A CASE OF EMBRITTLEMENT OF SHEATHED ALUMEL THERMOELEMENTS IN LMFBR FUEL PIN SIMULATORS

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D. L. McElroy, B. C. Leslie, and D. L. Clark[1]

ABSTRACT

Alumel thermoelements sheathed in type 304 stainless steel with MgO insulation formed part of the instrumentation of a heater and were brittle after being heat treated to 975°C in hydrogen. Metallographic examinations, radiographs, electrical resistance measurements, and chemical analyses established the probable cause for this behavior. A critical amount of cold work was produced in forming the Alumel assembly and the subsequent heat treatment resulted in very large grains that spanned the diameter of the wire. The grain boundaries, which traversed the wire, were weak, and this led to the brittleness. There is no known way to restore the ductility, since the assembly cannot be worked and reannealed without fracture.

INTRODUCTION

Background Information

The current design of heaters for LMFBR research and development work included five sheathed thermoelements. The sheath is 0.015-in.-OD type 304 stainless steel containing MgO insulation and 0.005-in.-diam Chromel-P or Alumel wire. Each heater contains two sheathed Chromel-P thermoelements and three sheathed Alumel thermoelements.

The particular six heaters that led to the current problem were to be heat treated to effect stress relief and straightening. The five sheathed thermoelements of each heater had been wrapped around a 0.093-in.-diam copper electrode to prevent any damage to them during subsequent electron-beam welding of the heater sheath to a surrounding tubesheet. This wrapping is sufficient to produce some permanent deformation of the

[1]Reactor Division.

wire. For instance, if 0.005-in.-diam wire is wrapped directly on a 0.093-in. rod, then the outer fibers of the wire are exposed to about (0.103 − 0.098)/0.098 or 5% cold work. Inside the sheath, the wire would be exposed to slightly less than 5% cold work.

These heater assemblies with the deformed thermoelements were heat treated in a continuous hydrogen furnace with inlet hydrogen dried to a −75°C dew point. The belt drive was 4.2 in./min, and the heating cycle was:

5 min to 900°C (1652°F),
3 min to 975°C (1787°F),
3 min at 975°C,
5 min down to 900°C,
5 min down to 350°C (662°F).

This gives an exposure of 11 min above 900°C.

After this straightening heat treatment and further fabrication steps, attempts to unwind the sheathed Alumel thermoelements and strip off the stainless steel sheath revealed brittle Alumel wires. Stripping attempts on three of the six heater assemblies were unsuccessful. Either the stripping action sheared the Alumel or the exposed Alumel wire was too weak to allow any mechanical connection to electrical circuitry.

This was the history at the onset of the reported program of tests.

Comment on Background Information

Documentation on the heater components and exposures was complete and assisted the interpretation of the results.

Exposure to Hydrogen

RDT Standard C7-6T (April 1972) (Ref. 2) describes annealing procedures for assemblies of Chromel-P vs Alumel thermocouples sheathed in stainless steel and insulated with magnesium oxide in Section 3.5.2 as follows:

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[2]RDT Standard — Thermocouple Material and Thermocouple Assembly, Chromel-P versus Alumel, Stainless Steel Sheathed, Magnesium Oxide Insulated, C7-6T, April 1972. Supersedes RDT C7-6T, July 1970.

"3.5.2 Anneal. Each assembly shall be heat treated to fully anneal the wire and the sheath. Annealing shall be performed either in a vacuum or in an atmosphere of hydrogen or hydrogen plus inert gas. Heat treatment data shall be supplied for all material annealed giving the treatment temperatures, the length of time at each temperature, and the atmosphere in which the material was treated. A recorder chart will suffice for time and temperature requirements."

This specification which was applicable at the time of the subject heat treatments (May 1973) would indicate that no deleterious effects due to the hydrogen atmosphere would be expected. It is interesting that temperature is only indirectly specified in the terms "fully anneal".

Exposure to Copper

Some concern was expressed by the heater fabricators that copper could have penetrated the stainless steel sheath (0.003 in. thick) and the MgO insulation (0.002 in. thick) to contaminate the Alumel wire. The copper-chromium phase diagram indicates a eutectic at 1075°C (1967°F), and the copper-iron diagram indicates a monotectic at 1094°C (2001°F). The copper melting point is 1083°C (1981°F). Copper is soluble in γ-iron to about 9.5 wt %. The 3-min exposure at 975°C (1787°F) is believed to be sufficiently short and sufficiently removed ($\sim$100°C or 180°F) from these reaction temperatures to preclude copper contamination of the Alumel wire.

Effect of Cold Work on Final Grain Size

The annealing of cold-worked metals and alloys is often used to control the final grain size of the product. Generally increasing the amount of cold work yields a finer final grain size, as schematically shown in Fig. 1. It should be noted that for small amounts of cold work (<3%), there is no effect on the final grain size. However, there is a critical amount of cold work, about 5%, that yields excessively large final grains. This phenomenon is often illustrated by the microstructure of an annealed sheet that has been penetrated by a bullet. The resulting structure usually shows a ring of very coarse grains in the region experiencing the critical amount of cold work. This phenomenon is the result of a balance between the rate of nucleation (or number of nuclei

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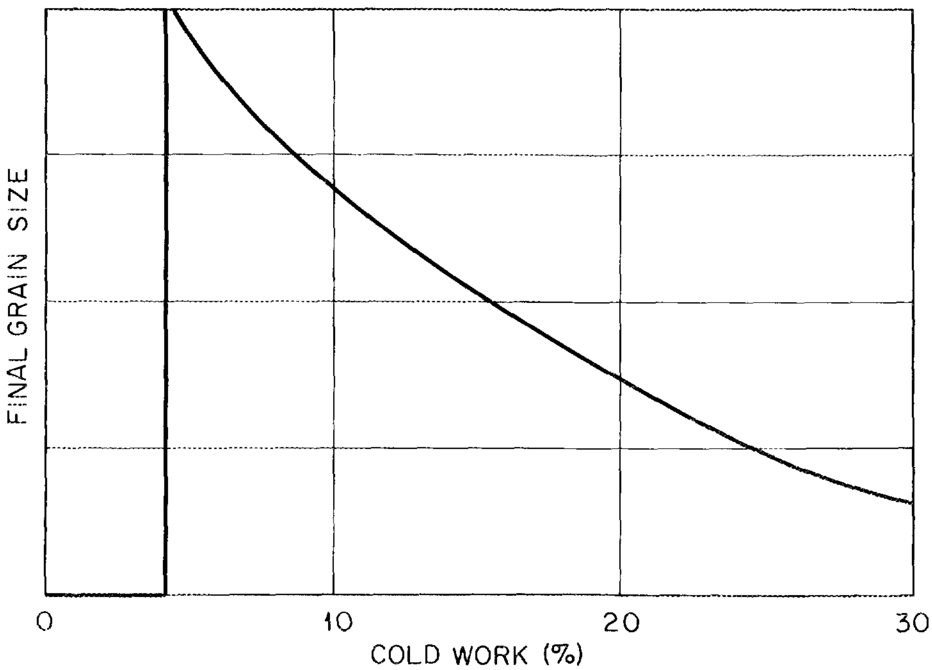

Fig. 1. Variation of Final Grain Size with Cold Work.

present) and the rate of grain growth. Increasing the alloy content displaces the curve in Fig. 1 to higher degrees of cold work for the same final grain size.

Previous studies[3] on Chromel-P and Alumel have shown the recrystallization temperature for a 4-hr exposure for 20%-cold-worked material to be 720 and 660°C (1330 and 1220°F), respectively. The exposure above 900°C (1652°F) for 11 min is certainly high enough to cause recrystallization, even for the short exposure. This is probably a low enough temperature to preclude secondary grain growth.

This description is presented because it is believed to be responsible for the observed Alumel behavior.

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[3]J. F. Potts and D. L. McElroy, Thermocouple Research to 1000°C — Final Report November 1, 1957, through June 30, 1959, ORNL-2773 (January 16, 1961).

Chromel-P Behavior

Although not stated above, the Chromel-P wires survived the wrapping, heat treatment, and unwinding operations. These wires had adequate ductility for the desired mechanical operations to complete the heater fabrication.

TESTS COMPLETED AND RESULTS OBTAINED

The following program was undertaken to determine the cause and possible solutions for the thermocouple wire embrittlement. Sections of the wires were examined metallographically after various thermal and mechanical treatments which represented the assembly fabrication. Radiography and electrical resistance measurements were used to detect flaws introduced by these treatments, and scanning electron microprobe analysis was used to seek possible chemical effects. Finally, additional metallographic and radiographic examinations were used to confirm the mechanism of embrittlement of Alumel during thermocouple assembly fabrication.

Metallographic Examination

Initially, metallographic specimens were prepared to examine transverse sections of the sheathed thermoelements. The as-polished views of as-received and heat-treated Chromel-P and Alumel did not reveal any unusual features.

The inside surfaces of the stainless steel sheaths and the outside surface of the thermoelement wires had irregular shapes; these will be apparent in the etched transverse sections to be shown. This is probably due to nonuniform resistance to deformation by the MgO insulation.

Observations on Etched Chromel-P Sections

Figure 2 compares the microstructures of Chromel-P as received and after heat treatment and uncoiling from the copper rod. The as-received 0.005-in.-diam wire shows about ten grains in the section, corresponding to a grain diameter of about 7×10^{-4} in. (15 μm). The section of the

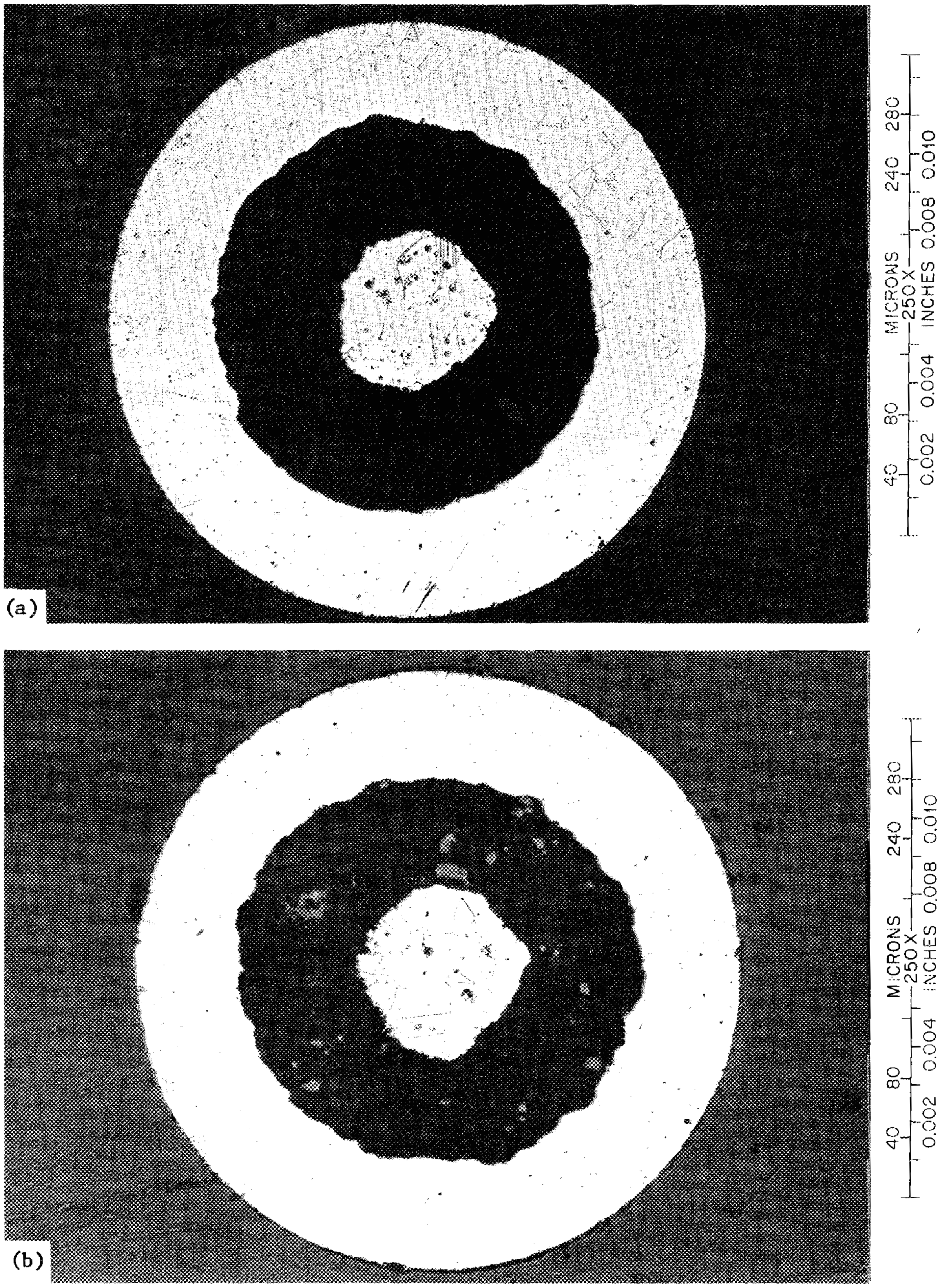


Fig. 2. Transverse Sections of Chromel-P Thermoelement, Showing Thermocouple Wire Surrounded by Stainless Steel Sheath, 250×, Etched. (a) As received. (b) Heat treated and then uncoiled from a copper rod.

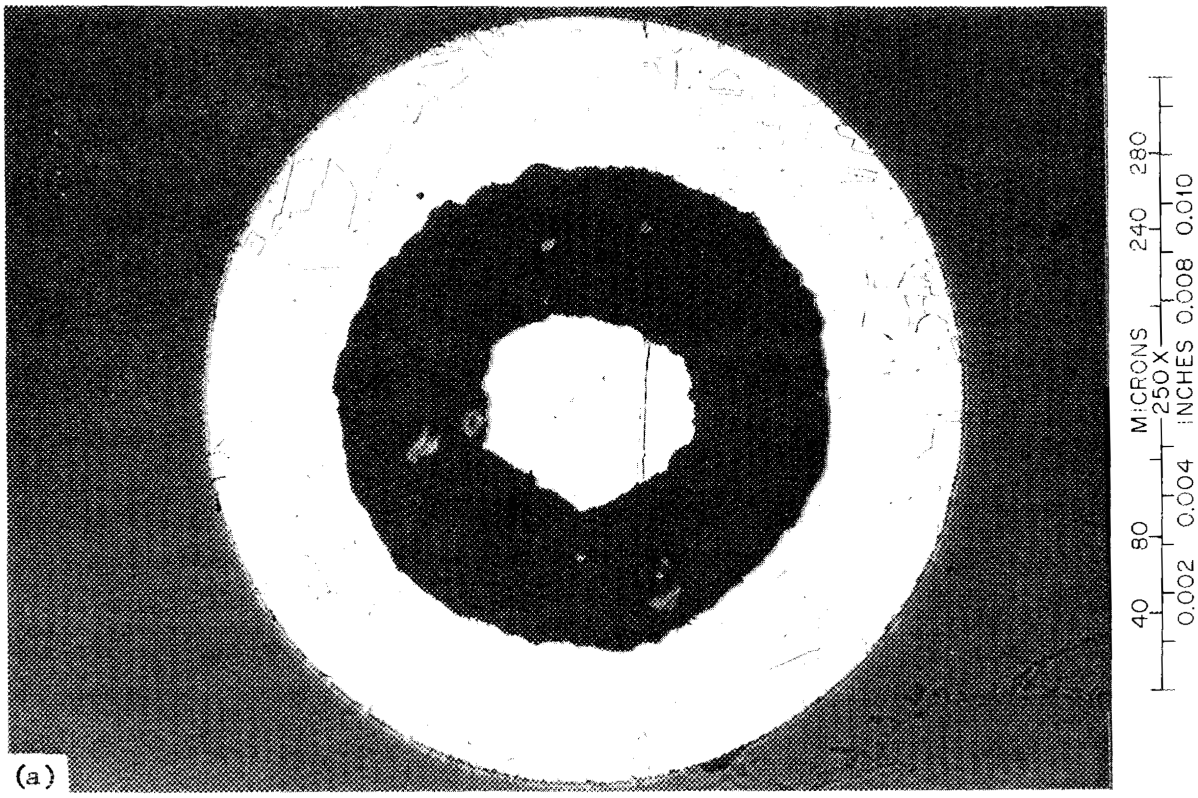
heat-treated and uncoiled thermoelement is similar to the as-received structure and shows that little had happened to the microstructure of the Chromel-P because of the heat treatment. Retention of this fine grain size is a requirement for ductility after heat treatment. It is interesting that the heat-treated stainless steel sheath developed a precipitate in the grain boundaries. This is because the subject heat treatment is very similar to a sensitizing heat treatment for stainless steels, which precipitates chromium carbide.

Observations on Alumel Sections

Figure 3 is the microstructure of the etched as-received Alumel. This transverse section shows only two grains spanning the wire cross section. Other transverse sections of the as-received Alumel contained three or four grains. Thus an early observation was that the as-received Alumel had a very much larger grain size than had the as-received or heat-treated Chromel-P. The longitudinal view shows the combination of large and medium-size grains.

Figure 4(a) shows the unetched heat-treated Alumel after it was uncoiled from the copper rod; this sample appears to have a single-phase microstructure. Oftentimes a second phase will be revealed in such a structure before etching. The same section etched, in Fig. 4(b), shows massive grains of nearly the wire diameter.

The structure of the heat-treated Alumel suggested that a longitudinal section might be more revealing. Figure 5 is a photograph of such a sample at one stage of sample preparation. The sheathed sample was intentionally bent 90° before mounting, causing the major fracture. Figure 6(a) is an unetched section of the bent sample showing an area removed from the main crack. Note the grain boundary cracks in this sample. These cracks must have formed during the uncoiling operation. Since fractures such as this can develop, we will see later how this influenced the resistance results. Figure 6(b) is an unetched view of the fracture at the bent part of the heat-treated Alumel. Figure 7 shows etched views of this fracture. The main fracture appears to be along a grain boundary, as was noted for the fractures in Fig. 6(a).



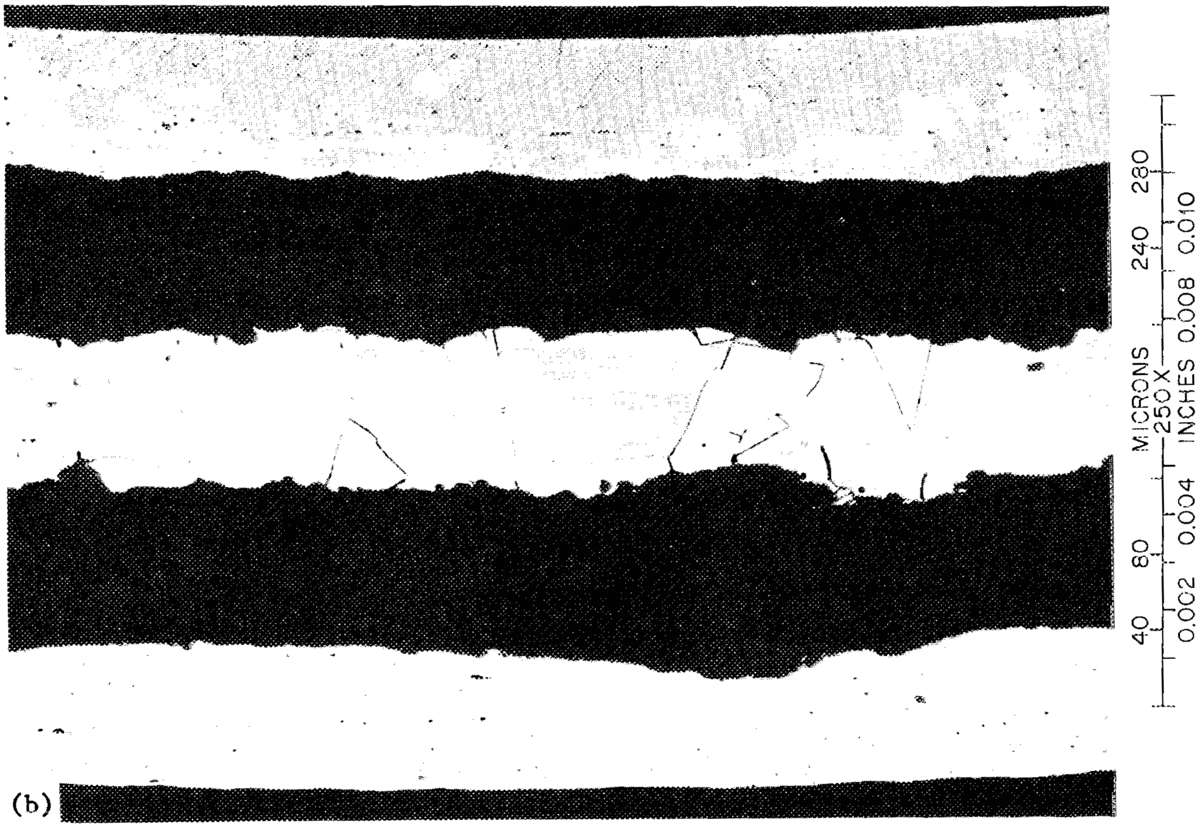


Fig. 3. As-Received Alumel, 250×, Etched. (a) Transverse. (b) Longitudinal.

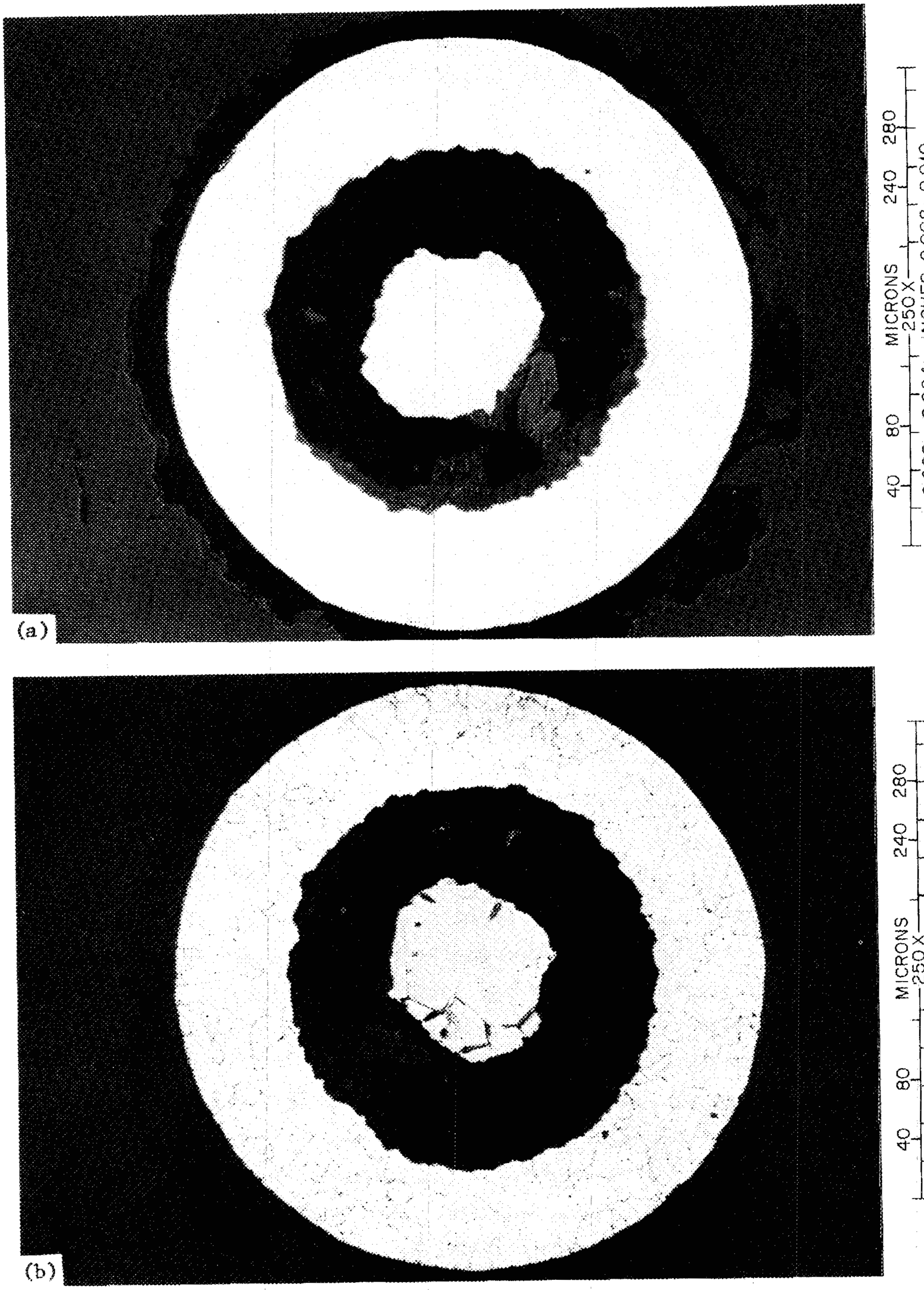


Fig. 4. Heat Treated Alumel, 250×. (a) Unetched. (b) Etched.

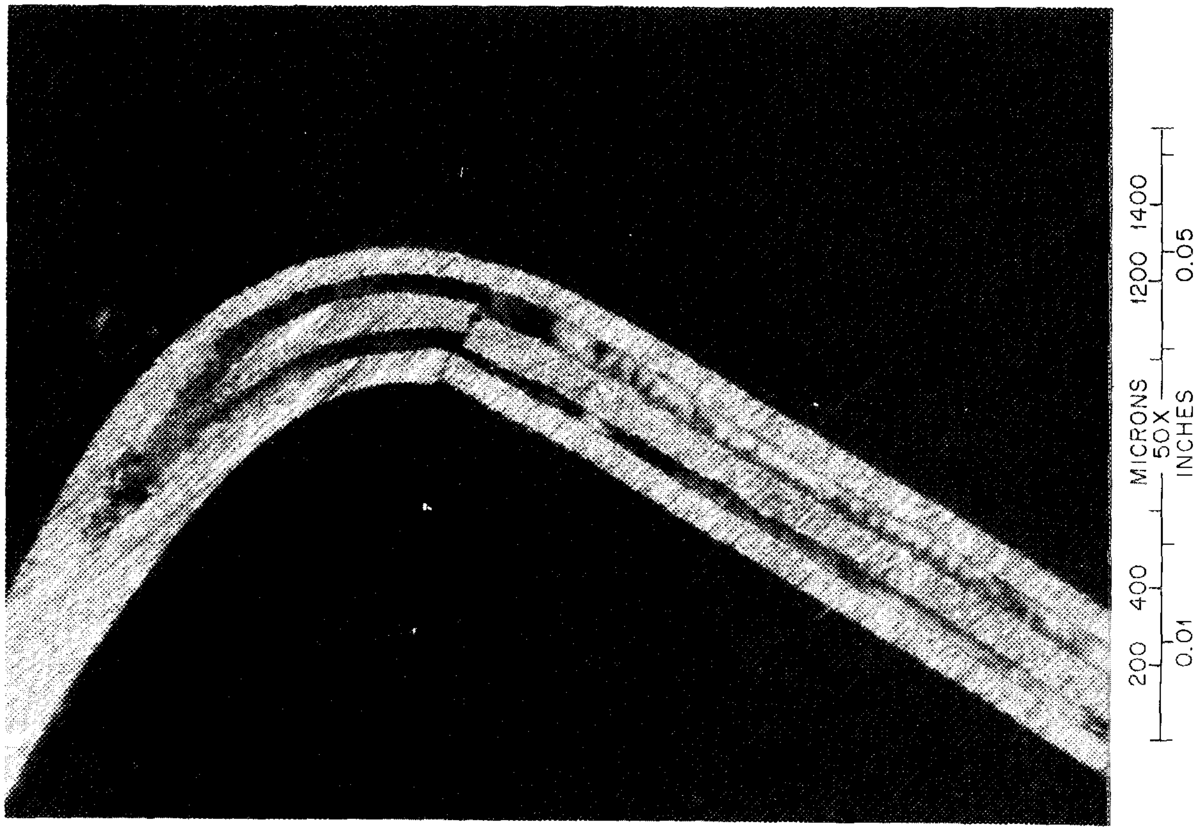


Fig. 5. Longitudinal Section of Heat-Treated Alumel After Rough Grinding of the Bent Section, Unetched, 50×.

Thus the lack of ductility of the Alumel is caused by grain boundary fractures. Figure 7 also shows evidence for a cold-worked structure in the stainless steel.

These metallographic observations were consistent with the idea that winding Alumel into the coils introduced the critical amount of cold work that on subsequent heat treatment led to excessive grain growth. Following this lead we performed the radiographic, electrical, and chemical tests described in subsequent sections as well as metallographic examination of uncoiled Alumel.

Four samples of Alumel were heat treated under the same conditions and in the same facility originally used for the heaters. Two of the samples were coils for the electrical measurements described later. The others were straight segments, one bare and the other insulated and sheathed as in the thermocouple assemblies.

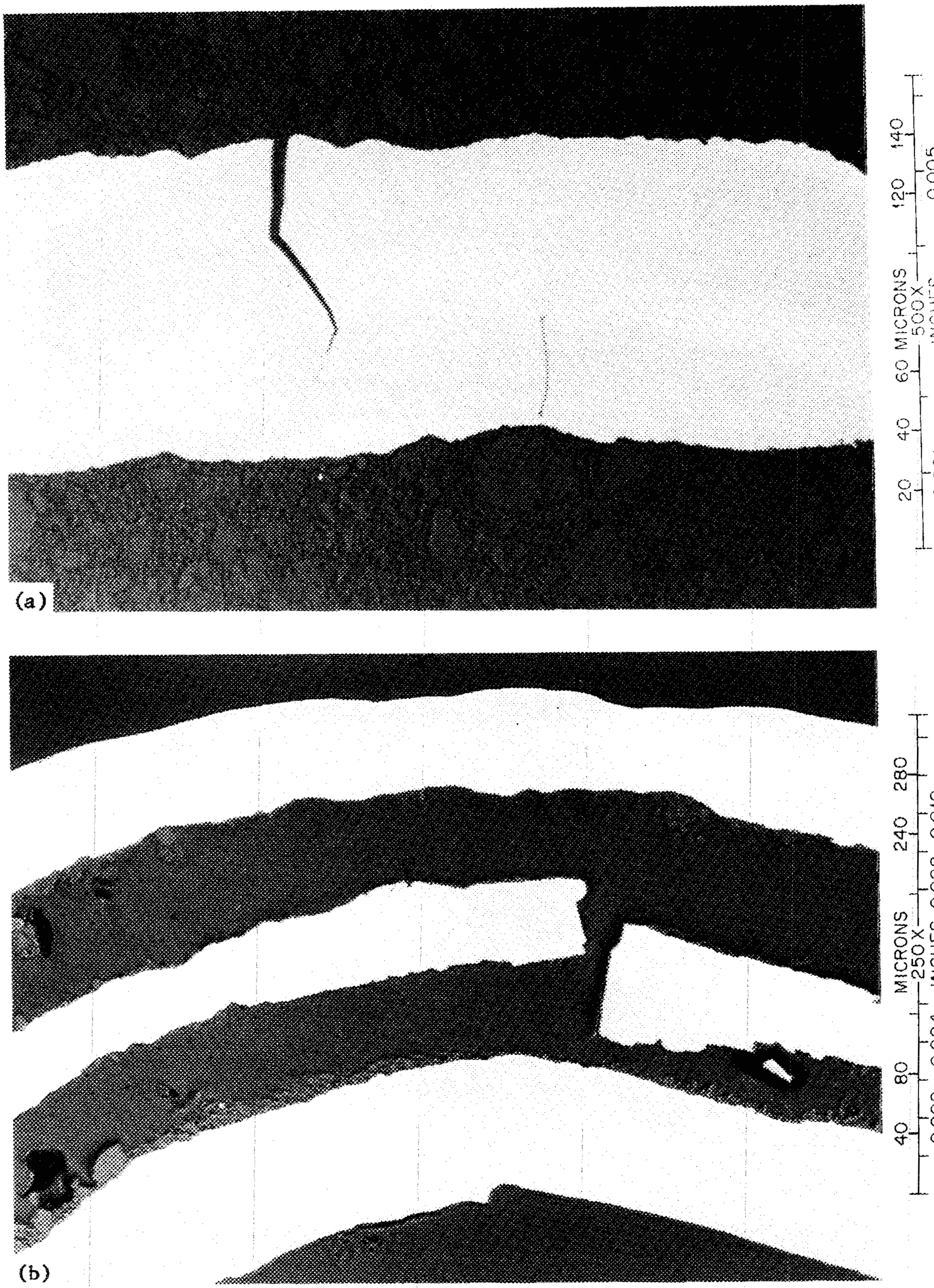


Fig. 6. Longitudinal Section of Bent Heat-Treated Alumel, Unetched. (a) Section away from bend, 500×. (b) Section at bend, 250×.

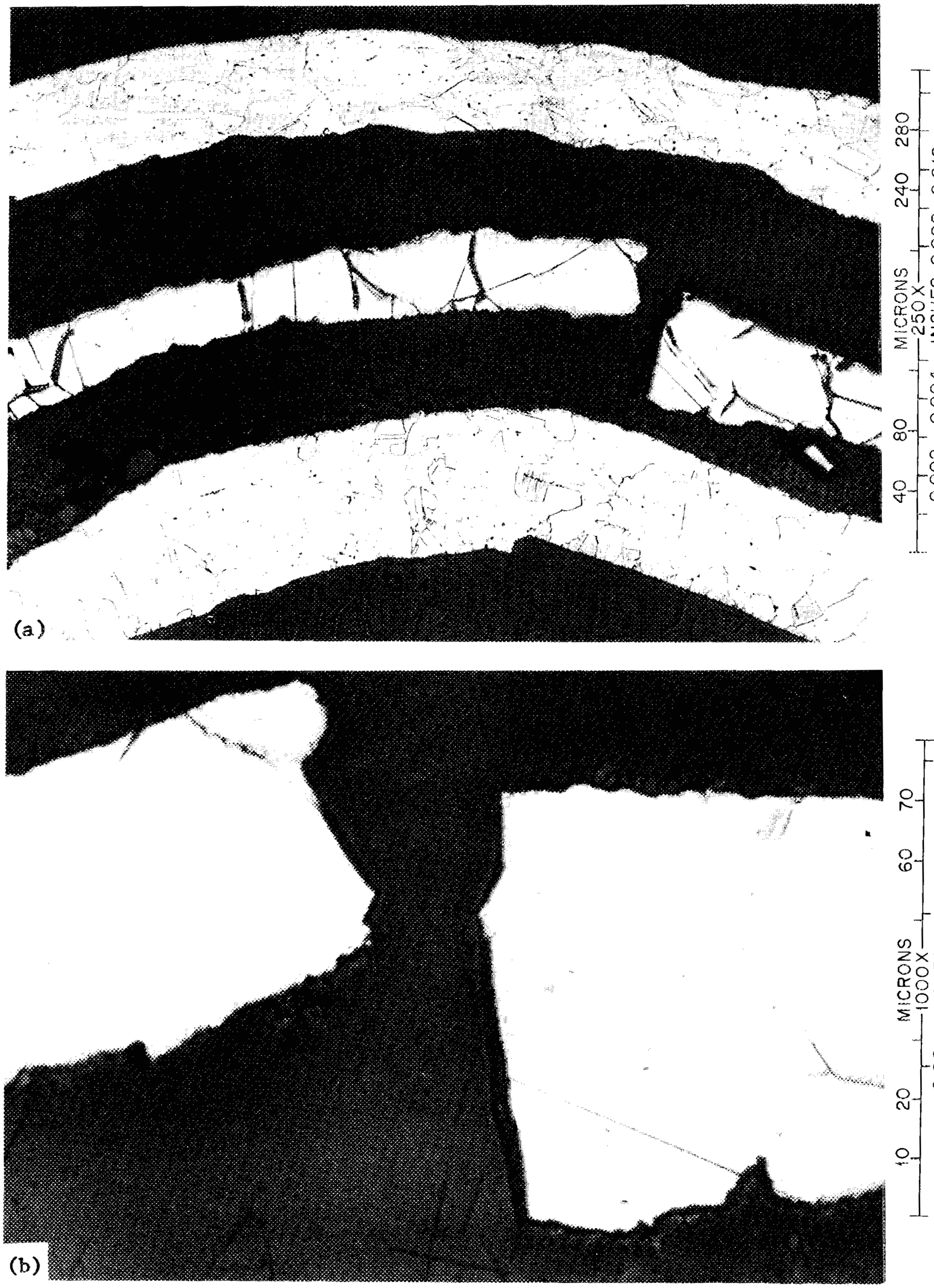


Fig. 7. Etched Microstructure of Bent Heat-Treated Alumel. (a) 250×. (b) 1000×.

Figure 8 is a longitudinal view of the straight sheathed Alumel assembly. It shows a duplex structure of large and small grains. One would expect this Alumel to have adequate ductility. The fact that this sample, which did not experience any cold working and did not develop the large-grained structure characteristic of the coiled and heat-treated Alumel, establishes the necessity for the critical cold working to obtain the brittle single-crystal structure. Figure 9 is a view of a bare Alumel wire heat treated at the same time. This straight Alumel wire confirms the behavior noted in Fig. 8.

Radiography

Radiographs of the sheathed thermoelements described above were obtained. No significant features were noted when these films were examined at 35×. Figure 10 is typical of the observed film and is a view of the heat treated Alumel at 35×. These radiographs did not

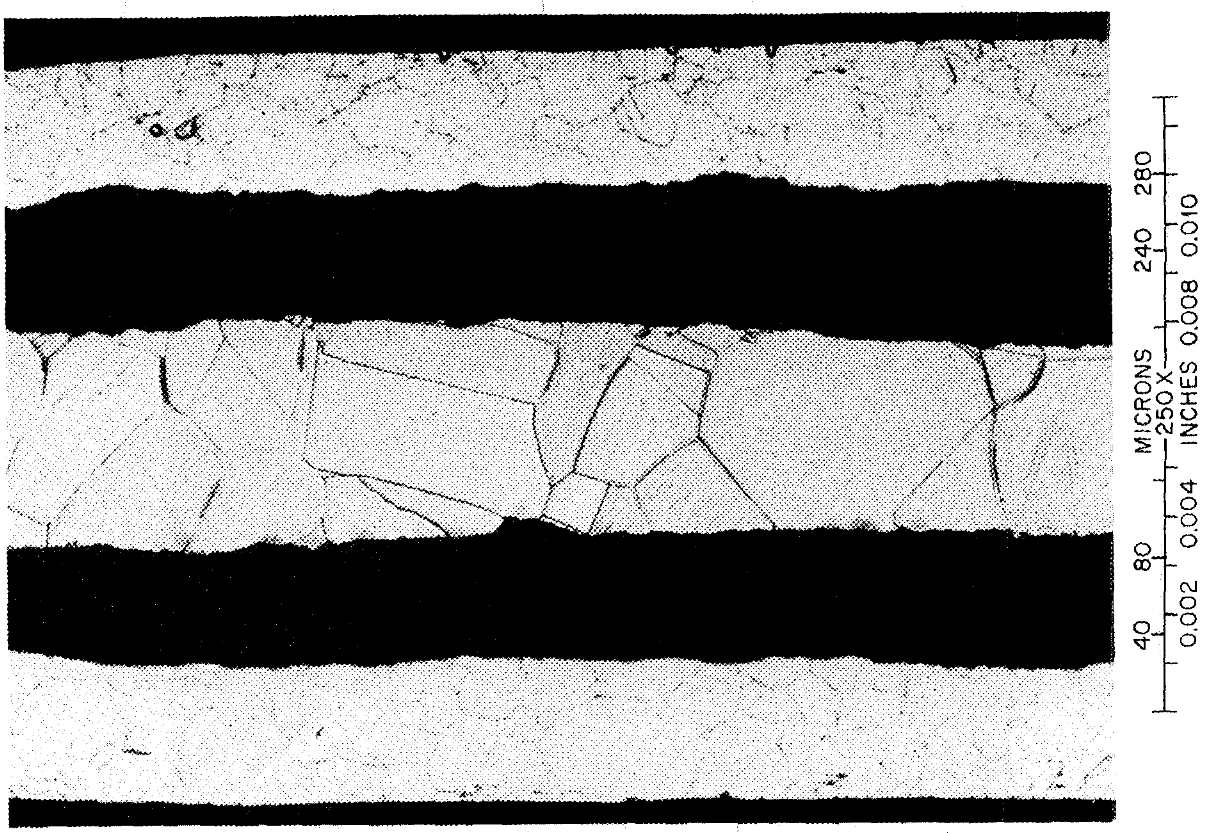


Fig. 8. Longitudinal View of Alumel after Heat Treatment as a Straight Sheathed Assembly, 250×, Etched.

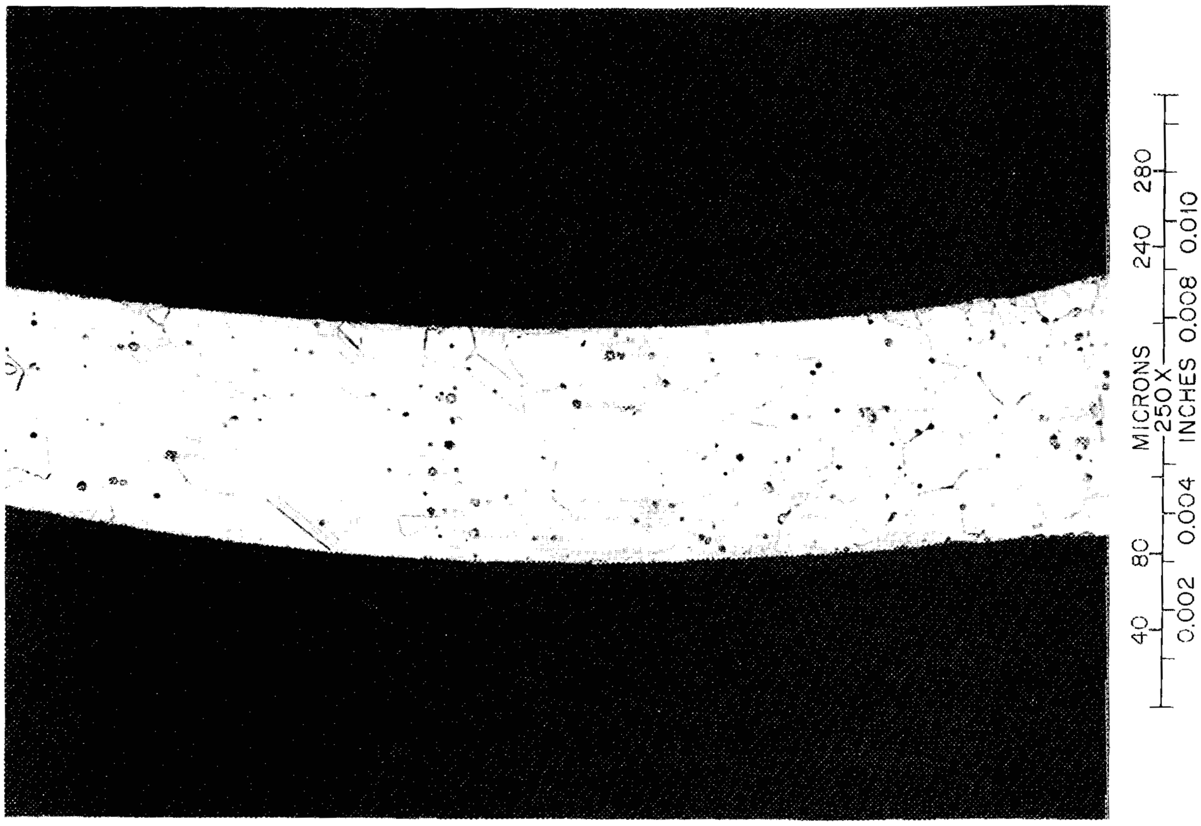


Fig. 9. Longitudinal View or a Bare Alumel Wire atter Heat Treatment as a Straight Section, 250×, Etched.

Fig. 10. Radiograph of Heat-Treated Alumel, 35×.

reveal the grain boundary fractures noted in Fig. 6(a). However, when this sample was bent 90° and restraightened the radiograph in Fig. 11 was obtained. This picture shows the Alumel wire to contain at least three fractures. This observation confirmed the transverse fractures detected metallographically.

Electrical Resistance Measurements

Two coils of Alumel were heat treated along with the straight segments for metallographic examination. Coil A was wrapped on a copper electrode taken from the original test. The Alumel of this coil had a room-temperature electrical resistance of 13.77 Ω before the heat treatment. Coil B was initially wrapped on a 0.1-in.-diam tube and was heat treated as a coil after being slipped from this tube. This uncored coil had a room-temperature resistance of 19.72 Ω before the heat treatment. These differences merely represent different lengths of Alumel.

Following the heat treatment, Coil A (Cu core) had a resistance of 15.08 Ω, a 9.4% increase, and Coil B (no electrode) had a resistance of 21.28 Ω, a 7.9% increase. When these coils were uncoiled for about half their coiled length, each resistance became infinite, indicating that an open circuit was created by the uncoiling action. The wire-to-sheath resistance was 100,000 Ω in the pre-heat-treated condition and nearly 3×10^6 Ω after heat treatment.

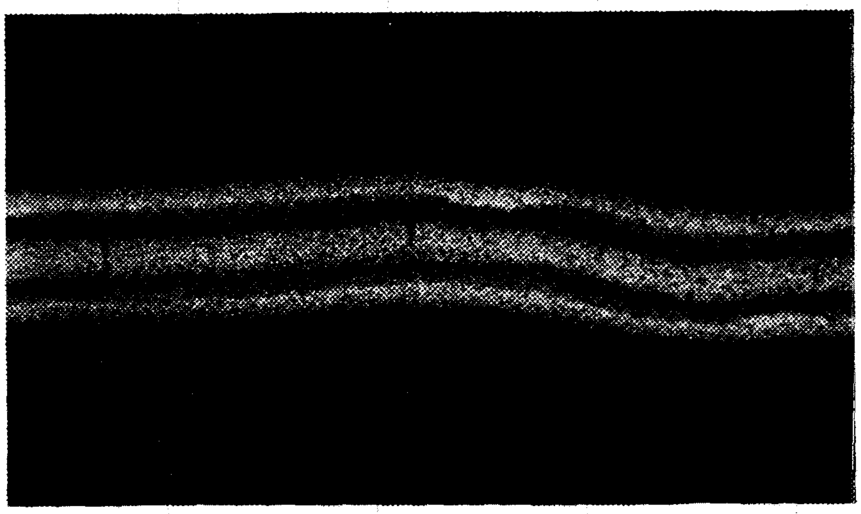


Fig. 11. Radiograph of Bent and Straightened Alumel, 50×.

Kollie[4] has observed about 0.6% increase in resistance for heat treating Alumel at 850°C. Similarly Potts and McElroy[5] have observed resistance changes of about 1% for heat treatment of cold-worked Alumel. Thus the observed increase of 8 to 9% far exceeds expectations for Alumel. A logical explanation is that fractures occurred during the heat treatment, and this decreased the effective conduction area. This explanation agrees with the open-circuit behavior found after uncoiling.

Radiographs were taken of the open-circuited uncoiled lengths of the heat treated coils. Figure 12, a magnified portion of the x-ray film, shows a fracture in the Alumel wire near the center of the print. This verifies that these coiled wires could not be uncoiled without the wire fracturing.

Since Coil B was brittle, the resistance tests indicate that the copper electrode was not a necessary ingredient for the subsequent Alumel behavior. That is, copper contamination was not necessary for the loss of ductility in the Alumel wire.

Scanning Electron Microprobe Analyses

Two chemical analyses of the heat-treated Alumel wire were obtained. Previous analyses obtained by McElroy[6] show Alumel to contain: 94.2% Ni, 1.1% Si, 1.3% Al, 2.0% Mn, 0.02% Fe, and 0.38% Co.

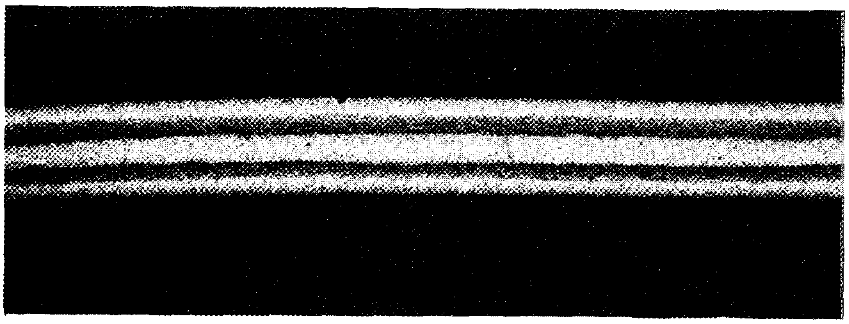


Fig. 12. Radiograph of Uncoiled Alumel, 35×.

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[4]T. G. Kollie, Intra-Laboratory Correspondence to K. R. Carr, May 17, 1973.

[5]Same as 3.

[6]D. L. McElroy, Progress Report 1, Thermocouple Research Report for the Period November 1, 1956, to October 31, 1957, ORNL-2467 (March 5, 1958).

The central area (~0.1 of the wire area) of the end of the heat-treated Alumel was analyzed in a scanning electron microprobe with x-ray fluorescence detection with a Si-Li detector. This analysis indicated peaks associated with Si, Mn, Co, and Ni, all as expected in Alumel. This analysis showed no Cu or Mg present in the Alumel; the absence substantiates the expected lack of penetration of copper to the Alumel. This analysis did not reveal any aluminum above 0.1%, although Alumel contains about 1.3% Al. These analyses were conducted by L. Hulett (ORNL Analytical Chemistry Division).

Two regions in the longitudinal view of the heat-treated Alumel were analyzed, one in a grain and one in a grain boundary region. Figure 13 is a photograph of the intensity versus energy obtained in an energy dispersive x-ray analyzer. The eight peaks are identified in Table 1. Peaks 5 and 6 are about the same size, and Peak 5 could be due to iron or manganese. Previous chemical analysis showed iron to be present to less than 0.02%. The stainless steel could provide a source of iron contamination of Alumel. This is not clear at the present time. Any peak associated with copper would occur near Peak 8 at 8.05 eV, but this is not seen in the intensity pattern. This analysis, performed by R. S. Crouse (ORNL Metals and Ceramics Division), is consistent with the expected Alumel composition except for the iron-manganese dilemma. Furthermore there appears to be no difference in composition for the two examined regions.

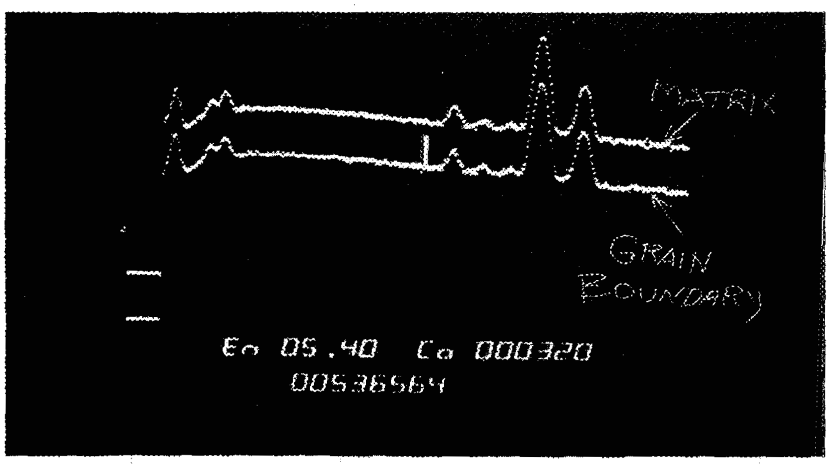

Fig. 13. Intensity as a Function of Energy of X-Rays on Section Shown in Fig. 9. Top curve is in grain. Bottom curve is in grain boundary.

Table 1. X-Ray Peaks from Alumel

Peak	Measured Energy (eV)	Expected Energy (eV)	X-Ray Line
1	0.82	0.85	Ni Lα
2	1.50	1.49	Al Kα
3	1.71	1.74	Si Kα
4	5.94	5.89	Mn Kα
5	6.47	6.40	Fe Kα
		6.49	Mn Kβ
6	6.97	6.93	Co Kα
7	7.51	7.48	Ni Kα
8	8.29	8.26	Ni Kβ

CONCLUSIONS

This study has established that the brittle behavior of the Alumel wire is primarily associated with its excessive grain size. Since cold working and annealing cannot be done to these assemblies, there is no known way to restore the needed ductility.

It is recommended that coiling operations such as experienced by the Alumel assemblies be avoided. Furthermore the specifications for these thermoelements should include a statement that prohibits acceptance of coarse-grained Alumel wire.[7]

[7]RDT C 7-6T (Ref. 2, p. 2) was amended in June 1973 as C 7-6T Amendment 1, June 1973. This conclusion suggests a further amendment may be appropriate.

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