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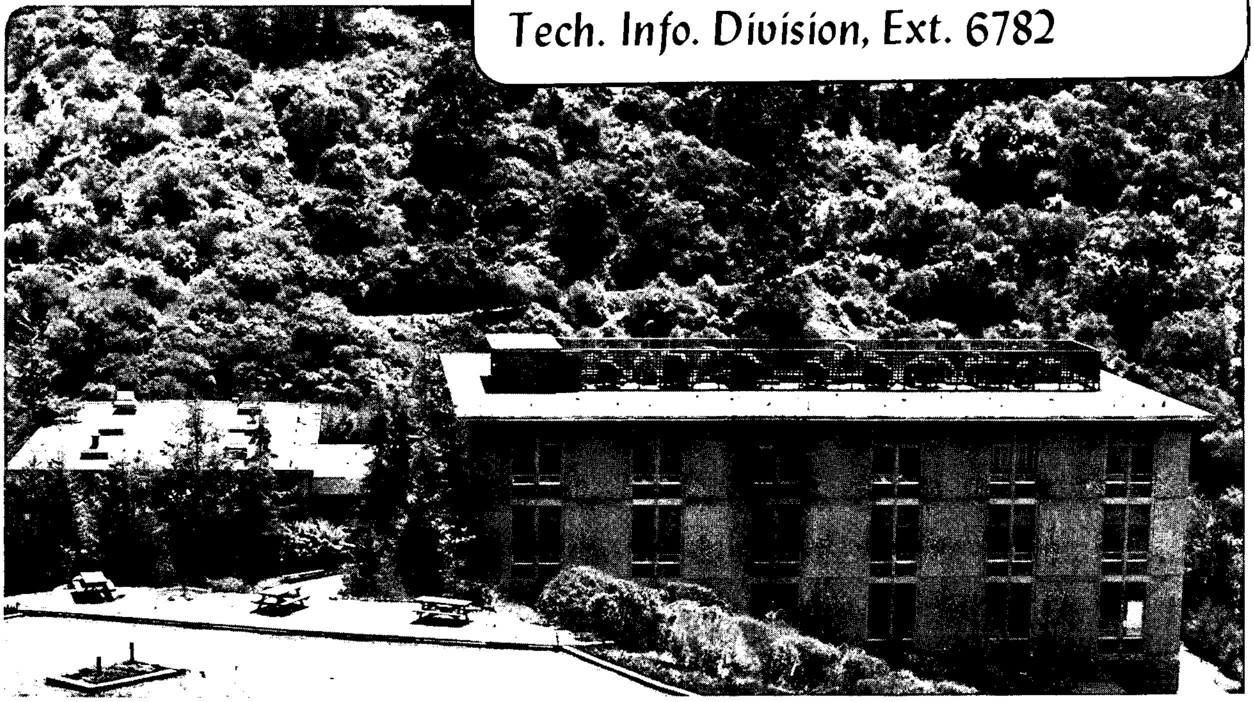

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Microstructures of Precipitation Hardened SmCo Permanent Magnets

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ABSTRACT

The microstructural features of isothermally aged and step-aged, and isothermally aged Sm(Co, Cu, Fe,Zr)$_{7.4}$ alloys are examined using electron microscopy and X-ray microanalysis. The microstructure is seen to consist of a cellular morphology with twinned rhombohedral 2:17 phase cell interiors, 1:5 phase cell boundaries and elongated thin platelets with a 1:3 structure. Upon prolonged aging, Zr preferentially goes into the 1:3 phase, Cu to both the 1:5 and the 1:3 phase, and Fe to the 2:17 phase. Isothermal aging at 850°C facilitates the growth of the cells and the low temperature step aging facilitates the chemical partitioning of the transition metals. The role of Zr in developing the morphology and the chemical partitioning is discussed.

PACS numbers: 81.40-z, 75.60 Gm, 81.40 Gh, 75.50 Bb

INTRODUCTION

Rare-earth cobalt alloy magnets with $(BH)_{MAX}$ values in excess of 30 MGOe have been designed recently[1]. Typically such magnets have an overall composition between those of the $SmCo_5$ and Sm_2Co_{17} phases, modified by additions of Cu, Fe and small amounts of Zr. These pentenary alloys are sintered and subsequently step aged to produce magnets with large saturation magnetization, large iHc and high energy product. Their microstructures generally consist of two phase cellular morphology where the

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2:17 phase forms the cell interiors and the 1:5 phase the cell boundaries. The high coercivity of the material is attributed to domain wall pinning. The chemical differentiation between the cell interiors and the cell walls is thought to be crucial in determining iHC and addition to Zr to the alloys plays a key role in aiding the chemical partitioning during step aging[2].

In this investigation, electron microscopy and chemical microanalysis techniques have been used to study the development of microstructure and chemical partitioning with thermal treatments. The role of Zr in the development of these microstructural features is considered. The results are consistent with the changes in the magnetic properties of these alloys due to alloying and thermal treatments.

EXPERIMENTAL

Alloys of compositions Co, 25.5%Sm, 8%Cu, 15%Fe, 1.5%Zr and Co, 25.2%Sm, 8%Cu, 15%Fe, 3%Zr were obtained from TDK Research and Development Laboratories, Chiba, Japan. Alloy preparation, magnetic properties measurements, and coercivity data for these alloys have been reported in a previous paper[2]. Thermal treatment of these alloys involves homogenization at temperatures between 1100 and 1220°C, quenching in Ar atmosphere, isothermal aging at 850°C and step aging. The step aging sequence is as follows: the specimens were continuously cooled from the isothermal aging temperature to 400°C at a cooling rate of 1-2°C per minute and subsequently aged at 400°C for 10 hours. Electron transparent foils for transmission electron microscope (TEM) were prepared by ion beam milling; electron microscopy was done with a Philips EM400 and a Philips EM301 operating at 100kV.

RESULTS

In alloys aged near peak coercivity, four microstructural features are generally present. This applies to alloys containing 1.5 or 3% Zr, heat treated isothermally with or without step aging. As previously reported[3], a coherent cellular structure of 1:5 walls and 2:17 cell interiors is present throughout the material. Occasionally, superimposed on the cell structure are thin coherent plates of a third phase. These plates, which lie on the basal plane of the matrix, are enriched with Zr with respect to the matrix; they have therefore been dubbed the "Z phase". Finally, the 2:17 cell interiors are twinned.

Fig. 1a is a TEM micrograph taken at a $<0\bar{1}10>_{\text{Hexagonal}}$ pole (c-axis in the plane of the paper) in which all of the four features are visible. The corresponding selected area diffraction (SAD) pattern is included in Fig. 1b. Indexing of the SAD pattern is consistent with a combination of hexagonal 1:5 and rhombohedral 2:17 phases; no hexagonal 2:17 spots are noticeable. From the diffraction information, the usual hexagonal-rhombohedral orientation relationship is found to apply:

$$(0001)_{1:5} \ // \ (0001)_{2:17}$$

$$[11\bar{2}0]_{1:5} \ // \ [1\bar{1}00]_{2:17}$$

The higher intensity spots in the SAD are common to both phases; they appear as stars due to the shape effect of, or lattice strain associated with, the 1:5 cell walls. The actual image contrast of the cellular structure is due to the lattice strain which arises because of the misfit of the two coherent phases. The misfit is reflected in the SAD pattern by the slight splitting of spots in the higher order reflections.

The twinning within the rhombohedral 2:17 cells is visible in the micrograph as bands of alternating intensity running perpendicular to the c-axis. The twins can be explained fairly easily with reference to the crystallography of the 2:17 phase. The 2:17 is generated from the 1:5 phase by replacing one third of the Sm atoms with pairs of Co atoms. The two simplest ways of arranging these substitutions generate the hexagonal (2H) and rhombohedral (1R) 2:17 structures, the rhombohedral structure having an ... ABCABCA ... type stacking sequence. Occasional reverses in this stacking are possible; they, in fact, produce the coherent twins ... ABCABACBA ... . This twinning is totally conservative; although it is possible for it to compensate for lattice strain, it cannot, by itself allow for deviations from stoichiometry.

The thin Z-phase plates, visible in Fig. 1(a) as linear features running across the image, are responsible for the faint streaking of the spots at 8 inverse angstroms in the SAD pattern. The number of these plates is highest in the high Zr magnets; after step aging these magnets develop the highest iHc. However, because the Z phase occurs as plates which are usually less than 3nm thick, it is very difficult to characterize them. It was, therefore, necessary to overage a specimen in order to coarsen its microstructure. The image of one of these coarsened Z phase plates is shown in Fig. 2(a), with corresponding SAD pattern in Fig. 2(b). The matrix pattern is $\langle 11\bar{2}0 \rangle_{Hexagonal}$; the extra spots can be indexed as a rhombohedral phase with c $\sim$2.4nm and a $\sim$0.5nm. The reciprocal lattice of the Z phase is very similar to that of the binary $SmCo_3$ phase which has space group $R\bar{3}m$. The orientation relationship between the Z phase and the matrix hexagonal phase is:

$$(0001)_{1.5} \; // \; (0001)_{Z\ \mathrm{phase}}$$

$$[11\bar{2}0]_{1.5} \; // \; [11\bar{2}0]_{Z\ \mathrm{phase}}$$

The spots in the pattern correspond to two twin-related variants; the line at the center of the coarsened plate is presumably the twin interface. Tilting experiments indicate that the interfacial dislocation structure goes out of contrast for a diffracting vector parallel to the c-axis indicating that the primary lattice mismatch is perpendicular to the c-axis. This is in agreement with the direction of spot splitting in Figure 2(b).

In general, magnets with 3% Zr have smaller cells than the magnets with 1.5% Zr for similar thermal treatments. Since the 1:5 cell walls have nearly constant thickness, the 3% Zr alloys have a larger volume fraction of the 1:5 material. Furthermore, the 1:5 cell walls in the low Zr magnets are more disordered and more often curved than the walls in the high Zr magnets. Alloys with 3% Zr have more, and thicker, Z phase plates, but fewer twin interfaces than do the 1.5% Zr alloys. Step aging does not change cell size nor Z phase density.

X-ray fluorescent microanlaysis of overaged (860°C for 100 hours) alloys has revealed that the Cu tends to segregate to the Z phase as well as the 1:5 phase. The 2:17 phase is enriched in Fe and Zr is concentrated in the Z phase. An example of a spectrum comparing the Z phase with the 2:17 phase is shown in Fig. 3.

Figure 4, taken from Reference 2, shows the intrinsic coercivity as a function of time at 850°C isothermal aging temperature. The four curves are for the 1.5 and 3% Zr alloys, both isothermally aged and quenched and isothermally aged and step aged. As can be seen, the step aging treatment is essential for the development of high iHc. Additions of Zr are ineffective without a step aging treatment.

DISCUSSION

The development of useful microstructures involves essentially two different processes--growth and chemical redistribution. Growth occurs primarily during the 850°C isothermal anneals and necessarily involves the diffusion of Sm. It has been suggested[5] that it is a minimization of elastic strain energy during growth which produces the pyramidal habit of the 1:5 cell walls and the resulting cellular morphology. The fact that the presence or absence of step aging treatments does not change the cell size indicates that growth, and therefore diffusion of Sm, is essentially suppressed during step aging. However, because coercivity increases during step aging, there is strong reason to believe that the redistribution of the transition metals Fe-Cu-Co contains during step aging and that this redistribution is beneficial. The driving force for continued redistribution is the reduction of the extent of solid solubility at lower temperatures; that is, the equilibrium compositions at 400°C are more dissimilar than the equilibrium compositions at 850°C. Redistribution is accomplished by diffusion of the transition metals through the relatively open Co sites of the lattice. This, it can be concluded that growth during 850°C anneals determines the size of the cellular structure, but redistribution of the transition metals at 400°C is still necessary for ultimate intrinsic coercivity.

Zr has four major effects in these processes. At high temperatures, Zr tends to inhibit Sm diffusion; this can be seen from the differences in size of the microstructures for the 1.5 and 3% Zr alloys after similar heat treatments. Secondly, if the elastic strain energy origin of the cellular structure is correct, Zr must promote misfit between the 1:5 and 2:17 cellular structures. This conclusion is obtained from the fact that the pyramidal habit is more rigorously obeyed in the high Zr alloys. Probably the most important effect of Zr is that it ultimately leads to nucleation and formation of the Z phase plates. The approximate time of nucleation of the Z phase plates has been indicated in Fig. 4; one can see that step aging treatments are always more effective when there are significant numbers of Z phase plates in the matrix. Finally, Zr must further reduce the limits of solubility of Fe in 1:5 and Cu in 2:17 leading to even greater compositional differences between the two major phases. This can be seen in Fig. 4 where it is shown that, even in the presence of the Z phase, the 1.5% Zr step aged alloy never develops the coercivity of the 3% Zr step aged alloy.

Of these four effects, the intrinsic coercivity is not likely to be strongly dependent on either cell size or cell wall perfection. The coercivity as controlled by domain wall pinning should depend on the strength of the strongest pinning sites and not on their distribution. The remanence probably depends more strongly on these factors. The last two effects work together; Zr increases the driving force for diffusion and the Z phase plates serve as high diffusivity paths for the Cu, Fe and Co. Thus, these two effects should very strongly control the coercivity and an interpretation of the results of the previous paper[2] in these terms gives satisfactory results.

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REFERENCES

1. Ojima, T., Tomizawa, S., Yoneyama, T. and Hori, T., IEEE Trans. Magn. MAG-13, 1317 (1977).
2. Mishra, R. K., Thomas, G., Yoneyama, T., Fukuno, A., and T. Ojima, J. Appl. Phys. 52, 2517 (1981).
3. Mishra, R. K., and Thomas, G., Proc. 4th. International Workshop R-Co Magnets, p. 301 (1979).
4. Bertaut, E. F., Lemaire, R., and Schweizer, J., Bull. Soc. franc Miner. Crist. 88, 580 (1965).
5. Livingston, J. D. and Martin, D. L., J. Appl. Phys. 48, 1350 (1977).

FIGURE CAPTIONS

Fig. 1a Transmission electron micrograph (symmetric $[01\bar{1}0]$ orientation) showing the microstructure of a 3% Zr alloy near peak aging. The c-axis is in the plane of the paper in the direction indicated. (b) Selected area diffraction pattern and indexing showing hexagonal 1:5 and rhombohedral 2:17 spots. Solid triangles correspond to spots common to all phases; solid circles are from one 2:17 variant, open circles are from the other.

Fig. 2a Transmission electron micrograph (symmetric $[11\bar{2}0]$ orientation) showing a Z phase plate after overaging. (b) Selected area diffraction pattern and indexing. Solid triangles denote 1:5 and 2:17 phase spots; circles are from the Z phase. For simplicity, only one Z phase variant has been indicated.

Fig. 3 X-ray microanalysis spectra comparing the 2:17 phase with the Z phase.

Fig. 4 Intrinsic coercivity as a function of isothermal aging time for 1.5 and 3% Zr alloys with and without step aging. The approximate time of nucleation of the majority of the Z phase plates has been indicated by a Z on each curve.

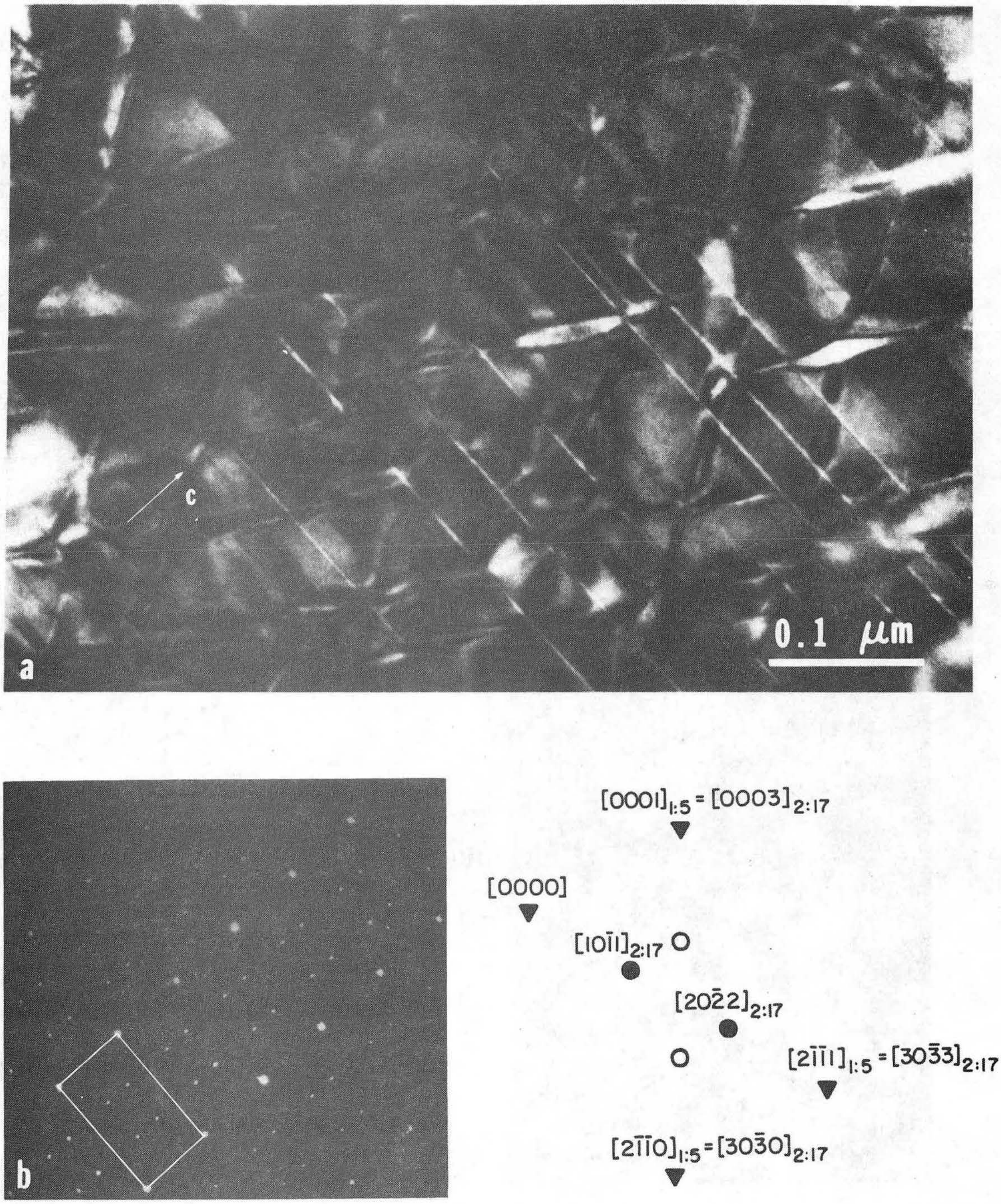

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Fig. 1

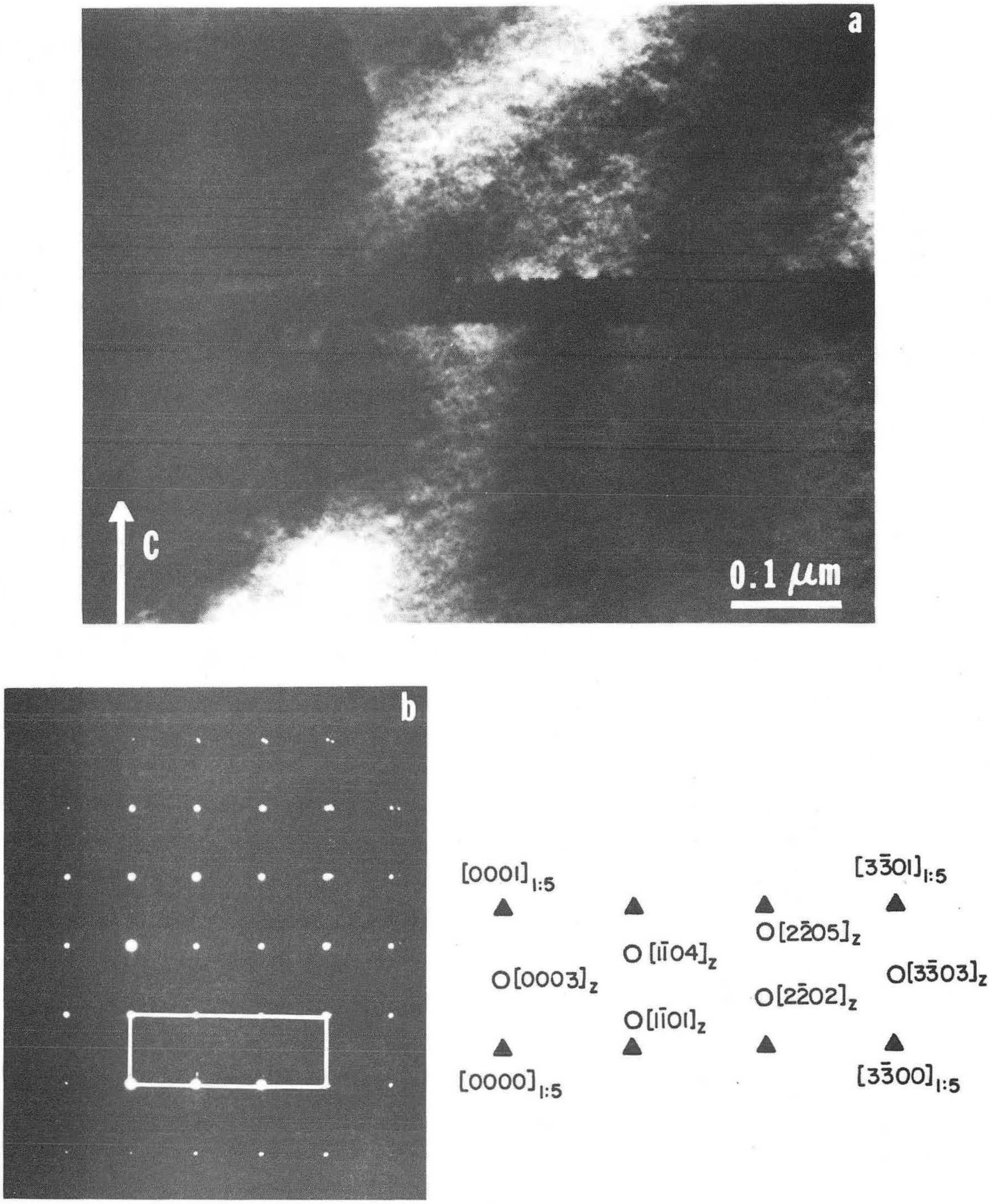

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Fig. 2

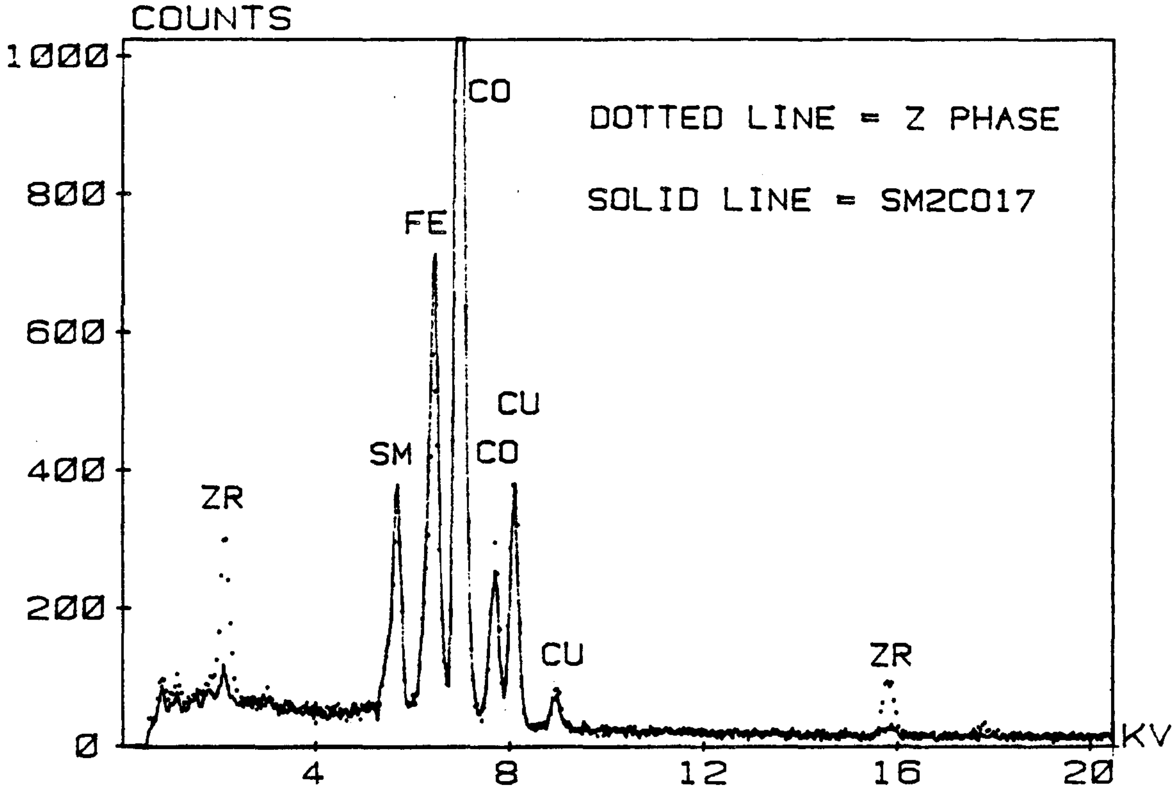

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Fig. 3

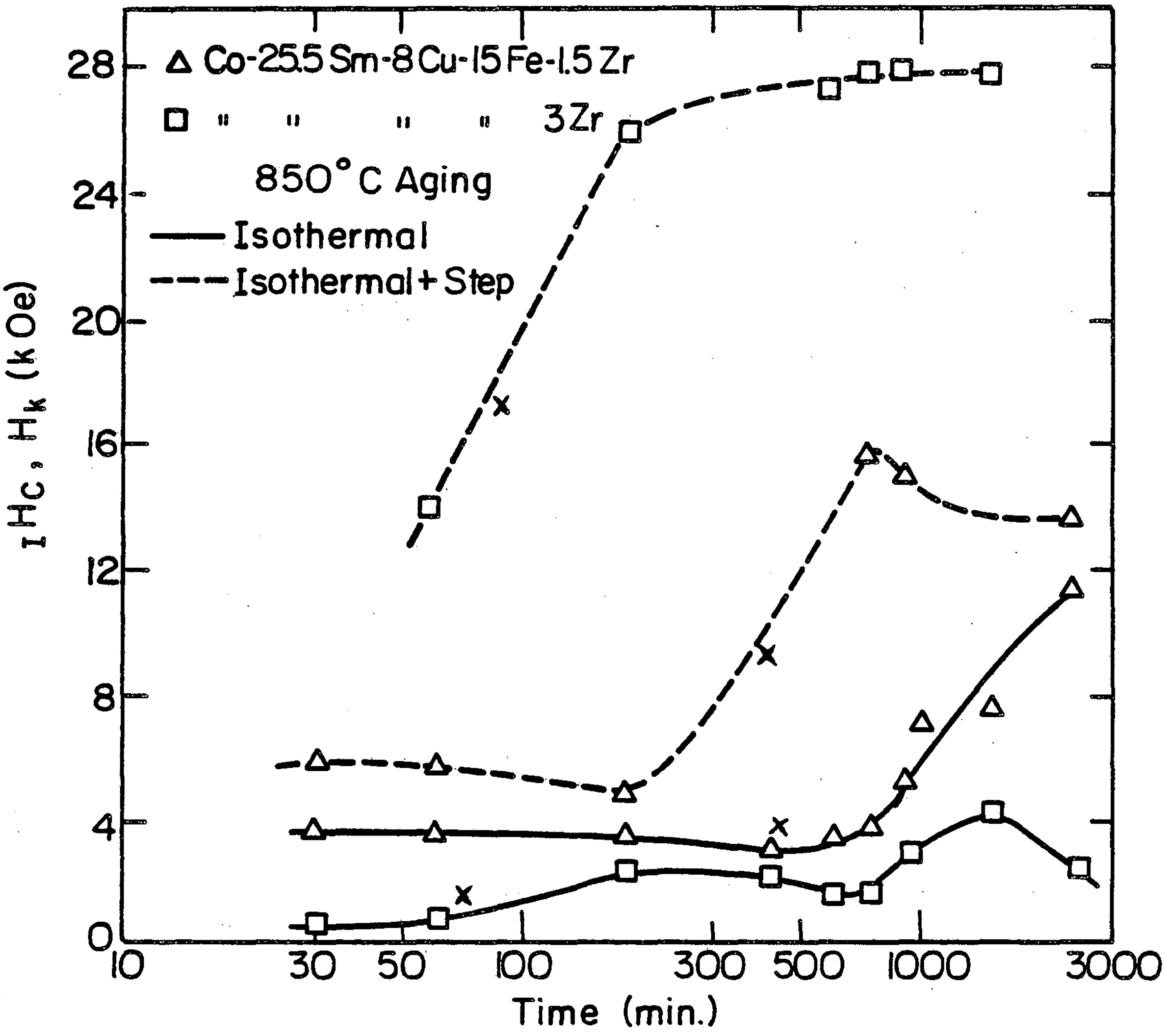

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Fig. 4

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