	18	7 3 0	1.1639	10
3 2 1	2.371	43	6 0 0	1.4775	15	7 3 2	1.1259	15
4 0 0	2.217	31	6 1 1	1.4381	28	8 0 0	1.1080	6
4 1 1	2.090	100	6 2 2	1.3364	38	8 1 1	1.0962	17

*Up to $2\theta = 90^\circ$ with Cu-K radiation.

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Table II. LATTICE PARAMETERS OF $R_{12}Fe_{32}O_{24}$ COMPOUNDS

R	a(Å)
Gd	8.919 ± 0.002
Tb	8.885 ± 0.002
Dy	8.8692 ± 0.0005
Ho	8.8435 ± 0.001
Er	8.815 ± 0.002
Y	8.8832 ± 0.0005

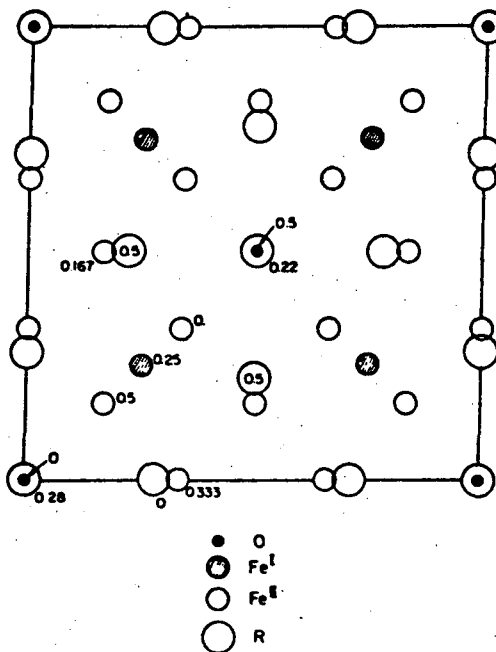


Fig. 1. Projection on the (001) plane.

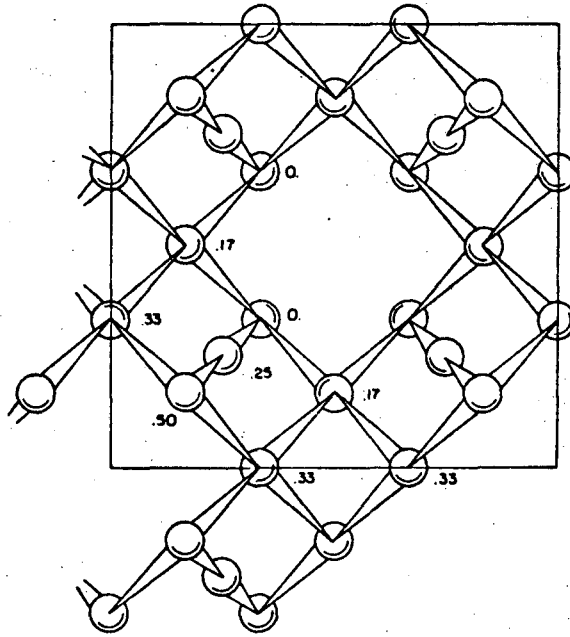


Fig. 2. Network of iron atoms projected on the (001) plane.

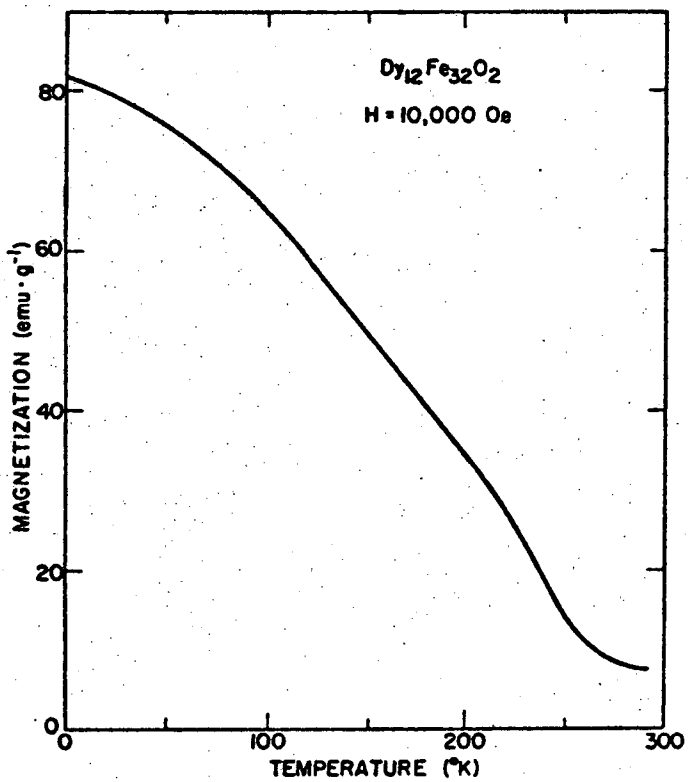


Fig. 3. Temperature dependence of the magnetization in nearly single phase Dy₁₂Fe₃₂O₂.

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