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MICROSTPUCTURAL CHARACTERIZATION OF RARE EARTH-COBALT MAGNETS

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MICROSTRUCTURAL CHARACTERIZATION OF RARE EARTH-COBALT MAGNETS

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ABSTRACT

Structural faults and phase transformations in R_2-Co_{17} magnets are studied using transmission electron microscopy. The magnetization mechanism in a step aged Sm (Co, Fe, Cu, Zr) alloy is determined to be by domain wall pinning in the 1:5 phase of the cellular microstructure. Limitations of the electron metallography technique to study these materials are pointed out.

INTRO TION

Properties of materials are structure-sensitive. Structure is in turn determined by composition, heat treatment and processing. Hence, it is necessary to characterize both structure and composition at the highest levels of resolution possible in order to understand materials behaviour. Such characterization requires advanced and sophisticated techniques of characterization using microscopic, diffraction and spectroscopic techniques. For this, of course, electron microscopy is particularly versatile, since we are now routinely synthesizing structures at atomic levels of resolutions. The interaction between heat treatment and properties is complex, but this interaction must be understood if materials are to be improved or new materials designed.

In the case of rare earth-cobalt very hard magnets, the study of the microstructures has received considerable attention (1-4) in the last few

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years and some progress has already been made in establishing microstructure-property relationships. Recent development of new heat treatments and compositions (5,6) giving still higher magnetic energy product ($(BH)_{max}$) values has necessitated further research to understand the detailed microstructural features (phases) and the magnetization reversal mechanisms in these materials and hence identify the microstructural features responsible for good magnetic properties.

In this paper, the results of an investigation of the microstructure of Sm_2 (Co-Cu-Fe-Zr)$_{17}$ alloy (especially after step aging) using transmission electron microscopy are presented. The study of defects and phase transformations are emphasized and the limitations of the present electron analytical techniques for further characterization of these materials, are discussed.

STRUCTURAL DEFECTS

The various structures exhibited by R-Co magnets have already been studied systematically and the possible magnetic significance of the faults and polytypes in R_2Co_{17} compounds have been discussed by Allen, et al. (7,8). Occurrence of the stacking faults and polytypes in 2:17 alloys of $(Co_{.8}Fe_{.1}Mn_{.1})_{17}$ Sm_2 have been observed by Mishra and Thomas (4). Figure 1(a) shows an example of faults as the boundaries between hexagonal and rhombohedral regions in this material which was prepared by sintering magnetically aligned pellets of $(Co_{0.8}Fe_{0.1}Mn_{0.1})_{17}$ Sm_2 at 1135°C. The interfaces between the two phases can be made to go out of contrast by tilting the specimen in the microscope. The boundary can be described as a fault in the rhombohedral structure with the fault vector R = 1/3[0001] normal to the boundary. Such a fault can be shown to accommodate nonstoichiometry with excess Co atoms at the fault. The other type of faults found in 2:17 magnets is shown in Fig. 1(b). These are nonconservative antiphase

boundaries on the prism planes with a displacement vector 1/4 <10$\bar{1}$0> and can be shown to accommodate nonstoichiometry. These faults extend through the matrix material and hence no evidence of partial dislocations bounding the faults have been found so far.

Such boundaries and faults may create regions of material with anisotropy different from that of the matrix. Stresses developed at the end of such regions (Fig. 1(a)) due to different magnetrostrictive behaviour can serve to assist the nucleation of domains. Formation of large regions of hexagonal material in the rhombohedral matrix can provide a similar source for domain nucleation. The magnetization data confirm that, in fact, in these materials, coercivity is controlled by domain nucleation (4).

PHASE TRANSFORMATIONS

Phase transformations in R-Co magnets are of primary importance, since nearly all the rare earth-cobalt magnets with good magnetic properties are multiphase alloys (1,3,9). However, identification of various phases that are present is generally not straight forward (10), particularly for the multicomponent alloys that are being developed presently (6). Determination of the structure, chemical composition and magnetic domain behaviour of the various phases in the material can be approached with electron microscopy techniques. Electron diffraction in conjunction with dark field techniques are essential for phase identification whilst Lorentz microscopy is very useful to study the magnetic domain patterns, and hence the mechanism of hardening.

Here the microstructure of sintered $(Co, Cu, Fe, Zr)_{11}\ Sm_2$ alloy solution treated between 1100-1250°C and step tempered between 750°C to 400°C has been investigated. The step aging heat treatment scheme is described elsewhere (5). The microstructure of the step aged alloy after aging at 400°C is shown in Figs. 2(a) and (b). The microstructure in

Fig. 2(a) taken from a section of the aged material containing the c-axis consists of a cellular microstructure (3) with cell interiors having a 2:17 structure and cell boundaries with a 1:5 structure. The cells are approximately 300Å in size and the cell walls are 40Å in width, making it difficult to determine the chemical composition of these phases using the available STEM. Closely spaced stacking faults on the basal planes are present in the cell interiors in Fig. 2(a) and these faults generally do not continue through the 1:5 phase at the boundary. In Fig. 2(b), taken from a section of the same magnet, normal to the c-axis, these faults are not seen. The cell morphology is not isotropic in this section, just as that in Fig. 2(a) where cell walls are parallel to crystallographic planes.

The microstructures from alloys step aged up to 600°C and 500°C (ref. 5) are similar to those shown in Figs. 2(a) and (b).

The magnetic domain walls are imaged by Lorentz microscopy in Fig. 3 from a specimen of the aged alloy, sectioned parallel to the c-axis. The domain wall is seen to be wavy in nature and lies parallel to the c-axis (easy axis). The Fresnel micrograph is taken at a low magnification and large defocus of the objective lens and hence the microstructural features cannot be seen directly. However, careful comparison of these images with the focussed images shows that the wavy domain wall in Fig. 3 follows the cell boundaries. This is the case if the boundary phase is magnetically softer/harder than the cell interiors so that the domain walls are preferred energetically to lie in the soft phase. The observations confirm the model of Livingston and Martin (3).

It can be concluded that the coercivity is controlled by domain wall motion and not by single domain particles in this magnet. The high coercivity is a result of the changes in the chemical composition between the two phases during step tempering. This in turn affects the magnetic anisotropy

and exchange energy. Such an effect has been observed in Fe-Cr-Co magnets which is known to decompose spinodally (11,12). Upon step tempering the spinodally decomposed Fe-Cr-Co alloys inside the miscibility gap, the morphology of the microstructure remains almost unchanged, but changes in the chemical composition of the phases take place (12). It is suspected that the initial phase separation in this R-Co system proceeds via a similar mechanism where the two phases first separate out and any further step aging only enhances the composition differences. It must be remarked here that this analogy may be a simple one and may be the only possible analogy between Fe-Cr-Co system and the R_2Co_{17} system. Further work in the characterization of the microstructure produced during aging of the R-Co alloys and the domain wall configurations in the partially aged alloys is necessary to discuss these points further, and is currently in progress.

DISCUSSION

In the preceeding sections, the microstructural features as studied using transmission electron microscopy have been characterized. However, several key questions remain unanswered even now, and these are due to the limitations in the techniques used (13). In Fig. 1(a) the boundary separating the two phases of 2:17 material is curved at A, although the displacement vector is the same there as at the straight regions of the boundary. High resolution imaging of (001) lattice fringes can be used to study the nature of this curved interface. Also, it is concluded that, near this boundary as well as near the antiphase boundary of Fig. 1(b), excess amounts of Co atoms are present, and the faults accommodate this nonstoichiometry. Since the electron scattering powers of F atoms and Co atoms differ significantly, atomic resolution microscopy should be able to provide direct experimental evidence but this will require instruments with better that 2Å resolution. At present the best reported is 2.2Å (14-17).

In the case of the phase transformation studies, the nature of the interface between the 1:5 phase and 2:17 phase can be examined using lattice imaging at 2.5Å which is now possible. Polytypism (4) in these alloys can also be studied at lattice resolution to investigate the regions where the anisotropy is altered due to nonstoichiometry, thereby affecting the domain wall properties.

Although current efforts are being devoted to these latter projects, obtaining high resolution images from these very hard magnetic materials is difficult. The magnetic field of the material alters the focussing conditions of the objective lens by interacting with the magnetic field of the pole piece. Our attempts to obtain lattice fringe images from ion thinned specimens using the Siemens 102 electron microscope have been unsuccessful solely due to the difficulties associated with the altered focussing conditions. This problem may be overcome by using high voltage high resolution microscopes with strong objective lenses and higher energy electrons. Such an instrument will be available at Berkeley in 1980.

A fundamental understanding of the magnetization mechanisms and mechanisms of the interaction of the domain wall with the defects/phases require high resolution studies of the microstructure as well as the domain wall structure. The domain walls in these very hard magnets will not be affected by the stronger magnetic field in high voltage microscopes, and in fact, with less defocusing necessary to image domains from thick specimens, one may be able to study the interaction between the domain walls and the microstructure directly, provided the essential resolution is also achieved.

As can be seen from the previous section, characterization of the chemical composition of the 1:5 phase and 2:17 phase accurately is essential to understand the contributing factors to high coercivity in the

newly developed magnets. EDAX in the STEM is limited by the small regions of 1:5 phase to be examined. Difficulties associated with the lattice fringe imaging make it impossible to derive the approximate compositions from local lattice parameter measurements also. High resolution chemical microanalysis in STEM must be developed to obtain chemical composition from 30-50Å regions to characterize the 1:5 phase.

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REFERENCES

1. H. Nagel, A. J. Perry and A. Menth, J. Appl. Phys., 47, 2662, 1976.

2. K. N. Melton and H. Nagel, J. Appl. Phys., 48, 2608, 1977.

3. J. D. Livingston and D. L. Martin, J. Appl. Phys., 48, 1350, 1977.

4. R. K. Mishra and G. Thomas, J. Appl. Phys., 49 2067, 1978.

5. T. Ojima, S. Tomizava, T. Yoneyama and T. Hori, IEEE Trans. Magnetics, 13, 1317, 1977.

6. R. L. Bergner, et al., Enhancement of the Magnetic Properties of the $Sm_2Cu_{1.6}Zr_{0.1}Fe_{3.3}Co_{12}$ Compound, J. Appl Phys., 50, p. 2352, 1979.

7. C. W. Allen, D. L. Kurusar and A. E. Miller, IEEE Trans. Magnetics, 10, 716, 1974.

8. C. W. Allen, K. C. Liao and A. E. Miller, J. Less Common Metals, 52, 109, 1977.

9. K. N. Melton and R. S. Perkins, J. Appl. Phys., 47, 2671, 1976.

10. P. Rao and R. P. Boehner, J. Appl Crystallography, 7, 487, 1974.

11. H. Kaneko, M. Homma, K. Nakamura, M. Okada and G. Thomas, IEEE Trans. Magnetics, 13, 1325, 1977.

12. Y. Belli, M. Okada, G. Thomas, M. Homma and H. Kaneko, J. Appl. Phys., 49, 2049, 1978.

13. G. Thomas, Characterization of Alloys and Ceramics, Electron Microscopy, 1978, Vol III, J. M. Sturgess (ed.), 392, Microscopical Society of Canada, Toronto.

14. S. Horiuchi, 1 MV Super High Resolution EM of Nb_2O_5-WO_3 Complex Compounds, 9th International Congress Electron Microscopy Proc., 1978, Vol. I, J. M. Sturgess (ed.), 298, Microscopical Society of Canada, Toronto.

15. N. Uyeda, E. Kirkland, Y. Fujiyoshi and B. Siegel, Atomic Resolution from 500kV Electron Micrographs by Computer Image Processing, 9th International Congress Electron Microscopy Proc., 1978, Vol. I, 220, Microscopical Society of Canada, Toronto.

16. H. Hashimoto, A. Kumao and E. Endoh, Single Atoms in Molecules and Crystals Observed by TEM, 9th International Congress of Electron Microscopy Proc., 1978, Vol. III, J. M. Sturgess (ed.), 244, Microscopical Society of Canada, Toronto.

17. H. Hirabayashi, et al., High Resolution Electron Microscopy of Long Period Superstructures of Hexagonal Au-Cd Alloys, Proc. of the 5th International Conference on High Voltage Electron Microscopy, Kyoto, Japan, Vol. 26 (1977), pp. 309-312, (see also pp. 313-316).

FIGURES

Fig. 1(a). BF micrograph taken from a sintered $Sm_2(Co_{0.8}Mn_{0.1}Fe_{0.1})_{17}$ sample sectioned parallel to the c-axis showing regions of hexagonal 2:17 phase (H) in the rhombohedral 2:17 matrix. The boundary between the phases can be described by a 1/3 <0001> fault, which is not straight on a macroscopic scale. (Specimen courtesy of D. Fry of General Motors Lab, Michigan).

Fig. 1(b). B.F. image of α faults in rhombohedral 2:17 phase with fault vector $\vec{R} = 1/4 \langle 10\bar{1}0 \rangle$. (Specimen courtesy of D. Fry of General Motors Lab, Michigan).

Fig. 2(a). BF image of a step aged $Sm_2(Cu\text{-}Fe\text{-}Co\text{-}Zr)_{17}$ alloy, sectioned parallel to the c-axis (easy axis) showing the cellular microstructure. The cell interior (I) has the 2:17 structure and the cell boundary C has the 1:5 structure. The cell interiors are heavily faulted (F) on (0001) planes.

Fig. 2(b). Same as (a), from the alloy sectioned normal to the c-axis. The cell interiors are not faulted. The cell boundaries are aligned crystallographically.

Fig. 3. Fresnel micrograph from a step aged $Sm_2(Co\text{-}Cu\text{-}Fe\text{-}Zr)_{17}$ alloy showing the domain walls in an over focussed condition. Note the wavy nature of the domain wall AB which tries to remain near the 1:5 phase preferentially.

XBB 770-9734A

Fig. 1(a)

XBB 770 9735A

Fig. 1(b)

XBB 795 6615

Fig. 2

XBB 795 6614

Fig. 3