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ANODIZING AS A METALLOGRAPHIC TECHNIQUE FOR ZIRCONIUM BASE ALLOYS

M. L. Picklesimer

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ANODIZING AS A METALLOGRAPHIC TECHNIQUE FOR ZIRCONIUM BASE ALLOYS

M. L. Picklesimer
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Summary

A modification of the anodizing technique developed by Margolin and Ence[1] for titanium base alloys has permitted its utilization on zirconium base alloys for phase identification, improvement of optical contrast of microstructures in both bright field and polarized light examination, and as a permanent preservative for the etched surface of a specimen.

A thin film of oxide is formed on the surface of the specimen in an electrolytic bath. The interference colors resulting are a function of the anodizing voltage and the phases present in the specimen. The technique can be used to positively identify zirconium hydride needles and to permit accurate lineal analyses of TTT specimens from very near 0 per cent to over 99 per cent transformation. Similar techniques have been used for uranium and titanium alloys.

Introduction

Margolin and Ence published a paper[1] giving their technique for phase identification in titanium alloys by "cumulative etching". Their technique is somewhat complicated and the composition of the solution used, the applied voltage, and the distance between the specimen surface and the cathode of the bath are all critical for reproducible results.

Difficulties encountered in the examination of TTT specimens of a Zr-Ag eutectoid alloy led to the experimentation with their technique and solution. Considerable experimentation resulted in a different technique and a composition that, for Zr base alloys, gave reproducible results without an exacting procedure or a critical composition of the solution.

Experimental Procedure

The specimen to be anodized is usually mounted in the conventional manner, (i.e., in a standard bakelite mount or with an epoxy resin that will harden at room temperature), the mount is drilled from the back with a small drill until the specimen is contacted, a piece of solid solder is inserted into the drilled hole until it is in good electrical contact with the specimen and is set in place with a pin punch, the specimen is polished and etched as desired, the etched specimen is inserted in a standard electropolishing unit as an anode and, with the electrical connection being made through the solder plug, the selected voltage is applied for 5 to 10 sec. The specimen is removed from the bath and washed and dried. The specimen surface is usually placed at approximately 1/2-in. from the stainless steel cathode for convenience although the distance is not critical. It is important that the only electrical path possible through the bath is that through the specimen, since any electrical contact of the specimen holder with the solution will permit most of the current to be carried by that holder and the specimen will be "shaded" with non-reproducible results.

The batch composition used for zirconium base alloys is 60 ml ethyl alcohol, 35 ml water, 5 ml phosphoric acid, 10 ml lactic acid (85 per cent), 20 ml glycerine, and 2 g citric acid. The composition is not critical but the bath should not be kept overnight because of the evaporation of the alcohol.

Voltages from 20 to 140 v are used, depending on the purpose and the color desired. Voltages around 20 v provide excellent contrast for fine details for both bright field and polarized light examination. No strong color distinction occurs at 20 v except for zirconium hydrides, in which case the matrix is colored blue to purple and the hydrides are colored a bright golden yellow. As the anodizing voltage is increased, two or more orders of interference colors appear. The anodizing voltage is usually selected by trial and error, using

successively higher voltages, on the basis of the greatest color contrast between the phases present. Once the proper voltage is selected, that voltage is used for other specimens of the same alloy. The time of anodizing used is always greater than 3 sec so that the oxide film has time to reach the thickness characteristic of the applied voltage. Times longer than 10 sec usually show no appreciable change in the color until fairly long times are reached. The higher anodizing voltages seem to "cover over" very fine details of the structures and do not give the best contrast for examination in polarized light, but may provide the color contrast desired in bright field. The zirconium hydrides are covered with what appears to be a fine powder at the higher anodizing voltages and are no longer sharply delineated.

Zirconium alloy specimens examined three years after anodizing still show the same color contrast and delineation of microstructure as on the day they were anodized. All zirconium specimens are now anodized as a routine procedure for the preservation of the etched surface and for most of the metallographic examination.

Results

The increase in contrast in both polarized light and bright field examination of the etched and anodized specimens is shown in Fig. 1. An air bubble was inadvertently trapped on the etched surface of the specimen, and as a result, the region covered by the air bubble was not anodized. The specimen was a Zr-3 at per cent Ag alloy isothermally transformed for 4 min at 799°C to give structures quite similar to the pearlitic, bainitic, and martensitic structures occurring in steels. The specimen was anodized at 20 v for 5 sec. The effect of anodizing a similar specimen at a higher voltage is shown in Fig. 2, where an isothermally transformed specimen was anodized at 120 v. The pearlitic phase is colored red, the bainitic dark red, and the martensitic yellow.

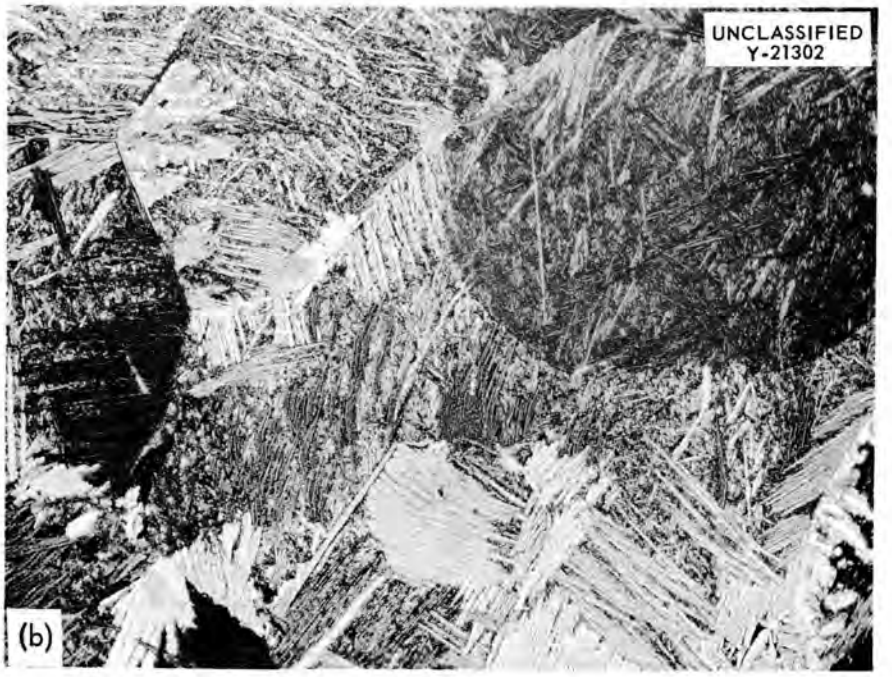

Fig. 1. Zr-Ag-36 Zr-3 Atomic per cent Ag, 902°C 30 min, 800°C 4 min, Hg Quenched. 75X. (a) Bright Field. (b) Polarized Light.

The use of the anodizing procedure for contrast of phases for lineal analyses of specimens is shown in Figs. 2, 3, 4, and 5. The microstructure shown in Fig. 3 is that of a Zr-Ag specimen isothermally transformed for 23.3 sec at 799°C. Unanodized, there appeared to be no transformation to the pearlitic phase. By anodizing, the start of the transformation was shown by the small red structure appearing in the grain boundary. Less than 0.1 per cent total transformation to the pearlitic phase had occurred. The microstructure of a specimen transformed for 1221 sec at 799°C is shown in Fig. 4. More than 95 per cent transformation has occurred. The structure at 750X is shown in Fig. 5. The yellow phase is martensitic, the red needles are bainitic, and the pearlitic phase is shown between the bainitic needles as the lamellar structure.

The use of the anodizing procedure for phase identification is shown in Figs. 6 through 10. Crystal bar zirconium was vacuum annealed to less than 5 ppm H_2, various amounts of hydrogen added in a modified Sievert's apparatus, and the specimens step-cooled 100°C every 30 min. All of these specimens were electropolished and anodized at 20 v. The structure of a specimen containing 160 ppm H_2 is shown in Fig. 6. The golden yellow phase is the zirconium hydride. That of a specimen containing 500 ppm H_2 is shown in Fig. 7. Again the yellow phase is hydride. Specimens of Zircaloy-2 were hydrided in the same manner in the same equipment. The structure of a specimen containing 100 ppm H_2 is shown in Fig. 8 and that of one containing 870 ppm H_2 in Fig. 9. The yellow phase in each case is hydride. A crystal bar specimen containing 530 ppm H_2 was mercury quenched from 900°C. The structure is shown in Fig. 10. The clearly resolved particles are colored yellow. All of the precipitate must be hydride. It is thought that the failure of the small, irresolvable needles to take on the yellow color is because of their size and the fact that they cannot be clearly resolved. Higher magnification is not possible without using oil immersion

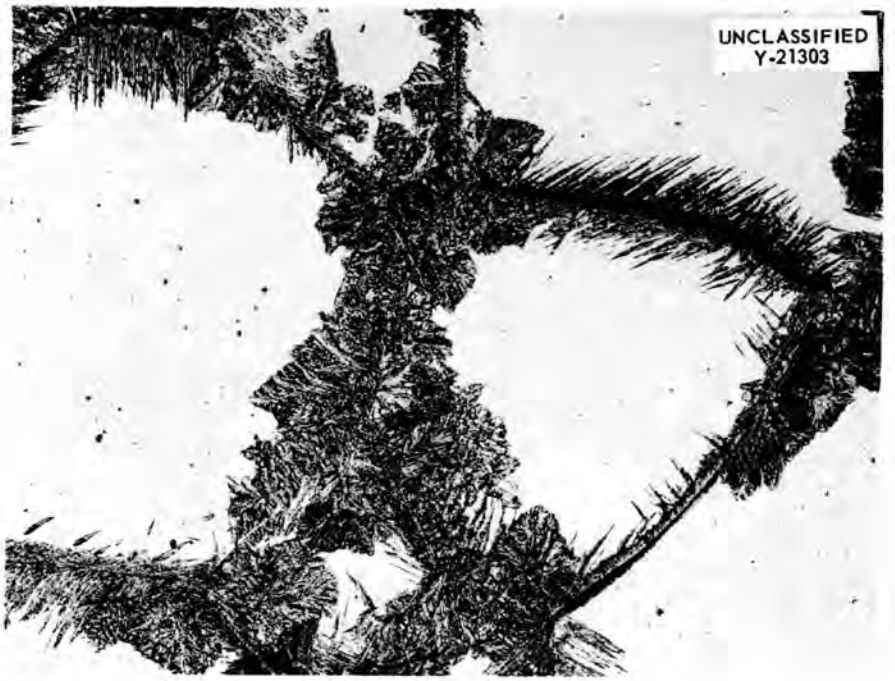

Fig. 2. Zr-Ag-34 Zr-3 Atomic per cent Ag, 902°C 30 min, 800°C 60 sec, Hg Quenched, Bright Field. 75X.

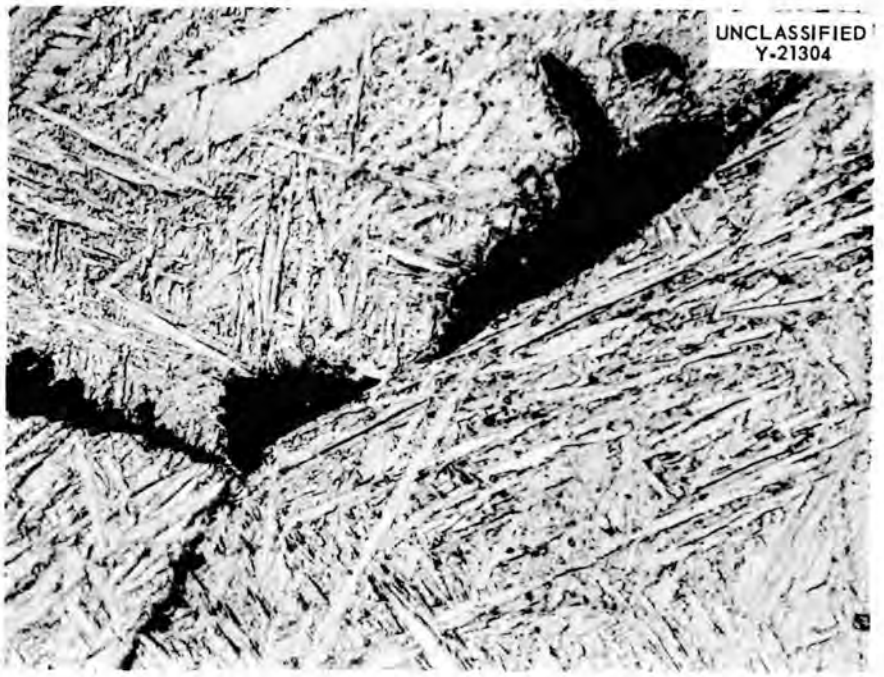

Fig. 3. Zr-Ag-3-48 Zr-3 Atomic per cent Ag, 901°C 30 min, 799.5°C 23.3 sec, Hg Quenched, Bright Field. 750X.

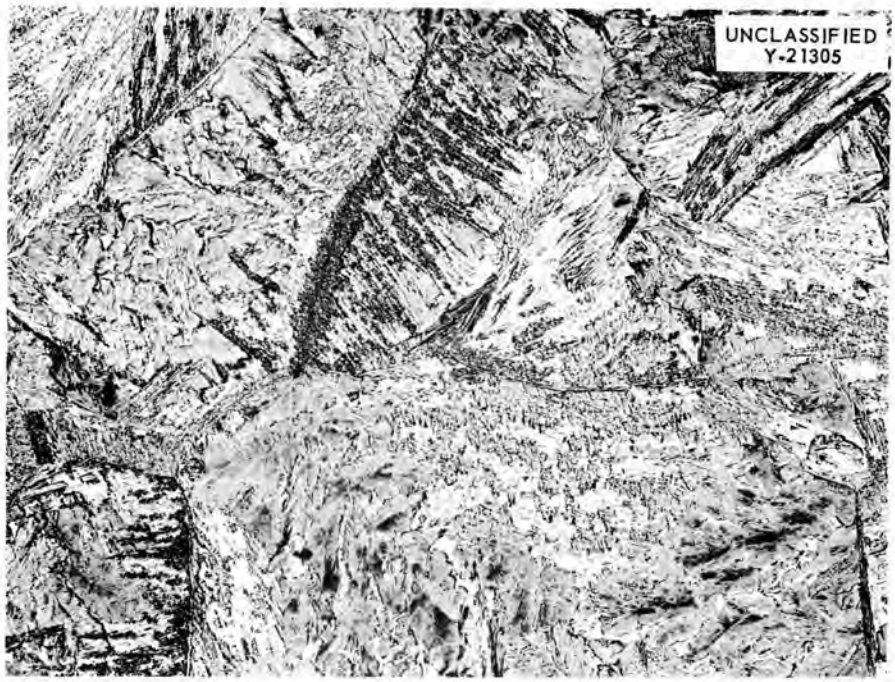

Fig. 4. Zr-Ag-38 Zr-3 Atomic per cent Ag, 901°C 30 min, 799.5°C 1221 sec, Hg Quenched, Bright Field. 75X.

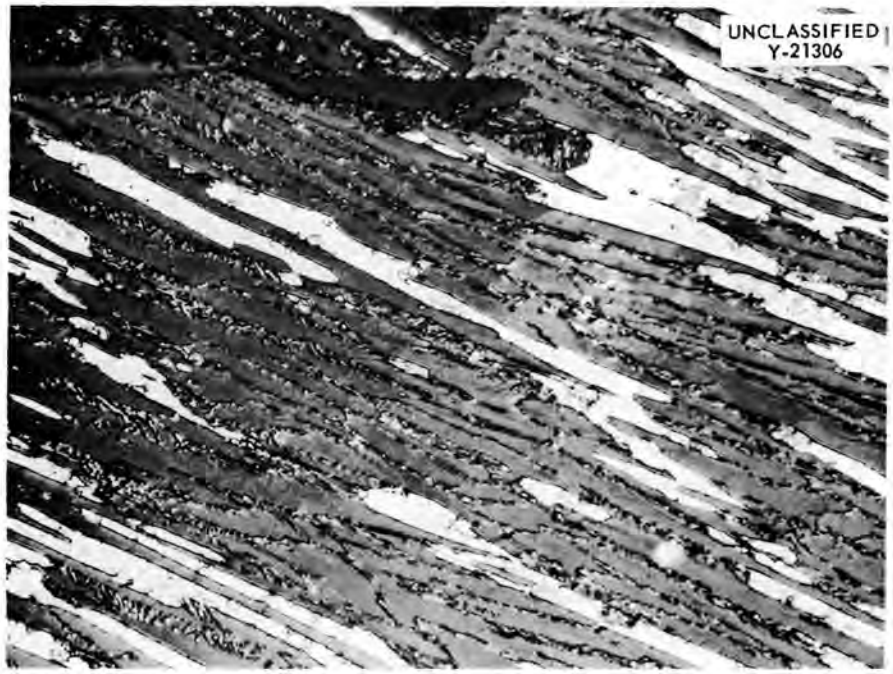

Fig. 5. Zr-Ag-38 Zr-3 Atomic per cent Ag, 901°C 30 min, 799.5°C 1221 sec, Hg Quenched, Bright Field. 750X.

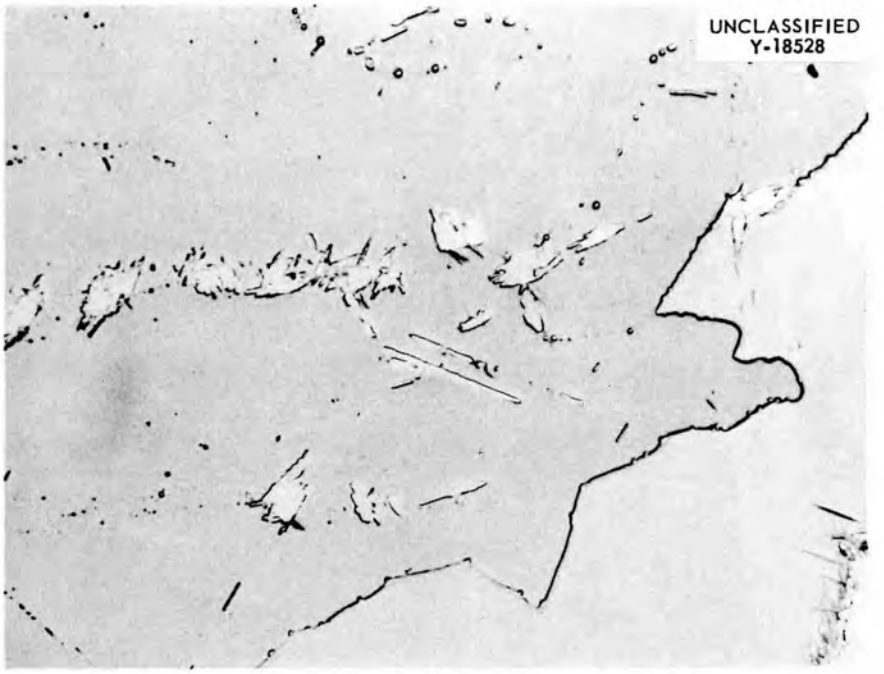

Fig. 6. B-11 Iodide Zr, 160 ppm H_2 Step Cooled, Bright Field. 500X.

Fig. 7. B-5 Iodide Zr, 500 ppm H_2 Step Cooled, Bright Field. 500X.

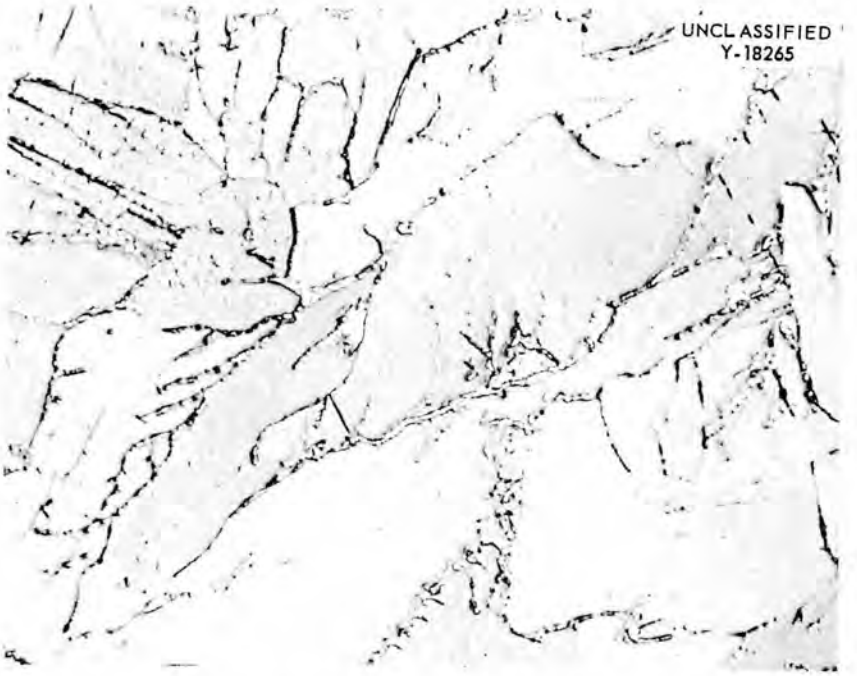

Fig. 8. D-5 Zircaloy-2, 100 ppm H_2 Step Cooled, Bright Field. 500X.

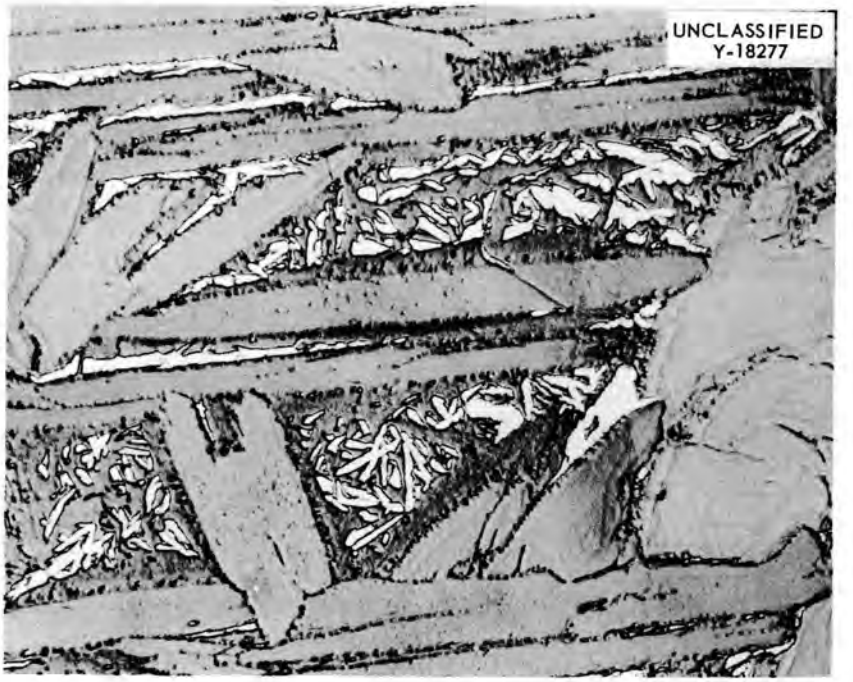

Fig. 9. D-8 Zircaloy-2, 870 ppm H_2 Step Cooled, Bright Field. 500X.

lens in which case the oil destroys the color contrast.

The use of the anodizing procedure for color contrast of phases for phase diagram work is shown in Fig. 11. The specimen was Zircaloy-2, held at 840°C for 30 min and water quenched. The structure is identical to that of a specimen held for two weeks at 840°C. The presence of the beta phase at temperature is shown by the yellow phase appearing in the grain boundaries and grain corners. Examination of this specimen in polarized light or in the unanodized condition in bright field does not reveal the presence of the prior beta phase. It is postulated that, although all of the structure seen in the micrograph was alpha after water quenching, the beta stabilizing elements Fe, Ni, and Cr, concentrated in the beta phase at temperature and being trapped there by water quenching, have so changed the chemical composition that a color difference is seen.

The delineation of microstructure in polarized light after anodizing at 20 v is shown in Figs. 12 and 13. Both specimens were Zircaloy-2 and neither showed a clearly resolvable structure in bright field examination.

It is believed by the author that the color contrast shown can be explained by the difference in oxidation rates of the different phases. Since the specimen, as a whole, is oxidized at the same voltage for the same period of time, each phase present in the microstructure will be oxidized to a different thickness of oxide film, characteristic of the voltage, the composition of the solution, and the composition and/or structure of the phase. If the oxide film can show interference colors, is adherent and non-porous, and its thickness is characteristic of the applied voltage, it is believed that this technique may be used for any alloy system. A very small amount of work has been done on uranium base alloys and one successful anodizing solution has been developed.

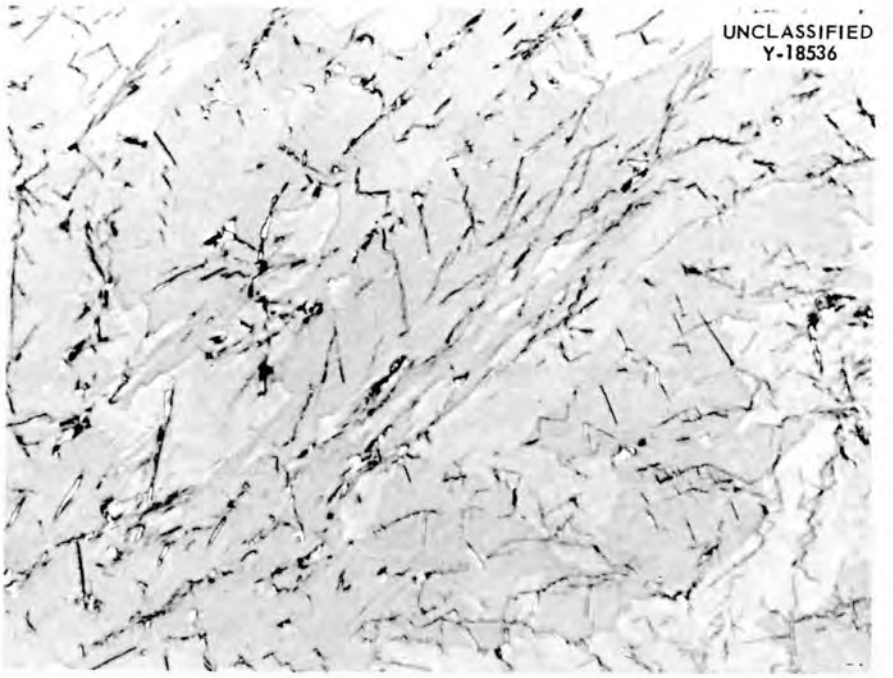

Fig. 10. J-3 Iodide Zr, 530 ppm H_2, Hg Quenched 900°C, Bright Field. 500X.

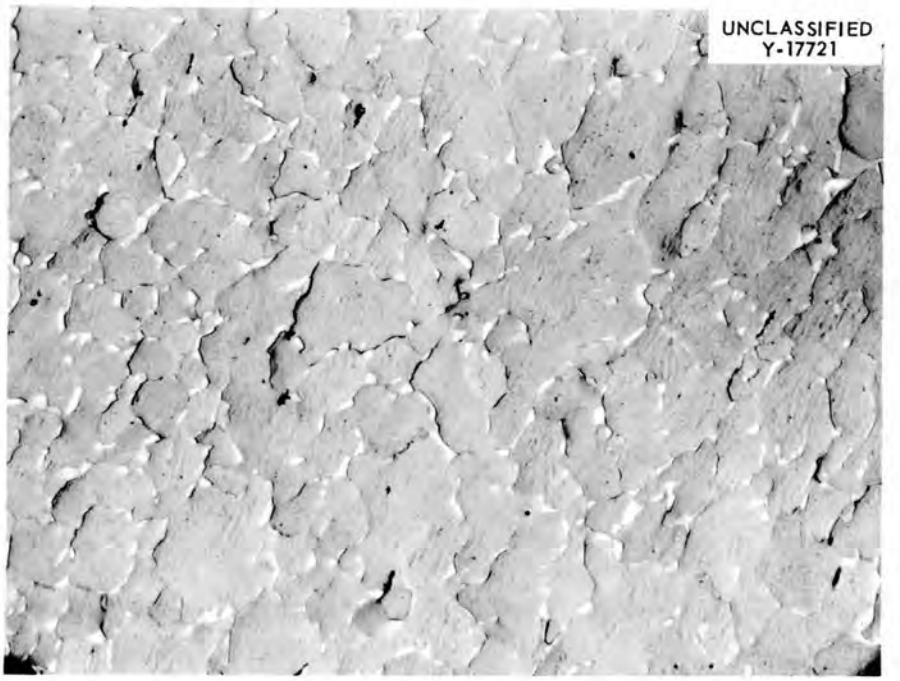

Fig. 11. Zr-2-58 Zircaloy-2, 840°C 30 min, Water Quenched, Bright Field. 200X.

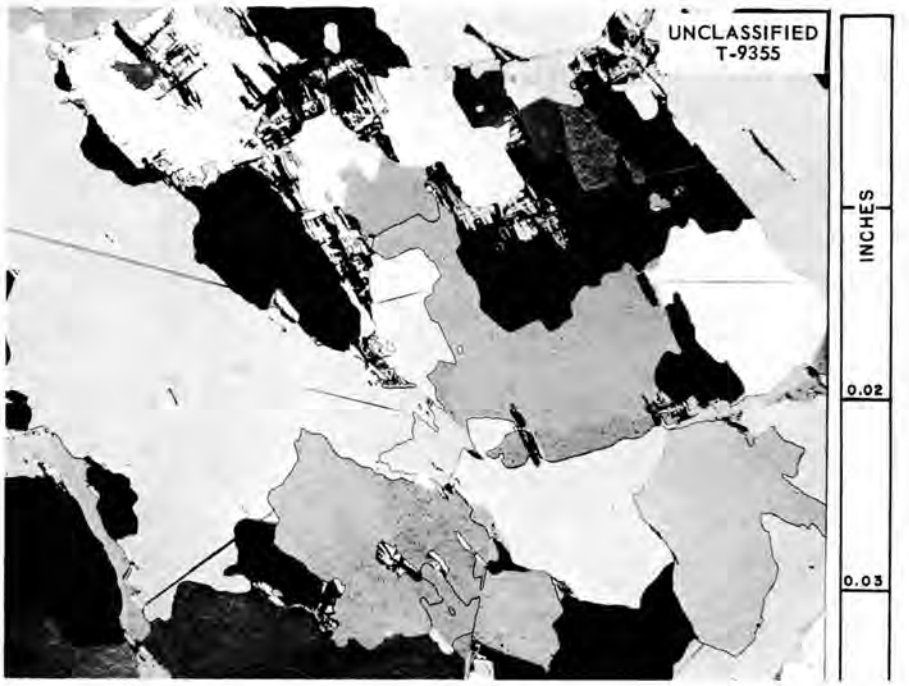

Fig. 12. Zr-2-51 Zircaloy-2, 1000°C 30 min, Water Quenched, 800°C 15 min, Water Quenched, Polarized Light. 100X.

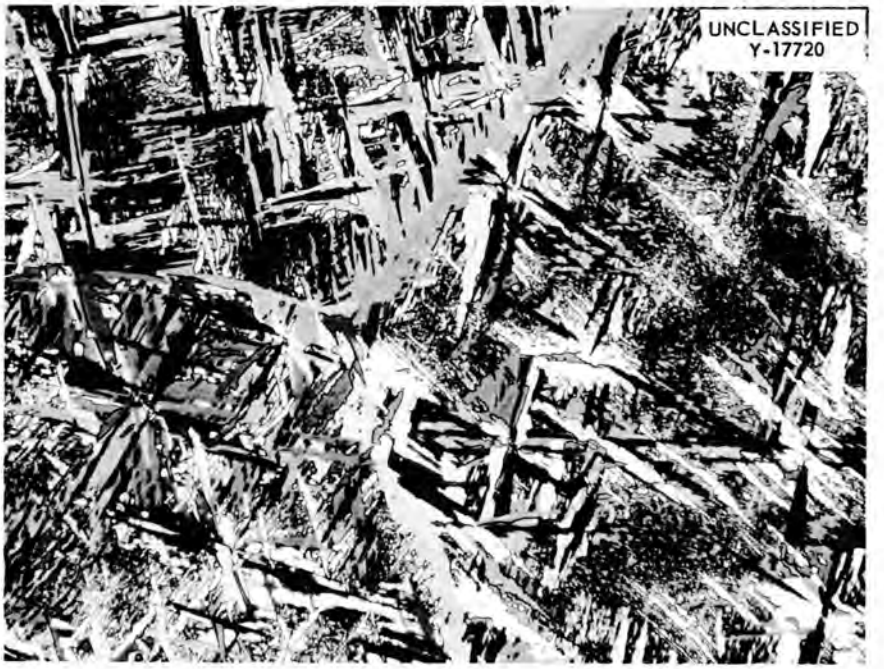

Fig. 13. Zr-2-43 Zircaloy-2, 1000°C 30 min, Water Quenched, 600°C 2 hr, Water Quenched, Polarized Light. 200X.

Its composition is 20 ml of concentrated ammonium hydroxide and 80 ml of absolute ethly alcohol. No phase identification work has been done although color contrast has been observed. An increase in contrast in polarized light and the preservation of the etched surface were also observed. The solution reported by Margolin and Ence has been used on titanium alloys with the technique described herein with good results. No phase identification work has been done on titanium alloys by the author as yet.

Conclusions

The anodizing technique and solution reported herein have been shown to be useful in phase identification, in providing color contrast of microstructures, increased anistropy in polarized light, and as a preservative for etched surfaces for the metallographic examination of zirconium base alloys. The technique has also been used on uranium and titanium base alloys.

References

1. Margolin and Ence, "Cumulative Etching of Titanium Alloys," Journal of Metals, March, 1953.