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J.S. Gau, R.K. Mishra, and G. Thomas

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Study of Precipitation and Fracture in Air-Cast Mn-Al-C Magnets

J. S. Gau*, R. K. Mishra and G. Thomas

Department of Materials Science and Mineral Engineering

and the

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

*Present address: Eastman Kodak Company, Rochester, N. Y.

Mn-Al-C alloys with suitable alloying and thermomechanical treatments exhibit hard magnetic properties comparable to those of Alnico and Fe-Cr-Co magnets [1]. Although the theoretically predicted values of $(BH)_{max}$ have not yet been achieved in practice [2], a combination of factors such as low cost, energy density per unit weight, mechanical properties in the magnetic state, etc. have necessitated further research to understand the microstructural and other aspects of this magnet system. In this paper, results of an electron analytical study of precipitation and fracture in air cast warm extruded Mn-Al-C alloys are presented. Details of this alloy can be found in Ref. 2.

Although earlier investigators had suggested that carbides precipitate out from the Mn-Al-C solid solution [3,4] during warm extrusion, subsequent investigation has shown it not to be true [2]. Instead, a new class of precipitates has been observed in materials which were originally melted and cast in air. The scanning electron micrograph and the transmission electron micrograph in Fig. 1 show these precipitates, their size and distribution in the material. The precipitates are about 10-50nm in size and distributed inhomogeneously in the material. To examine these particles further, they were extracted from the alloy using the carbon extraction replica technique [5]. Fig. 2a is a bright field image of the replica containing few precipitates. The corresponding EDX spectrum recorded using a Philips EM400 analytical microscope is shown in Fig. 2b. It can be seen that a strong Al signal arises from the precipitates. A small amount of S is also detected. The EDX technique using an EM400 cannot detect x-ray signals from oxygen atoms, but Auger electron spectrosocpy can detect an oxygen signal. In order to complete the chemical characterization of the precipitates, a specimen was fractured in a Phi 590 scanning Auger microscope. The Auger specta recorded

from the fractured surface is shown in Figs. 3a, b and c. Fig. 3a is the spectrum obtained from a region free of the precipitates. Since the material fractures by intergranular mode (an SEM image of a fractured surface is shown in Fig. 4), the Auger spectrum in Fig. 3a shows that the grain boundary in Mn-Al-C has oxygen atoms present on it. If the fractured surface is sputtered with Al ions for a few seconds to remove a ~5nm layer of material, the oxygen signal decreases (Fig. 3b). The spectrum from an area containing the precipitates is shown in Fig. 3c and it contains the oxygen signal in addition to the Al signal. A point to note here is that although the Al signal is present in all cases, the fine structures of the Al signals in Figs. 3a and b are different from those in Fig. 3c. Comparing the five structures of the Al signal from the alloy with reference spectra [6] of pure Al and pure Al_2O_3, it can be seen that while the fine structures in Figs. 3a and b correspond to the reference spectrum from the Al metal in Fig. 3b, the signal in Fig. 3c arises from Al_2O_3 and thus corresponds closely to the reference spectrum from Al_2O_3 as shown in the inset of Fig. 3c. A small amount of S is also detected from these precipitates.

Two conclusions emerge from these observations. First, the particles seen in Fig. 1 are Al_2O_3 particles. The formation of these particles is related to the oxidation of Al atoms during processing, which consists of melting and casting. Al_2O_3 particles result from both oxidation of the melt surface and oxidation during casting when the melt is in contact with air. The surface oxides then mingle and disperse in the material during subsequent processing. Since the free energy of formation for Al_2O_3 is almost twice that of MnO at the melt temperature (-200 kcal and -100kcal respectively [7]), it is not surprising that no MnO particles are seen. S is present as an impurity in the starting material. Secondly, there is still some oxygen segregated near the grain boundary regions. This observation can

explain why the Mn-Al-C alloys are so brittle and the fracture mode is mainly intergranular in nature. In fact, since no second phase that can cause intergranular fracture has been detected at the grain boundaries, oxygen enhancement at the boundary is believed to be responsible for the intergranular mode of fracture and the consequent brittleness of the material.

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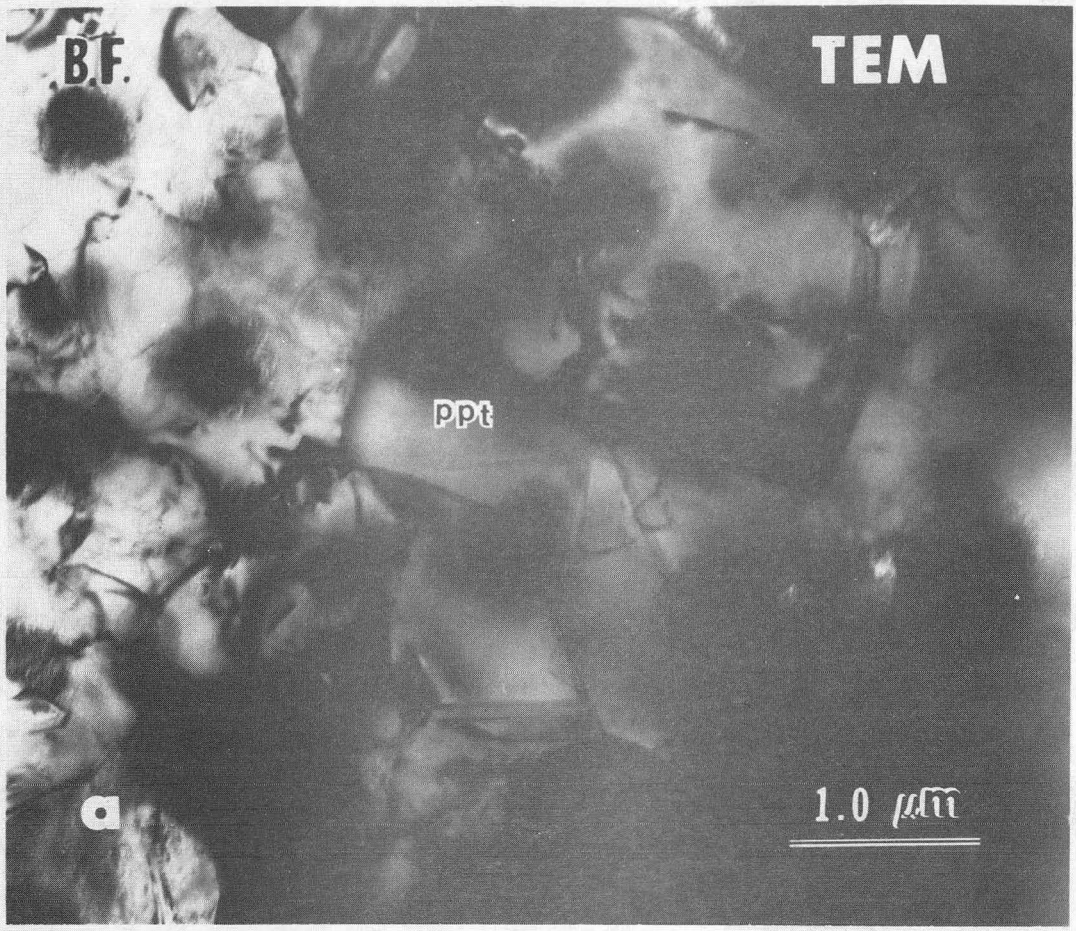
Figure Captions

Fig. 1. (a) Bright field image of Mn-Al-C alloy showing small precipitates (black regions) dispersed in the extruded material; (b) scanning electron micrograph showing the precipitates on a polished and etched surface.

Fig. 2. (a) Bright field image of a carbon extraction replica showing the Al_2O_3 precipitate; (b) corresponding x-ray fluorescence spectrum showing high Al content. Cu and Cr signals are from the background and the S signal arises from the Al_2O_3 particle.

Fig. 3. Auger electron spectra taken from (a) in-situ fractured surface; (b) after sputtering the surface with Ar ion showing reduced oxygen content and (c) from the precipitates. The inserts in (b) and (c) are reference Al spectra of pure Al and pure Al_2O_3 [6].

Fig. 4. In-situ fracture surface of the extruded Mn-Al-C magnet showing characteristic intergranular fracture.



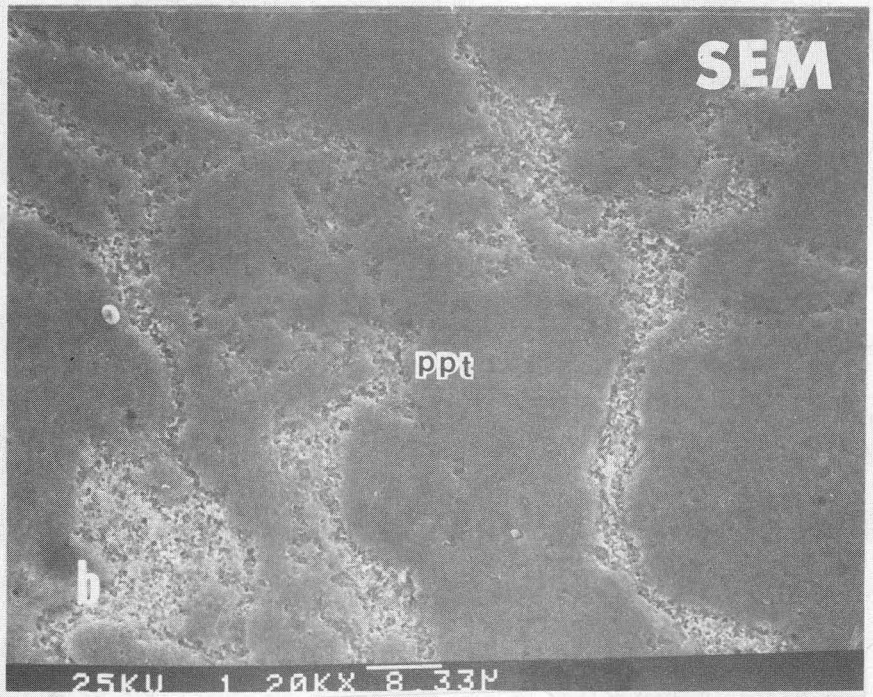


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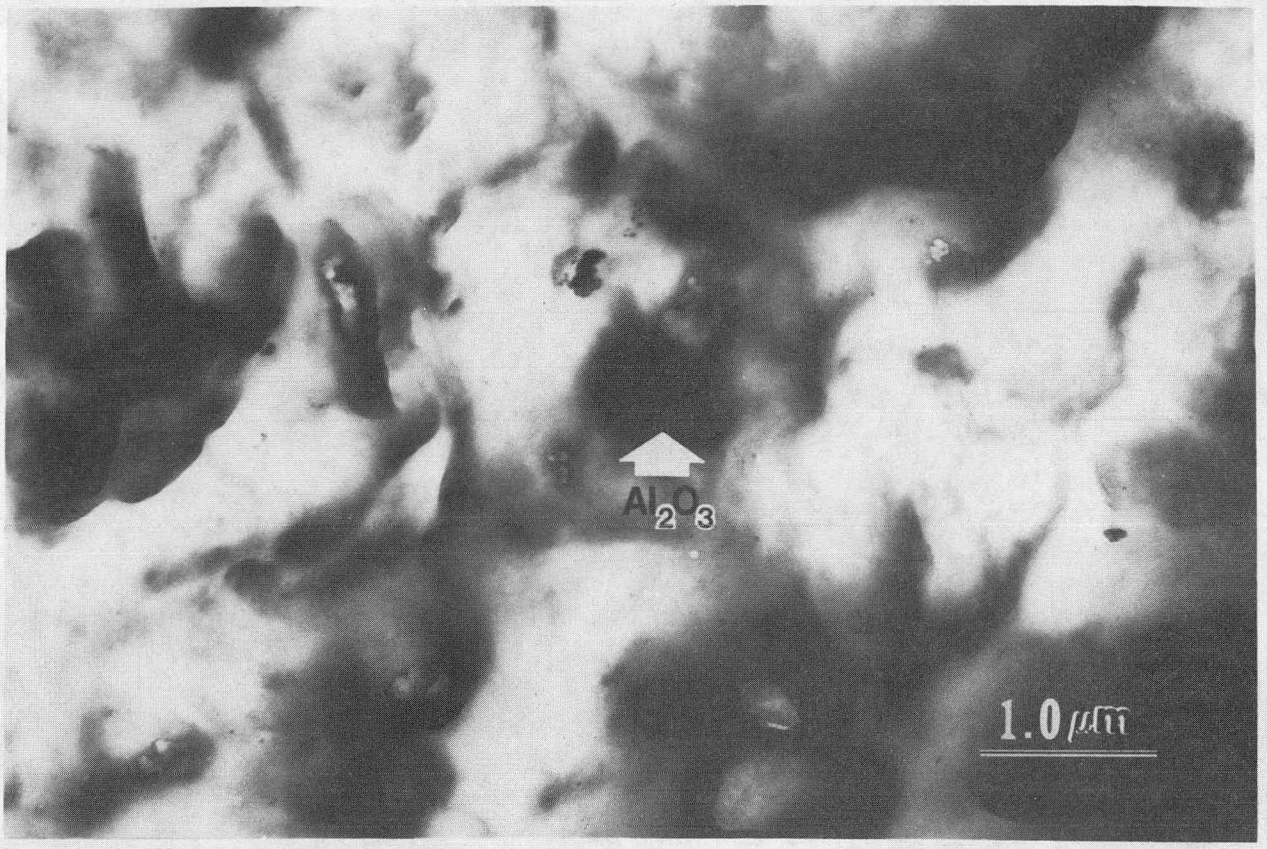
Fig. 1



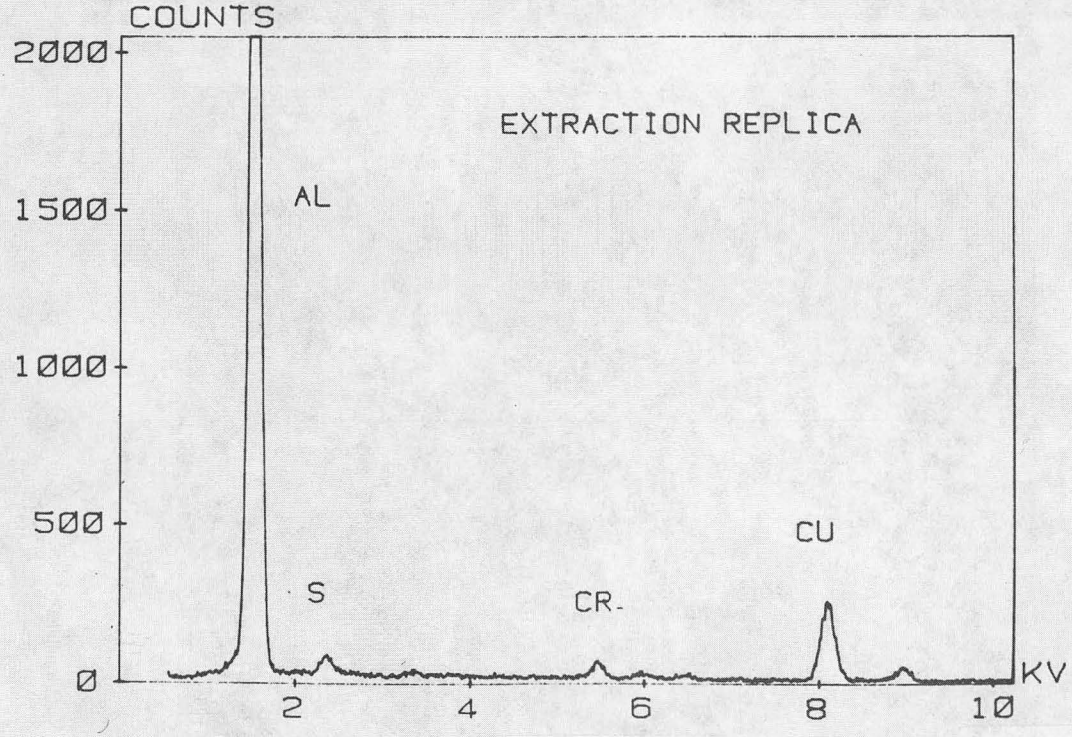


Fig. 2

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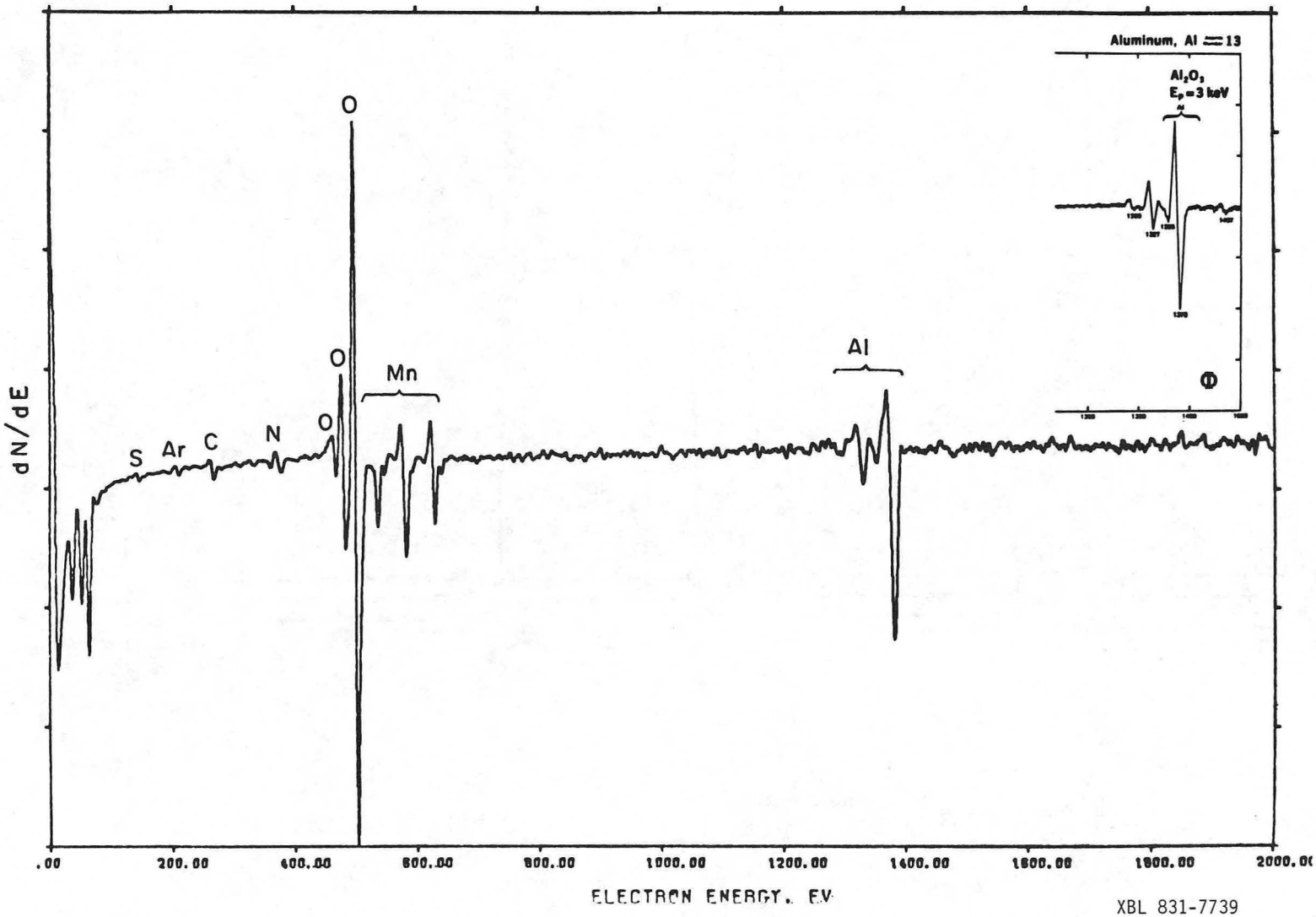

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Figs. 3a,b

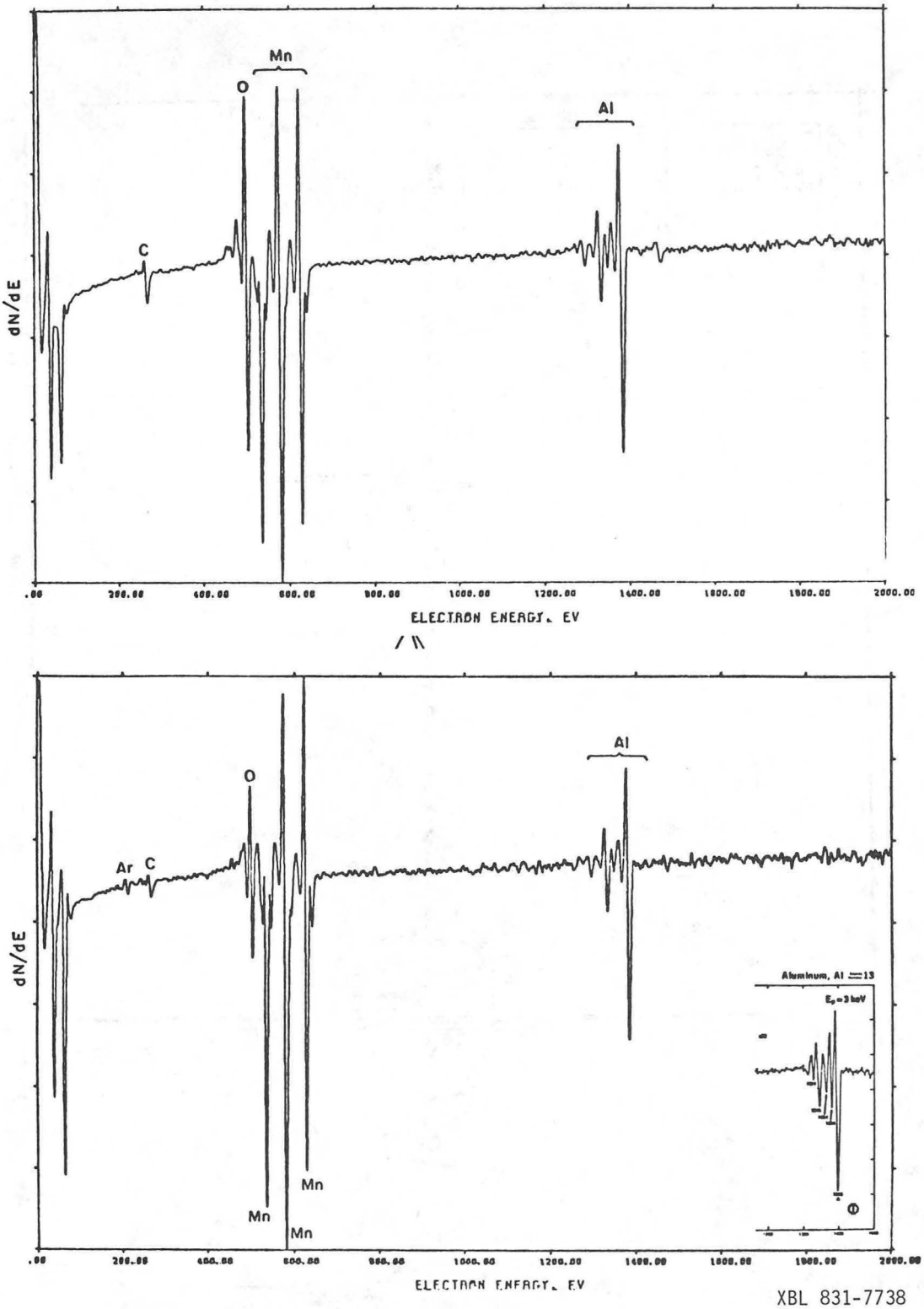

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Fig. 3c

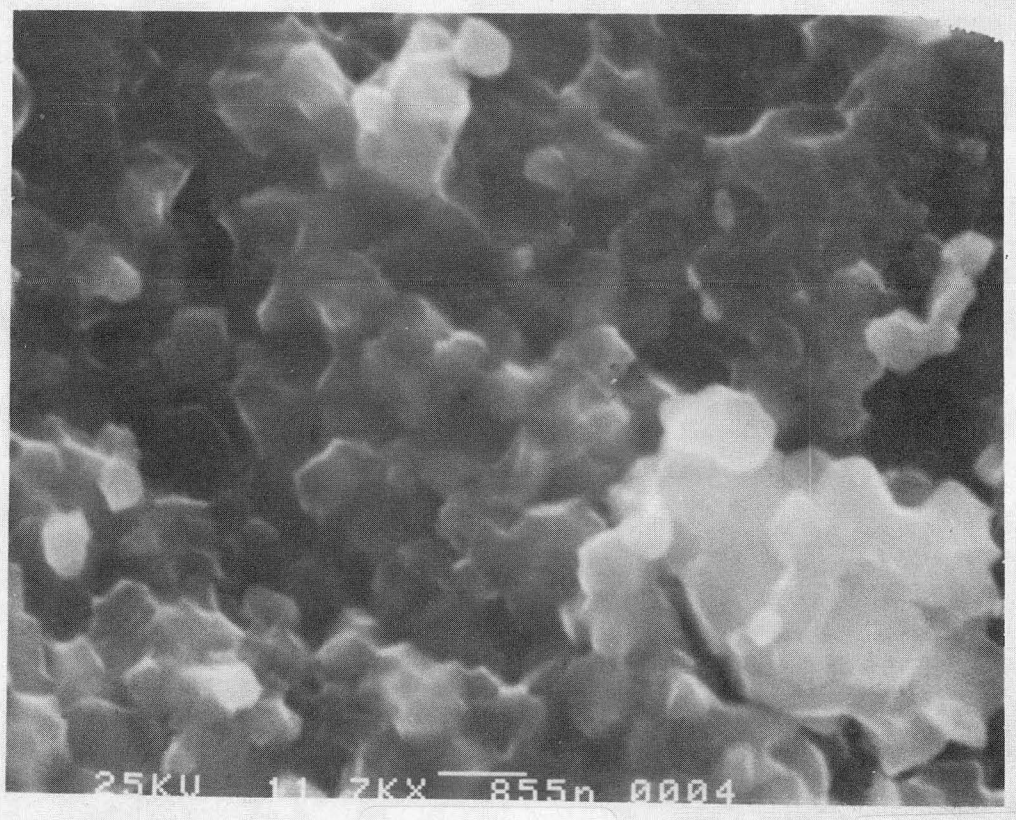

Fig. 4

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