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A new type of soft ferromagnetic alloys: $RFe_{12-x}Ge_x$

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Abstract

Ternary iron-rich rare earth germanides $RFe_{12-x}Ge_x$ with R=Y, La, Ce, Nd, Sm, Gd, Dy, Ho and Er reveal soft ferromagnetic properties. The structure, the microstructure and the soft magnetic properties of these materials have been studied versus the germanium content and the nature of the rare earth element. In the as-cast materials, at least three crystallized phases have been identified: α-Fe(Ge), RFe_2Ge_2 and traces of Fe_3Ge. The typical grain size is of some tens of micrometer. The Curie temperature of these alloys is rather high (i.e. >770 K). The transition temperature as well as the saturation magnetization are found to strongly depend on the nature of the R element. The rapidly quenched alloys appear fully homogenized compared with the as-cast materials and the grain size decreases to about one micrometer. Although X-ray diffraction patterns have shown that the two major phases remain present, the magnetic characteristics are fairly dependent on the earth rare element. For all the investigated materials, measurements of the hysterical behaviour reveal a very low coercivity level, i.e. $H_c<10$ Oe.

Keywords: New ferromagnetic alloys; Soft magnetic properties; R–Fe germanides

1. Introduction

Various $R_{12}M$ alloys exhibit potential permanent magnet properties. These materials crystallize in the $ThMn_{12}$-type structure. Binary iron compounds do not exist in the RFe_{12}-type form. The 'RFe_{12}' phase, however, is stabilized by adding small amounts of a substitution element according to the formula $RFe_{12-x}M_x$. The substitution element can be either a transition metal which has to be mainly more electropositive than iron, or non-metal element as silicon [1]. However the Curie temperatures of the compounds remain relatively low, limiting their ferromagnetic properties.

A ferromagnetic material with Curie temperature above 770 K results from the substitution of germanium. The structural analysis reveals that the $RFe_{12-x}Ge_x$ alloys do not crystallize with the $ThMn_{12}$-type structure instead they are almost constituted by two different phases: the α-Fe(Ge) solid solution and a RFe_2Ge_2 type of phase. Because the latter is paramagnetic [1], the former phase is responsible for the ferromagnetic behaviour of the alloy. By controlling the substitution degree and the thermal treatment (annealing or rapid quenching process), an homogeneous microstructure can be stabilized.

In order to improve and understand the softness properties of these new type of alloys systematic structural and magnetic experiments have been investigated on as-cast and fast-quenched materials varying the nature of the rare earth element, the germanium substitution degree.

2. Experimental procedures

As-cast materials were synthesised by high frequency melting using the so-cold crucible technique. Amorphous or microcrystallized $RFe_{8.5}Ge_{3.5}$ ribbons were prepared from the former materials by rapid quenching using the single-roller method at different roll speeds ranging from 30 to 50 $m\,s^{-1}$.

At each step of the synthesis, systematic structural and microstructural characterizations were performed using SEM and Philips 300 kV high-resolution electron microscopy (HREM) combined with microanalysis (EDX) techniques. Identification of the different phase present in the alloys was done using a powder X-ray diffractometer Philips with Fe-$K_{\alpha1}$ radiation. The lattice parameters of the different phases were derived from the X-ray patterns by means of a least-squares routine.

High temperature thermomagnetic analysis was carried out on a Faraday type of balance and the magnetization loops were recorded using an extraction type magnetometer from 4 to 300 K. The $RFe_{12-x}Ge_x$ alloys were

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milled and pressed into ring-shaped samples with outer and inner diameters of 14 and 6.2 mm, respectively, in order to determine the permeability spectra. The permeability components, μ'(f) and μ''(f) were measured at room temperature using a coaxial impedance analyser covering the 0.1 MHz–1 GHz frequencies range [2].

3. Results and discussion

3.1. Structural analysis

3.1.1. The as-cast compounds

For all the R elements (except for Ho and Er) and for a germanium content ranging between 2 and 3.5, the as-cast materials RFe$_{12-x}$Ge$_x$ reveal two major phases:

- XRD analysis of the dark parts (Fig. 1a to d) reveal an iron–germanium solid solution which contains amounts of germanium varying from 20 to 5 atomic percent according to the rare earth element and the initial germanium concentration (x) used. Previous investigations [3] indicate that the maximum atomic germanium content dissolved in the a-Fe(Ge) solid solution is about 20 atomic per cent.
- XRD analysis of the white parts leads to the following results: 40 at % Fe, 40 at % Ge and 20 at % R; it corresponds to the RFe$_2$Ge$_2$ type of phase.

For x=3.5, the SEM analysis indicates the presence of a minor phase identified as a Fe$_3$Ge phase according the XRD results. For germanium content less than 3.5, SEM observations have no longer revealed traces of Fe$_3$Ge. The

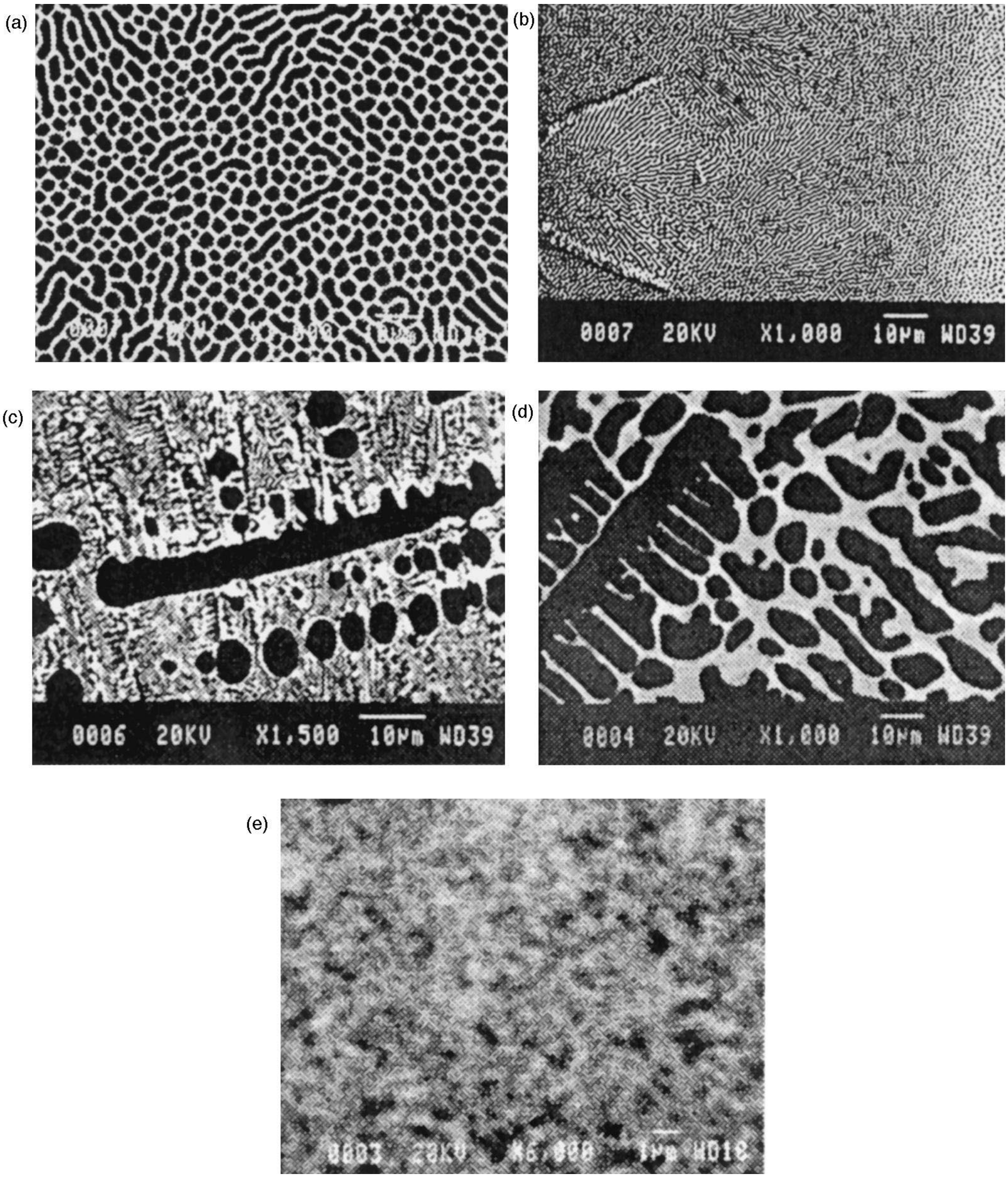

Fig. 1. (a) CeFe$_{8.5}$Ge$_{3.5}$ as-cast; (b) CeFe$_9$Ge$_3$ as-cast; CeFe$_{9.5}$Ge$_{2.5}$ as-cast; (d) CeFe$_{10}$Ge$_2$ as-cast; (e) GdFe$_{8.5}$Ge$_{3.5}$ fast-quenched.

occurrence of these impurities in $RFe_{8.5}Ge_{3.5}$ justifies the limit of $x=3.5$ for the maximum germanium content chosen in our studies. Indeed, above this limit the precipitation of Fe_3Ge increases markedly and because of its relative low Curie temperature it minimizes the properties of the bulk material. SEM observations of the $RFe_{12-x}Ge_x$ alloys lead to classify these materials in two different groups:

for $3\leq x\leq 3.5$ typical cellular systems are observed. They are more or less developed according to the rare earth element used. The mean size of the cell is about 10 μm for $x=3.5$ and close to 1 μm for $x=3$ (Fig. 1a,b).

Decrease of the germanium concentration promotes the demixing of the two different phases at a micrometric scale and should be correlated to the decrease of the cell sizes.

for $2\leq x\leq 2.5$ the decrease of the germanium (or increase of the iron) content does no longer promote the cellular systems but leads to the formation dendrites at a larger scale than these in the former germanium concentration range (Fig. 1c,d).

Except for R=Ho and Er, the microstructure of the $RFe_{12-x}Ge_x$ corresponds well to that described above. Therefore, special care has to be paid in the comparison of the structure and magnetic properties of R=Ho, Er compounds with the other ones.

For all the rare earth elements and from 2 to 3.5 germanium concentrations, the X-ray diffraction patterns reveal two phases identified as RFe_2Ge_2 and α-Fe(Ge). The α-Fe(Ge) solid solution crystallizes in b.c.c. system (the Fm3m S.G.). The lattice parameters vary linearly versus the germanium concentration [4]. Compared to the literature [4] on the b.c.c. Fe–Ge solid solution, the content of the dissolved germanium in our α-Fe(Ge) phases can be determined. The RFe_2Ge_2 type phase has the body centered tetragonal $ThCr_2Si_2$-type structure with the I4/mmm space group.

For $x=3.5$, no Fe_3Ge diffraction peak was found in the X-ray patterns. This result proves that presence of Fe_3Ge observed by SEM remains at a poor level in the $RFe_{8.5}Ge_{3.5}$ alloys. From X-ray data, the RFe_2Ge_2 phase constitutes the major one compared to the α-Fe(Ge) one. Decrease of x in $RFe_{12-x}Ge_x$ alloys leads to a relative decrease of the RFe_2Ge_2 phase, conversely a corresponding increase of α-Fe(Ge) is observed. The Ge content deduced from the lattice parameters versus x and R used is reported on Fig. 2 and Fig. 3, respectively. There is a good agreement between the results found from the XRD analysis and those deduced from the lattice parameters measurements. When the Ge substitution in the $RFe_{12-x}Ge_x$ alloys decreases, the Ge content, x_α, in the α-Fe(Ge) phase decreases. Furthermore, x_α is dependant on the rare earth element, the maximum x_α was found for La and Sm. Hence it is possible to control the Ge content in the micrometric α-Fe(Ge) grains both by the germanium content in the as-cast $RFe_{12-x}Ge_x$ alloys and the R element. These aspects reveal of prime importance in order to control and to understand the magnetic properties of the new materials.

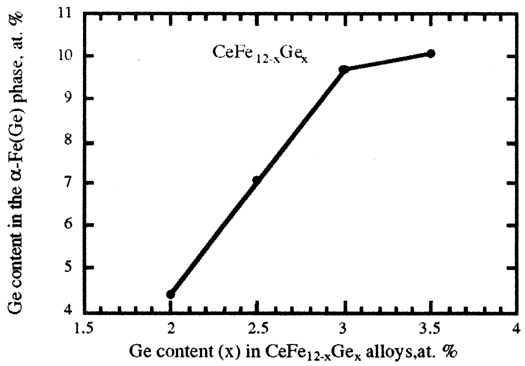

Fig. 2. Variation of the Ge content dissolved in the α-Fe(Ge) phase with the Ge concentration in $CeFe_{12-x}Ge_x$ as-cast alloys.

3.1.2. The rapidly-quenched alloys

At a higher magnification of SEM a black and white granular system can be detected on the Fig. 1e, the typical grain size being about 1 μm. As the XRD analysis resolution does not permit an accurate determination of the composition of the different phases, the high resolution TEM technique has been used. Microparticulate aggregations identified as α-Fe(Ge) and RFe_2Ge_2 phases have been detected. Preliminary results indicate that the rapid quenching method does not change the nature of the phases already found in the as-cast state but it leads to fully homogenize alloys.

In Fig. 4, comparisons of the X-ray diffraction patterns between the as-cast and fast quenched compounds are made confirming both the b.c.c. α-Fe(Ge) and RFe_2Ge_2 phases. The diffraction spectra show a systematic and strong decrease of the peaks in the fast quenched alloys (about 50%) compared to the as-cast state. Increase of the mid-height width of the peaks reveals atomic disorders and a decrease of the grain size. No accurate determination of

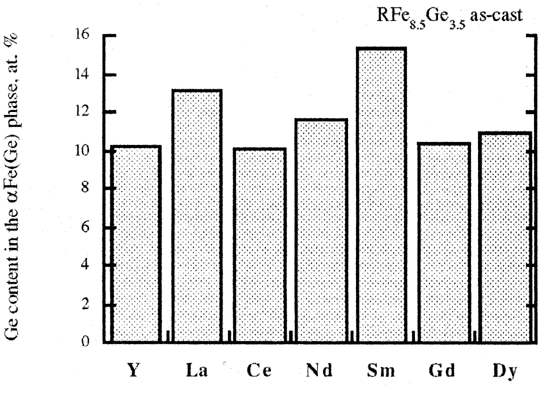

Fig. 3. Variation of Ge content in the α-Fe(Ge) phase with R used in the $RFe_{8.5}Ge_{3.5}$ as-cast alloys. R(=Ho and Er)$Fe_{8.5}Ge_{3.5}$ have not been inserted in the plot because of the difficulty to accurately determine the Ge content in the α-Fe(Ge) phase.

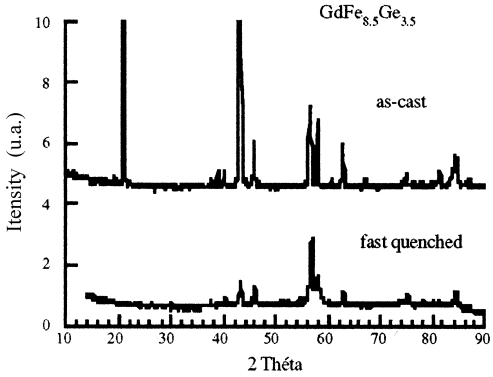

Fig. 4. X-ray diffraction spectra for the as-cast and fast quenched $GdFe_{8.5}Ge_{3.5}$ alloy.

the lattice parameters can be made from such broad diffraction peaks.

3.2. Magnetic properties

The results of thermomagnetic experiments are reported on the Fig. 5. The $RFe_{12-x}Ge_x$ alloys exhibit a single ferromagnetic phase with a high Curie temperature ranging above 870 K. The T_c determinations are in agreement with previous investigations [5]. Combining the structural results and thermomagnetic analysis, it can be concluded that the α-Fe(Ge) phase is responsible for the ferromagnetic behaviour. The Curie temperature of the α-Fe(Ge) solid solution decreases from 1038 K to 903°C for 0 to 19 at % of Ge content [3].

For fixed R element, the $RFe_{12-x}Ge_x$ Curie temperature decreases when x increases. This variation is directly related to the Ge content dissolved in the ferromagnetic phase (cf. Fig. 2).

For fixed x value, the $RFe_{12-x}Ge_x$ Curie temperatures vary with the nature of R. Because of the Curie temperature is an intrinsic property, in our investigated materials, the R element can not directly influence the T_c values. But the variation of x_α with the R element observed in Fig. 3. explains why x_α is the only factor affecting the T_c values.

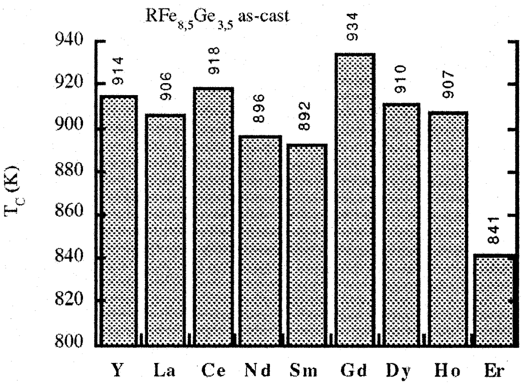

Fig. 5. Variation of the Curie temperature with R in the as-cast $RFe_{8.5}Ge_{3.5}$ alloys.

As the R element seems to modulate the solubility of the non metal element (Ge), a suitable choice of the R element and germanium substitution allow to control the ferromagnetic ordering temperature of the alloys.

As mentioned in the previous section the phases in the as-cast alloys are preserved after the rapidly quenching process. Thus a Curie temperature comparison between the fast quenched and the as-cast state can be made. It results that the fast quenched materials show a slight reduction of the Curie temperatures comparison with the as-cast ones ($[T_{\text{c-as-cast}} - T_{\text{c-fast-quenched}}]/T_{\text{c-as-cast}} \approx 10\%$).

The values of saturation magnetization were extracted from the magnetization loops using the high approach law for a polycrystalline material with randomly oriented grains [6] defined as:

$$M = M_s - \frac{a}{H^2} + \chi H$$

For R element fixed, the saturation magnetization of the $RFe_{12-x}Ge_x$ decreases when x increases. Two parameters should influence this M_s variation: the Ge content (x) and the quantitative ratio of α-Fe(Ge) phase. As discussed above, the Ge content dissolved in α-Fe(Ge) phase decreases with x. Furthermore previous investigations [3] have reported that the α-Fe(Ge) magnetic moment diminishes with the increase of the Ge content dissolved in the α-Fe(Ge) phase. Therefore a increase of x could explain a diminution of saturation magnetization. From the X-ray patterns discussion, it results that the quantitative ratio of the αFe(Ge) phase decreases when x increases in the $RFe_{12-x}Ge_x$ alloys. Consequently the increment of x is related to the decrease of the ferromagnetic contribution and is responsible of the diminution of the $RFe_{12-x}Ge_x$ magnetic moment.

For x fixed value, the saturation magnetization results are reported on Fig. 6. versus R in the as-cast and fast-quenched state. Firstly, it can be seen that M_s strongly depends on the rare earth element and secondly, rapid quenching process dramatically drops down the saturation

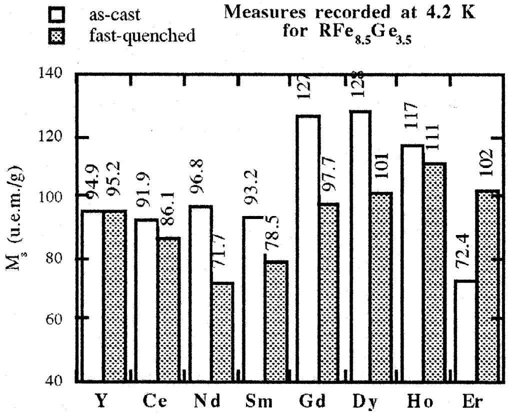

Fig. 6. M_s measured at 4.2 K versus R for as-cast and fast quenched $RFe_{8.5}Ge_{3.5}$ materials.

magnetization. While the Ge content explains well the T_c variations with the R elements, it does not appear to be the unique factor responsible for the variation of M_s with the R elements. At this point, we can express two hypotheses.

The first one is based on a metallurgical point of view. A high melting point of the R element should promote the quantitative increase of the ferromagnetic α-Fe(Ge) phase and consequently should increase the saturation magnetization. Furthermore higher the melting point of the R element is, more efficient the quenching treatment is, leading to the larger the decrease in M_s. Therefore the following question can be addressed: does the Fe(Ge) contains a significative amount of dissolved R atoms?

The second assumption is concerned to magnetism. For this hypothesis, it is supposed that some amounts of R atoms are dissolved in the αFe(Ge) lattice. In binary R–Fe intermetallics the magnetic moments are antiferromagnetic coupling between 3d spins and the R spins. For compounds in which R is a light rare earth element ($J=L-S$) this implies that the total rare earth moment ($gJ\mu_B$) is coupled parallel to the 3d moments (i.e. $M_{3d}\uparrow - M_{\text{light R}}\uparrow$). By contrast, when R is a heavy rare earth element ($J=L+S$) the total rare earth moment is coupled anti parallel to the 3d moment (i.e. $M_{3d}\uparrow - M_{\text{heavy R}}\downarrow$) [7]. Contrarily to this rule on exchange couplings, an opposite exchange scheme could apply in the present system. The relevant exchange Fe–R interaction should be of superexchange type via rare earth atoms preferentially co-ordinated by germanium (Fe–Ge–R). For R = Nd and Sm, M_s stands lower than for the non-magnetic rare earth element as Y or Ce, but for R = Gd, Dy, Ho, . . . M_s it is larger. This scheme applies rather well both for the as-cast and for the quenched materials.

Frequency-dependent measurements of complex permeability spectra have been performed on some $RFe_{12-x}Ge_x$ as-cast materials. Preliminary examinations lead to determine the maximum real part of the permeability μ' ranging between 4 and 7 at low frequency. At higher frequency, a clear absorption phenomenon was evidenced ranging between 40 to 200 MHz, with a maximum imaginary part of the permeability μ'' larger than 2 in some cases. The Ge content in the $RFe_{12-x}Ge_x$ clearly influence these parameters: when x (Ge) decreases, we observe increases of μ' and $\mu''_{\max}$, and the absorption frequency is shifted towards lower frequencies. Presently, works on the effects of the R element on the permeability components are in progress.

4. Conclusion

The structure, the microstructure and the magnetic properties on a new type of soft ferromagnetic materials with $RFe_{12-x}Ge_x$ composition have been analysed. From the measurements analysis, we can report the following conclusion:

- as-cast $RFe_{12-x}Ge_x$ alloys crystallize in a binary system composed of ferromagnetic α-Fe(Ge) grains surrounded by a paramagnetic RFe_2Ge_2-type of phase.
- the rapid quenching process does not affect the nature of the two phases but fully homogenizes alloys.
- Curie temperatures of the R–Fe–Ge alloys depend clearly on the germanium concentration, they are slightly dependent on the nature of the rare earth element.
- magnetization measurements reveal saturation magnetization values ranging from 72 to 128 $A\cdot m^2\cdot kg^{-1}$ varying with the germanium substitution degree and the nature of the rare earth element. The coercivity of all the investigated compounds remains low, typically about a few oersted. The initial complex permeability spectra were measured for $RFe_{8.5}Ge_{3.5}$ alloys in the 0.1 MHz–1 GHz frequency range.

The influence of the germanium substitution on the magnetic properties is well explained by the germanium content dissolved in the ferromagnetic phase. Even if the influence of the nature of the rare earth element on the static and dynamic properties clearly exists, no definitive conclusion can be drawn on this point and requires further investigation.

References

[1] K.H.J. Buschow, Handbook of Magnetic Materials no. 7, (1993), p. 235.
[2] V. Cagan, M. Guyot, IEEE Trans. Magn. 20(5) (1984) 1732.
[3] P. Pascal, Nouveau traité de Chimie Minérale, tome XX, Masson and cie, (1964), p. 872.
[4] H. Chessin, et al., J. Phys. Chem. Solids 24(2) (1963) 261.
[5] K.Y. Wang, et al., J. Alloys Comp. 233 (1996) L1.
[6] A. Bozorth, Ferromagnetism, D. Van Nostrand Company, Inc., (1963), p. 484.
[7] K.H.J. Buschow, Ferromagnetic Materials, vol. 4, North-Holland, (1988), p. 43.