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Author
Howe, J.

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Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

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J. Howe

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DISCLAIMER

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J. Howe*

Department of Materials Science and Mineral Engineering

and the

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720

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*formerly with Kaiser Aluminum and Chemical Corporation, Center for Technology, Pleasanton, CA 94566

Abstract

The size, type and distribution of insoluble dispersoids and age-hardening precipitates influence the processing and final properties of aluminum alloys and accurate characterization of these sub-micron precipitates is often required. A modified version of a relief etching technique introduced by Ryvola and Morris [1] now allows rapid determination of their size, shape and distribution in the SEM in addition to facilitating accurate chemical and microstructural analyses by TEM/STEM analytical and diffraction techniques. The etching procedure is applicable to almost all second phases commonly found in aluminum alloys and is simple to use.

Introduction

Several years ago, Ryvola and Morris [1] introduced a KI + methanol electrolytic etch which they used to selectively remove the aluminum matrix from around the intermetallic phases in direct-chill ingots of commercial purity aluminum, AA 6063 alloy and AA 356 casting alloy. This technique enabled them to study the effects of composition, solidification and thermal treatments on the intermetallic phases by scanning electron microscopy and x-ray diffraction.

We applied the KI + methanol etch to several different cast and wrought alloys according to the procedures outlined by Ryvola and Morris. The etch worked well for their intended applications, but etched surfaces were too rough to accurately determine such factors as the size and distribution of sub-micron precipitates. Collection of such precipitates for x-ray diffraction was also very difficult. We therefore tried different combinations of current, voltage and etching time and arrived at one which facilitates rapid characterization of both intermetallic dispersoids and soluble, age-hardening precipitates in the SEM. In addition, the KI + methanol solution was used to jet-polish thin foils for TEM examination. Preferential polishing of the aluminum matrix occurs, leaving sub-micron precipitates exposed and available for accurate chemical and microstructural analyses.

Materials and Procedures

The alloys investigated were 3003 homogenized billet, 3004 can stock, 5182 hot-rolled sheet, 2124 plate in differently aged conditions and 7475 extruded rod.

For SEM examination, etching was performed using a Hewlett-Packard, Harrison 6299A D. C. power supply. 6.4 grams of KI were dissolved in 0.32 liters of methanol in a 0.60 liter beaker to make a 2.5wt% solution. An aluminum sheet (cathode) was fitted inside the periphery of the beaker and the samples (anodes) were suspended in the center.

Typical metallographic samples with a 1µm diamond polish were etched. The etching was confined to about 3mm x 3mm areas by covering the remainder of the samples with plater's tape.

To begin etching, the current was turned all the way up. The voltage was then rapidly increased from 0 to 30 volts and samples etched for 30 seconds. A magnetic stirrer gently rotated the solution during etching. The current density averaged about $0.3A/mm^2$.

Immediately after etching, the samples were ultrasonically rinsed in methanol for 30 seconds. They were examined in an ISI Super IIIA SEM at 30 keV, in the secondary electron mode, with a 20° tilt and no evaporated coating.

The 2.5wt% solution was also used to prepare TEM specimens. 3mm discs were polished in a twin-jet Fischione apparatus at -30°C, with an applied potential of at least 90V. The current density averaged about 9.0 x 10^{-3} A/mm^2 and the foils were washed thoroughly in methanol immediately after polishing. The current density/voltage curve for the KI + methanol solution is roughly straight (Fig. 1) and polishing begins along the perimeter of the foil around 70V and encompasses the whole foil surface above about 90V. Foils were examined in a Philips EM301 microscope at 100keV.

Differential scanning calorimetry (DSC) analyses were performed on a DuPont 900 thermal analyzer equipped with a DSC cell. Rectangular specimens about 6mm x 5mm x 2mm thick were cut from each of the five aged 2124 samples and ground on a 400 grit SiC water wheel to about 319 mg weight. Instrument settings of: Heating Rate = 20°C/min, T = 100°C/in and ΔT = 0.5°C/in were employed. The samples were compared with a 319 mg, annealed 99.99% Al reference.

Results

Figs. 2a and b show SEM micrographs of the Mn constituents and dispersoids in 3003 homogenized billet. The state of the dispersoids crucially affects the subsequent recrystallization behavior of this alloy and the etched surface is smooth enough to determine their size, shape and distribution using both low and high magnifications.

In 5182 hot-rolled sheet, the Mg_2Al_3 phase is dissolved by the KI + methanol etch. This, however, facilitates direct observation of the Mn dispersoids, which also affect critical properties in this alloy (Figs. 3a and b). Mg_2Si precipitates are also revealed in this alloy as in 6000 series alloys, but can be eliminated by a short solution heat-treatment followed by a cold water quench. This does not alter the state of the Mn dispersoids significantly.

The KI + methanol etch also exposes Al_2CuMg precipitates in 2124 alloy, provided they are not coherent with the aluminum matrix. Figs. 4, 5 and 6 show optical and SEM micrographs and DSC thermograms of 2124 plate which was aged to produce a variety of precipitate structures according to the aging data of Silcock [2] (Fig. 7).

The optical micrographs in Fig. 4 show increased darkening with Keller's etch as precipitation progresses. In Fig. 4a only the Mn dispersoids appear as fine dark speckles but with further aging, as in b, the background darkens and grain boundaries are noticeably decorated. There is also slight decoration of slip bands which formed during quenching.

The precipitates are more clearly revealed by the series of SEM micrographs in Fig. 5. These micrographs show that with the KI + methanol etch: (1) G.P.B. and G.P.B. [2] zones are associated with smooth or slightly fuzzy areas; (2) the S' phase may be revealed as fine, oriented precipitate and, (3) the S phase is clearly visible as distinct laths. The grain boundary precipitates are also readily visible in these micrographs.

The DSC curves of Fig. 6 confirm the presence of the precipitate structures and show a progressive increase in reversion temperatures (i.e. 177°C for sample 1 to 255°C for sample 5) and decrease in size of the S' + S precipitation peak (305°C) as aging progresses.

Also, the KI + methanol etch was used to reveal the Cr dispersoids in 7475 extruded rod (Fig. 8). A short solution heat treatment and cold water quench was again used to eliminate the soluble precipitates (compare Figs. 8 and 9). The size and distribution of the Cr dispersoids influence the processing and properties of many aluminum products, particularly in high strength, corrosion resistant 7000 series alloys.

When the KI + methanol solution is used to prepare thin foils of aluminum alloys for TEM examination, a similar relief effect occurs. Figs. 10a and b show sub-micron Mn dispersoids protruding from the edge of a hole in a TEM foil of 3004 can stock. The edge of the Al matrix is visible along each precipitate showing that they are readily available for chemical and micro-structural analyses using TEM/STEM analytical and diffraction techniques.

Conclusions

The KI + methanol solution can be used to expose sub-micron, age-hardening and intermetallic precipitates in a wide variety of cast and wrought Al alloys. The solution does not attack most precipitates, thereby permitting accurate evaluation of their size, shape and distribution in the SEM and chemical composition or structure by TEM/STEM analytical and diffraction techniques. Etching or polishing is rapid and simple and therefore is particularly beneficial when a large number of samples need to be examined.

Acknowledgements

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References

1. M. Ryvola and L. R. Morris, Examination of insoluble intermetallic phases in aluminum alloys, in Microstructural Science, Vol. 5, Elsevier North-Holland, Inc., New York (1977), pp. 203-208.

2. J. M. Silcock, The structural aging characteristics of Al-Cu-Mg alloys with copper: magnesium weight ratios of 7:1 and 2.2:1, J. Inst. Met. 89: 203-210 (1977).

Figure Legends

Fig. 1. Electropolishing curves for 2.5wt% KI + methanol solution.

Fig. 2. Mn constituents and dispersoids in 3003 homogenized billet.

Fig. 3. Mn constituents and dispersoids in 5182 hot-rolled sheet. Notice the grain structure in (a).

Fig. 4. Optical microstructures of 2124 samples with different precipitates.

Fig. 5. SEM relief-etched structures of differently aged 2124 samples.

Fig. 6. DSC curves of five aged samples with different initial precipitate structures.

Fig. 7. Structure occurring at various points on the aging curves for an Al-3.15% Cu-1.52% Mg alloy (after J. M. Silcock, Ref. 2).

Fig. 8. Cr dispersoids in 7475 extruded rod. Cr dispersoids as small as 500Å are visible in the right micrograph.

Fig. 9. Cr dispersoids and soluble phases in -F temper 7475.

Fig. 10. Mn dispersoids at perforation in TEM foil of 3004 can stock.

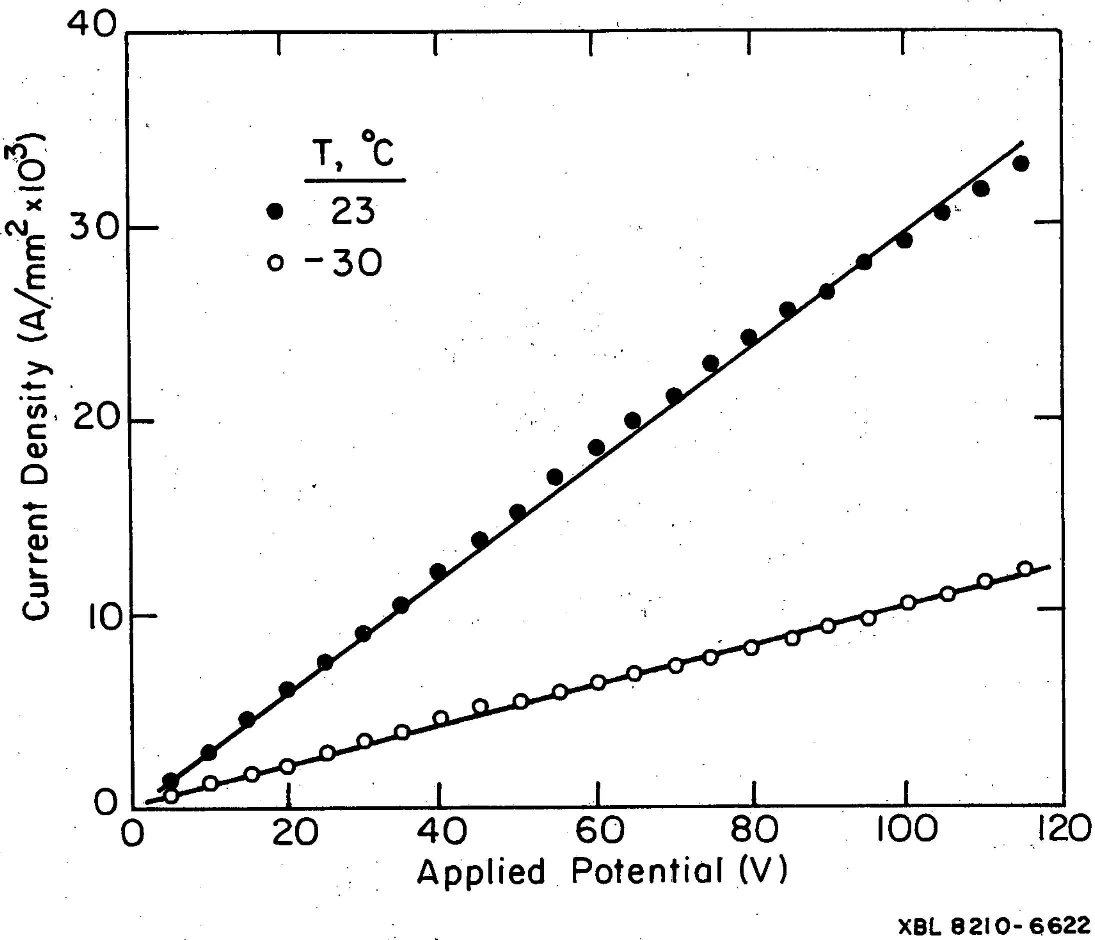

T, °C
23
-30
Current Density (A/mm^2 x 10^3)
Applied Potential (V)
0
10
20
30
40
0
20
40
60
80
100
120
XBL 8210-6622

Fig. 1

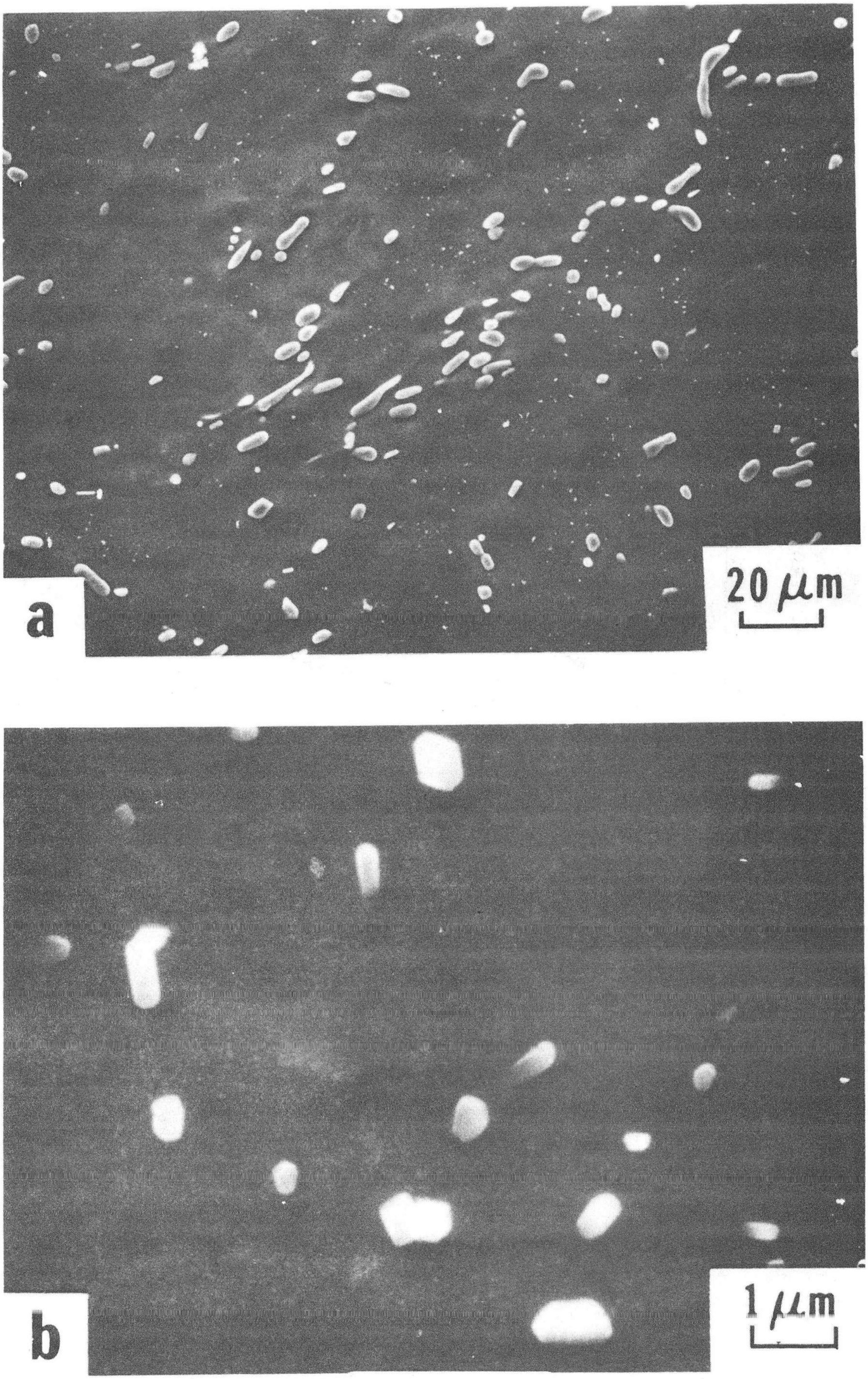


Fig. 2

XBB 820-8920

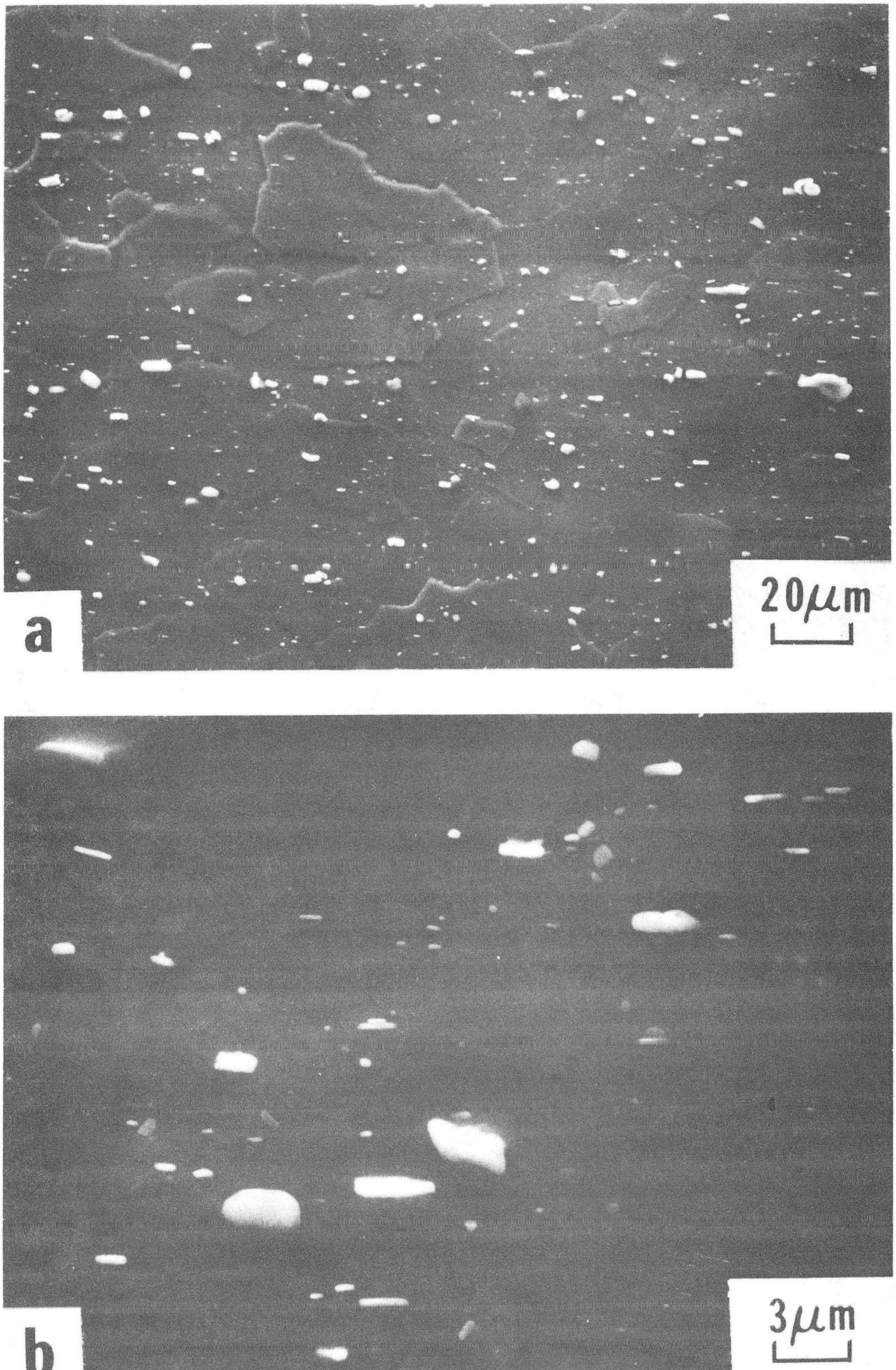
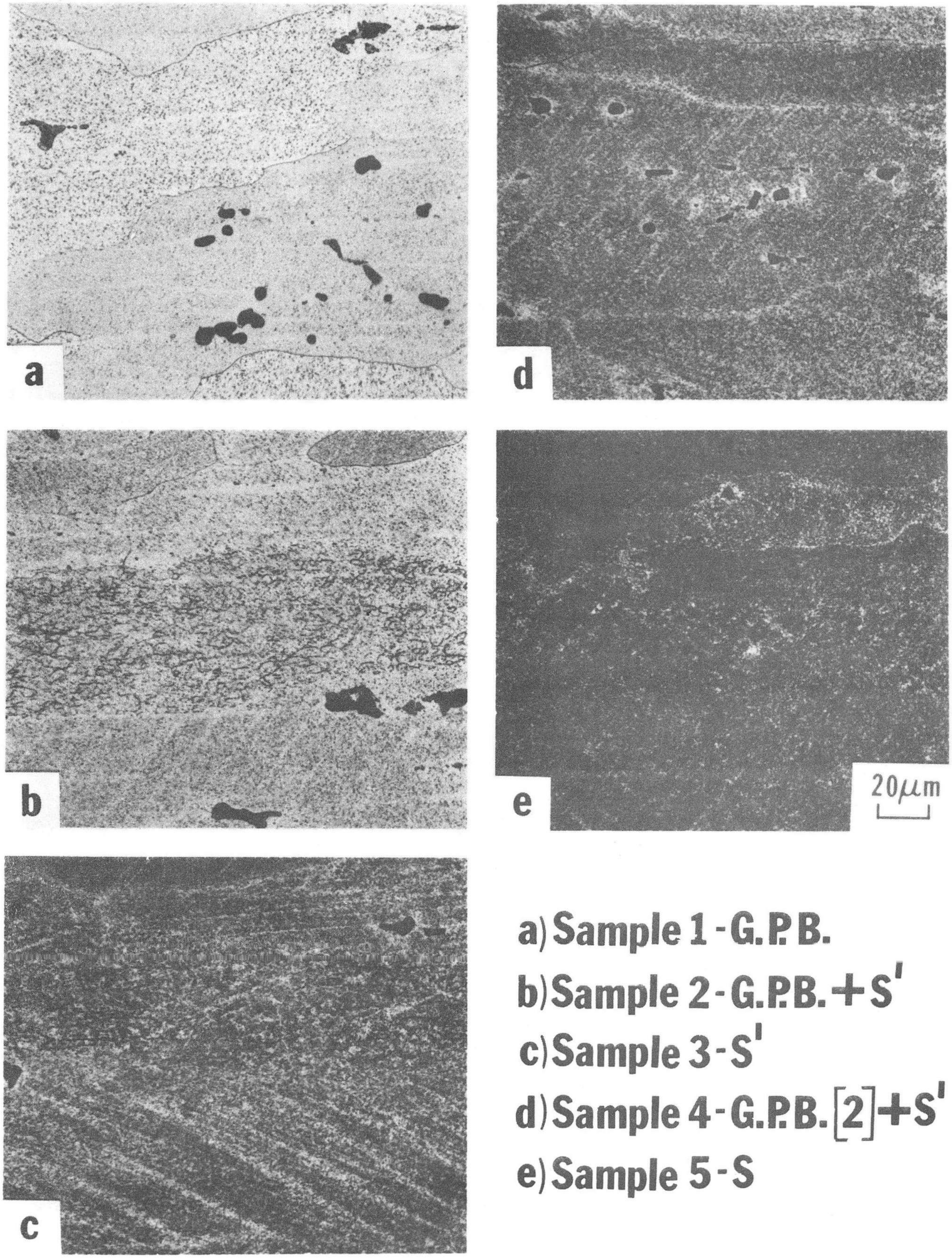


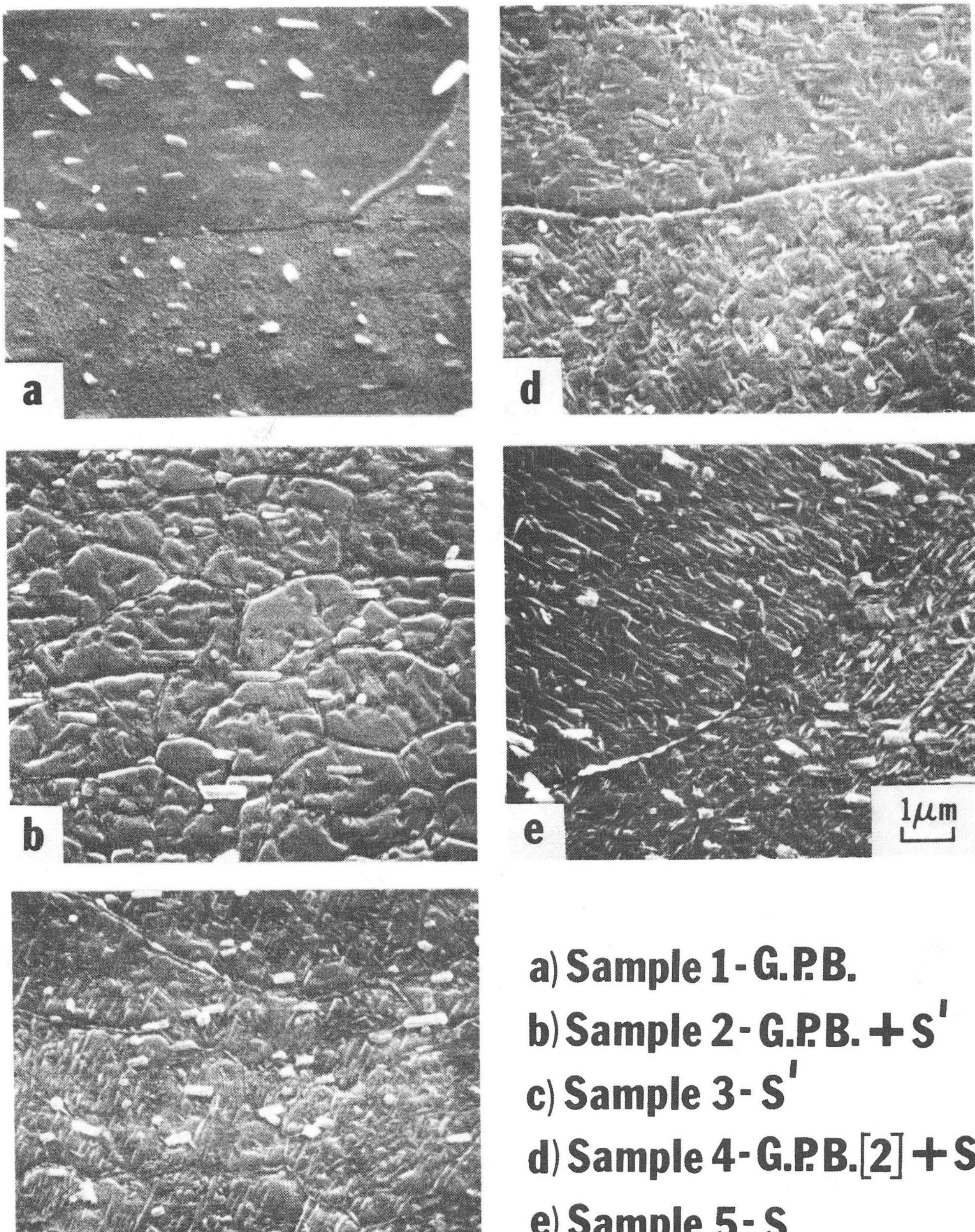
Fig. 3

XBB 820-8921



XBB 820-8916

Fig. 4



a) Sample 1 - G.P.B.

b) Sample 2 - G.P.B. + S'

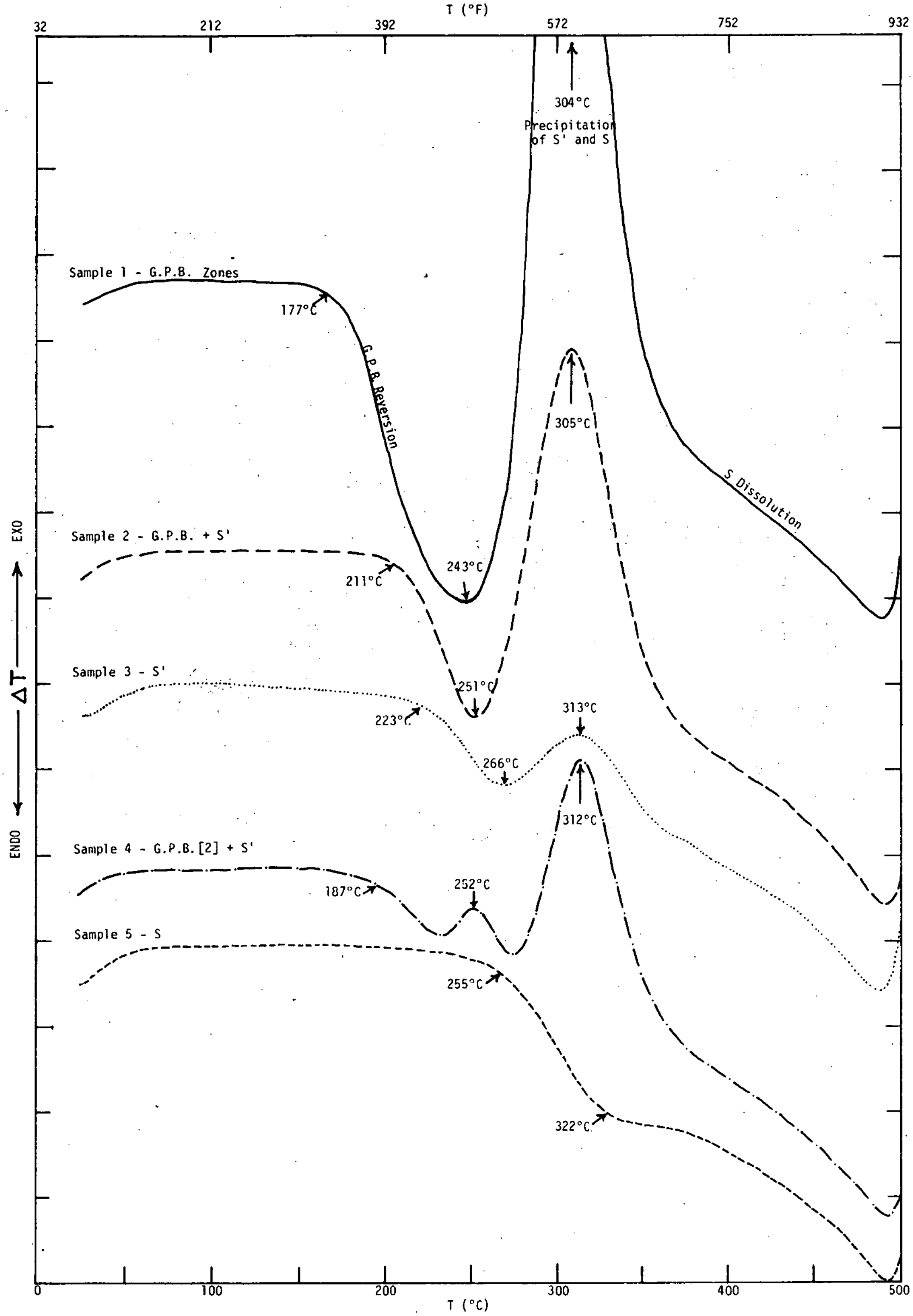
c) Sample 3 - S'

d) Sample 4 - G.P.B.[2] + S'

e) Sample 5 - S

Fig. 5

XBB 820-8917



XBL 8210-2858

Fig. 6

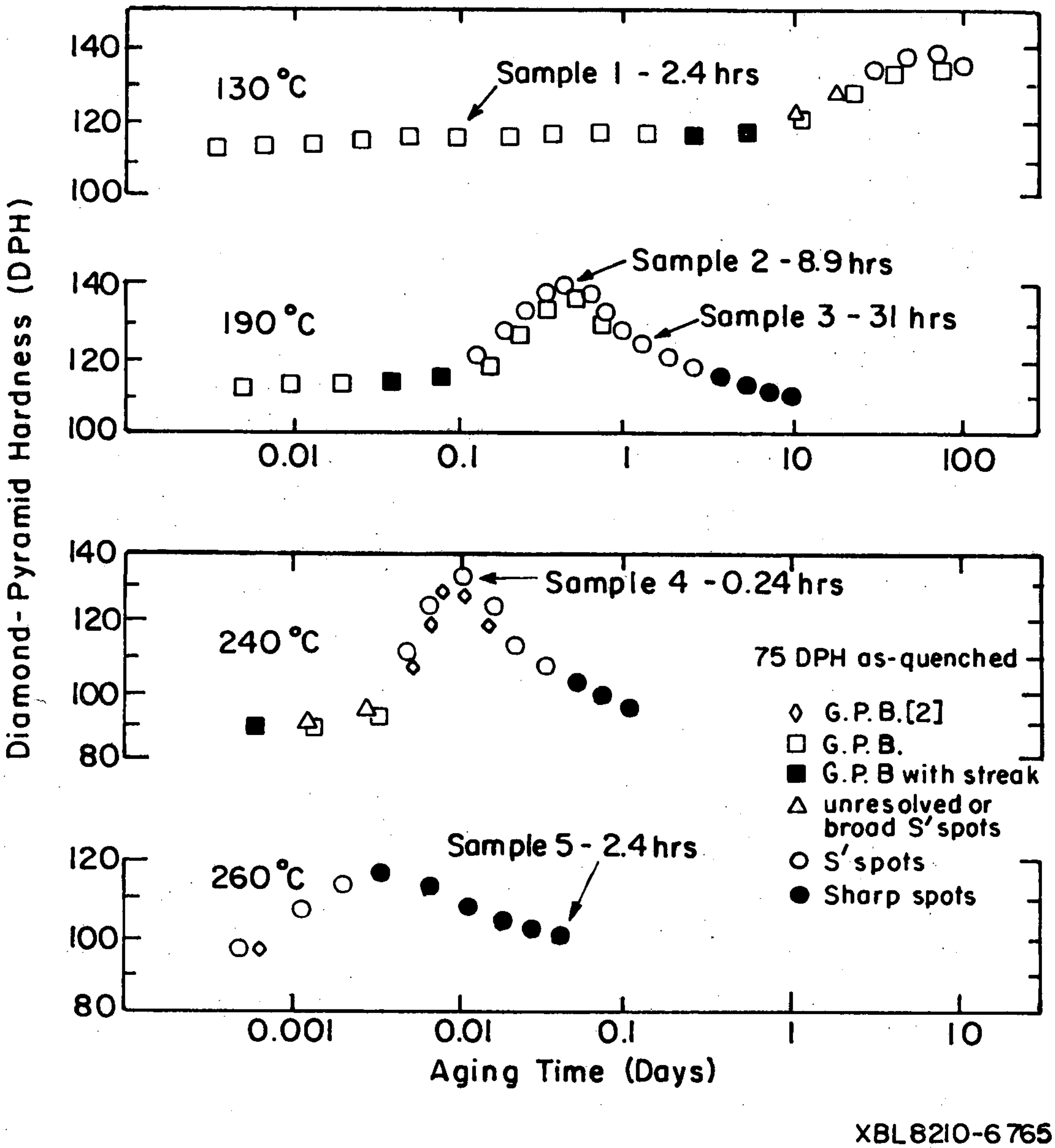
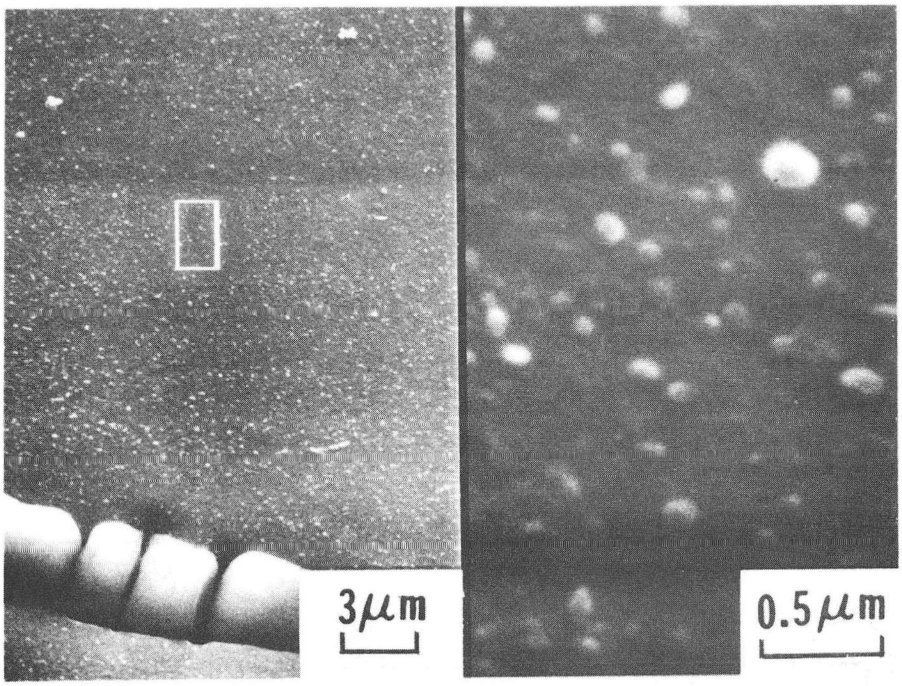
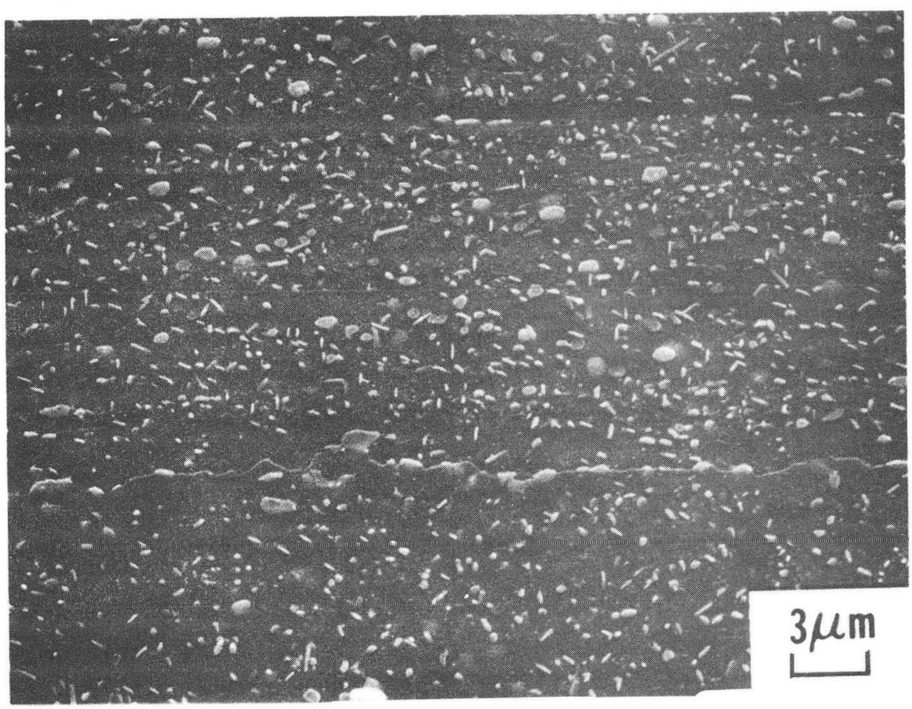
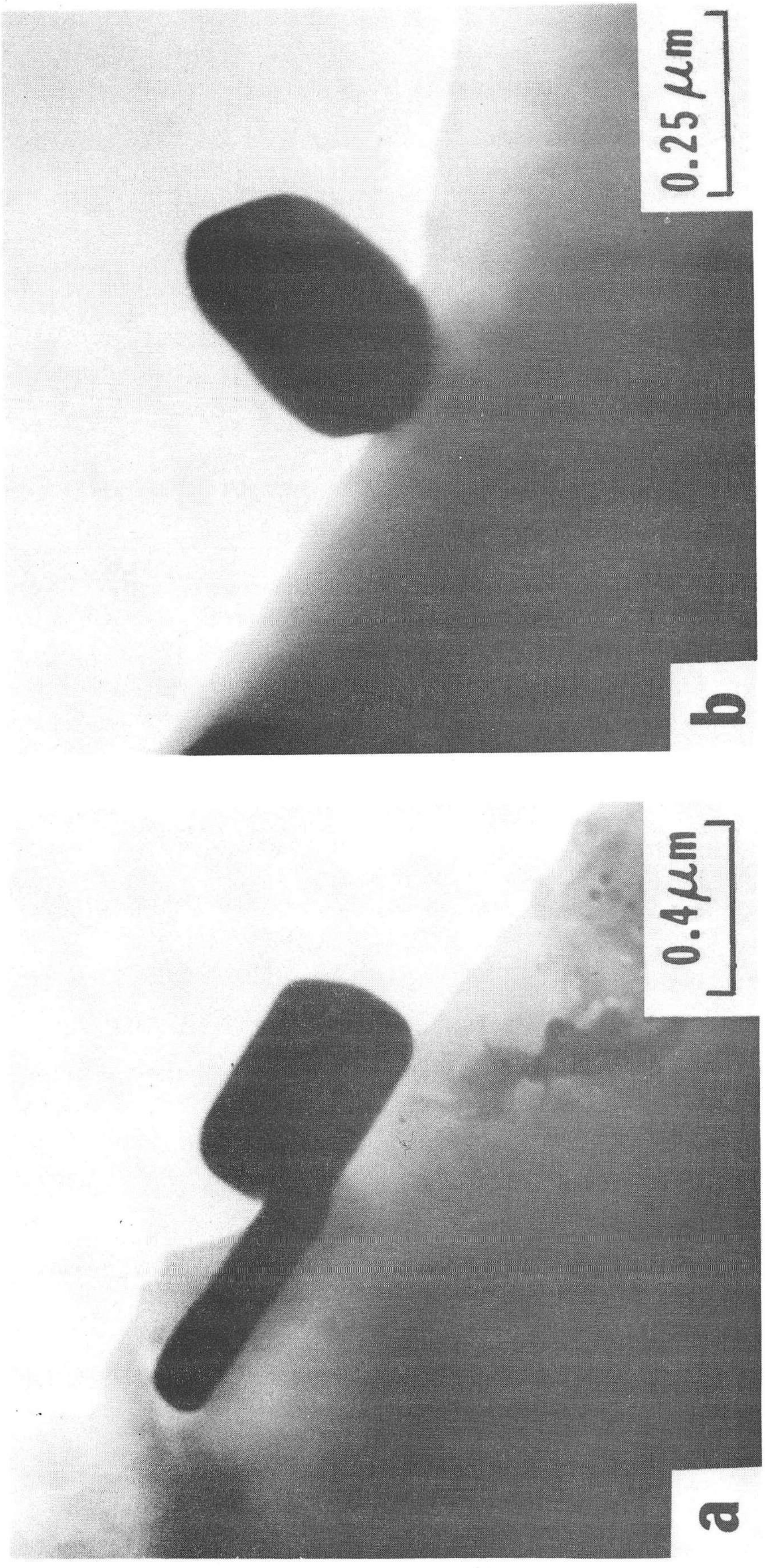

130 °C
Sample 1 - 2.4 hrs
190 °C
Sample 2 - 8.9 hrs
Sample 3 - 31 hrs
0.01
0.1
1
10
100
Diamond-Pyramid Hardness (DPH)
240 °C
Sample 4 - 0.24 hrs
75 DPH as-quenched
◊ G.P.B.[2]
□ G.P.B.
■ G.P.B with streak
△ unresolved or broad S′ spots
○ S′ spots
● Sharp spots
260 °C
Sample 5 - 2.4 hrs
0.001
0.01
0.1
1
10
Aging Time (Days)
XBL8210-6765

Fig. 7





Figs. 8 and 9 XBB 820-8918



XBB 820-3919

Fig. 10

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720