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Metallographic Preparation of Zr-2.5Nb Pressure Tube Material for Examination of Inclusions

Traitement métallographique du matériau (alliage Zr-Nb 2,5%) des tubes de force en vue de l'examen des inclusions

A.J. Lockley

Presented at the 27th Annual International Metallographic Society (IMS)/ASM Convention 1994 July 24-27 Le Centre Sheraton - Montreal

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TRAITEMENT MÉTALLOGRAPHIQUE DU MATÉRIAU (ALLIAGE Zr-Nb 2,5 %) DES TUBES DE FORCE EN VUE DE L'EXAMEN DES INCLUSIONS

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RÉSUMÉ

Traditionnellement, le traitement de polissage final de l'alliage Zr-Nb 2,5 % comprend un polissage d'attaque qui utilise un mélange d'alumine ou de cendres volantes (0,05 µm) et d'acide fluorhydrique dilué. Ce traitement effectue une attaque chimique sélective du matériau adjacent aux inclusions et provoque la déformation ou l'élimination de ces dernières. Un polissage final a été mis au point qui utilise une boue d'alumine caustique pour obtenir une attaque chimique-mécanique qui laisse les inclusions intactes. Ce traitement est reproductible, convient à l'automatisation et permet de conserver les petites inclusions.

Les travaux susmentionnés ont été parrainés par le Programme de R et D du GPC :

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Matériaux des réacteurs
Composants des canaux de combustible
Laboratoires de Chalk River
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ABSTRACT

The traditional final polish of Zr-2.5Nb alloy comprises an attack polish that contains a 0.05 μm alumina or fly-ash slurry with dilute hydrofluoric acid. This polish preferentially etches the material adjacent to the inclusions and distorts or removes the inclusions. A final polish has been developed that uses a caustic alumina slurry to produce a chemical-mechanical polish that keeps the inclusions intact. This preparation is reproducible, suitable for automation, and retains smaller inclusions.

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INTRODUCTION

The metallographic examination of inclusions in Zr-2.5Nb is required to determine their effect on the mechanical properties of CANDU[1] pressure tubes. Traditionally, the final polish used for zirconium alloys comprises a chemical-mechanical polish, referred to as an attack polish, that contains hydrofluoric acid (HF) as the aggressive etching agent, mixed with a fine abrasive of either 0.05 μm alumina or fly-ash, appropriately proportioned to provide the required balance of abrasion and etching. In samples prepared using a final polish comprising dilute HF and fly-ash the inclusions were damaged or removed. A similar method using alumina [1] has been used and has provided improved retention of the inclusions, but this technique requires much skill to ensure consistency. Neither method is suitable for automation.

Superior inclusion retention is obtained using colloidal silica during the final polish. This technique is suitable for automated polishing, but is not appropriate when surface mapping is required to determine the presence of silicon, as the colloidal silica becomes imbedded in the surface. An alternate metallographic preparation has been developed that reveals inclusions with geometric detail intact, retains small particles, does not contaminate the surface with silica, and is suitable for automation.

EXPERIMENTAL PROCEDURES

The cold-worked Zr-2.5Nb materials used in the development of the caustic polishing procedure were taken from production CANDU pressure tubes. Material containing inclusions was sectioned and mounted to present the plane normal to the transverse direction with respect to the pressure tube. The samples were mounted in Bakelite using a 32 mm diameter mounting press, and were ground through a standard progression of grits of 240, 320, 400, and 600 using an aliphatic hydrocarbon (Varsol)[2] as a lubricant. The samples were rough polished using a slurry comprising 1.0 μm alumina, water and hydrogen peroxide (H_2O_2), and were charged onto a napless chemotextile cloth. A polishing time of one to two minutes was usually sufficient to remove the 600 grit scratches.

Three formulations of slurries were used for the final polish. The first slurry comprised 0.05 μm alumina, water and H_2O_2, being similar in composition to the slurry used for the rough polish. In the two reformulations potassium hydroxide (KOH) was added to increase the alkalinity of the slurry. The final reformulation included aqueous ammonium hydroxide (NH_4OH). Two types of polishing cloths were used: a chemically resistant cloth and a synthetic velvet cloth.

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[1]CANada Deuterium Uranium, registered trademark of Atomic Energy of Canada Limited

[2]Registered Tradename of Imperial Oil Canada

The procedure was adapted for use on an automated polishing apparatus. The final polish could be consistently produced in about two minutes using an applied load of 4.5 kg per sample on a synthetic velvet cloth. The polish was considered complete when scratches could not be seen in bright field illumination. The contrast between the inclusions and the zirconium matrix was increased by the deposition of an anodized layer [2].

For the purpose of comparison, a sample was first prepared using the HF and fly-ash attack polish and then prepared using the caustic polish. The size distribution and population of the inclusions for each preparation were quantified using an image analyzer. About 100 observation fields were selected at random for each prepared surface; each field covered an area of 2500 μm^2.

The caustic prepared sample was prepared for chemical analysis. Areas around inclusions to be analysed were marked, using a microhardness indenter, and photographed before the anodized layer was removed using the caustic slurry. The sample was extracted from the Bakelite, ultrasonically cleaned in methanol and chemically analysed using a scanning auger microscope (SAM). Three elemental maps were made, for phosphorous, silicon, and carbon. The elemental maps were compared with the optical photomicrographs, to allow the inclusions to be identified and correlated.

RESULTS & DISCUSSION

Initially, a final polish comprising 0.05 μm alumina, water, and H_2O_2 was tried, but polishing times extended beyond ten minutes because the surface contained scratches that resulted from continued polishing. The alkalinity of the slurry was increased to a pH of 9.0 using KOH, which noticeably reduced the number of scratches, but not enough to eliminate their appearance in bright field illumination. In an attempt to further reduce the number of scratches, the amount of KOH was increased, which raised the alkalinity to a pH of 11.0. This did not appear to reduce the number of scratches, but it did induce surface pitting. The slurry was optimized when KOH was used to establish a pH of 9.0, followed by the addition of NH_4OH to increase the alkalinity to a pH of 11.0.

The best polishes were achieved when the optimized slurry was used with the synthetic velvet cloth. The chemically resistant cloth produced scratches on the surface regardless of the slurry's alkalinity or the duration of the polishing time. For automation, a final polish was achieved in two minutes when the synthetic velvet cloth was used. The slurry was charged to the cloth at 30-second intervals, to keep the surface wet, and an applied load of 4.5 kg per specimen was used.

In bright field illumination a properly polished surface was generally featureless. The only distinguishable features were small, dark angular objects, which interference contrast illumination revealed to be gaps within the inclusions. Interference contrast illumination also revealed a surface of fine scratches, with inclusions appearing as flat unscratched areas standing slightly proud of the scratched background (Figure 1).

After anodizing, the primary inclusions were pale blue and bright yellow, and the (αZr) and the (βZr) phases in the background Zr-2.5Nb matrix became visible (Figure 2). The cracks that occurred within the inclusions were observed without any deterioration in detail. Even inclusions perched at the edges of large cracks or voids retained their edges. The pale blue inclusions consisted of zirconium and carbon, while the yellow inclusions consisted of either phosphorous and zirconium, silicon and zirconium, or a combination of phosphorous and silicon with zirconium (Figure 3a). There was no surface contamination from silica, which allowed surface mapping for silicon without confusion (Figure 3b). Although colloidal silica provides an excellent final polish, the silicon imbeds in the surface confounding SAM examinations for fine silicon particles.

The sample prepared using the standard acid-attack polish showed preferential etching at the interface between the inclusions and the Zr-2.5Nb matrix and at the cracks within the inclusions. The edges of the inclusions appear to be more rounded, and the image is not as sharp and clear as the surface prepared using the caustic preparation. The caustic polish does not induce preferential etching at the interface between the Zr-2.5Nb, and the inclusion geometric detail is maintained at the edges of the inclusion.

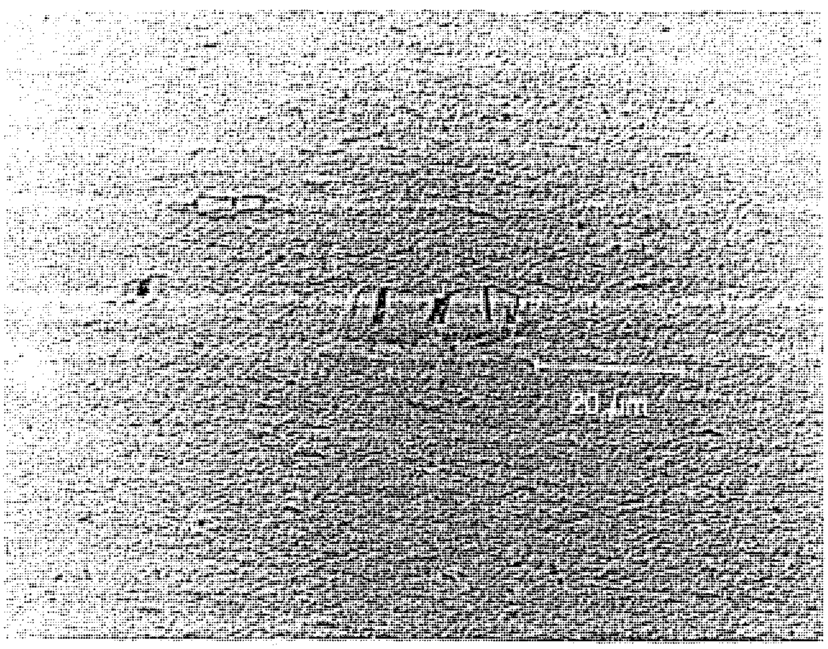

Figure 1. The caustic polished surface viewed using interference contrast illumination.

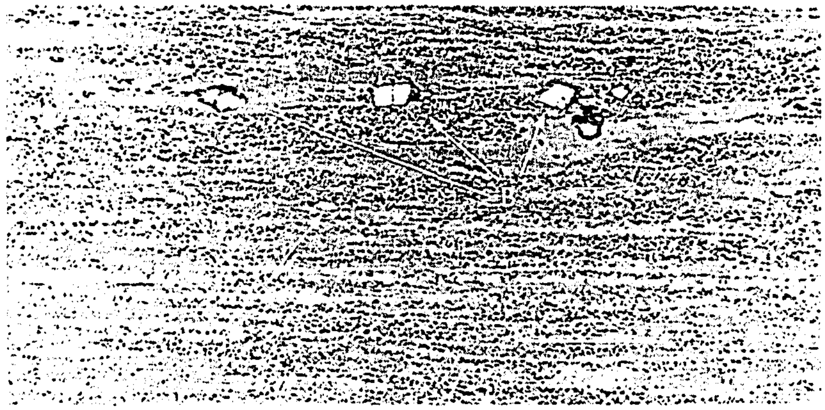

Figure 2. The same surface as in Figure 1, anodized and viewed in bright field illumination showing pale blue (A) and bright yellow (B) inclusions.

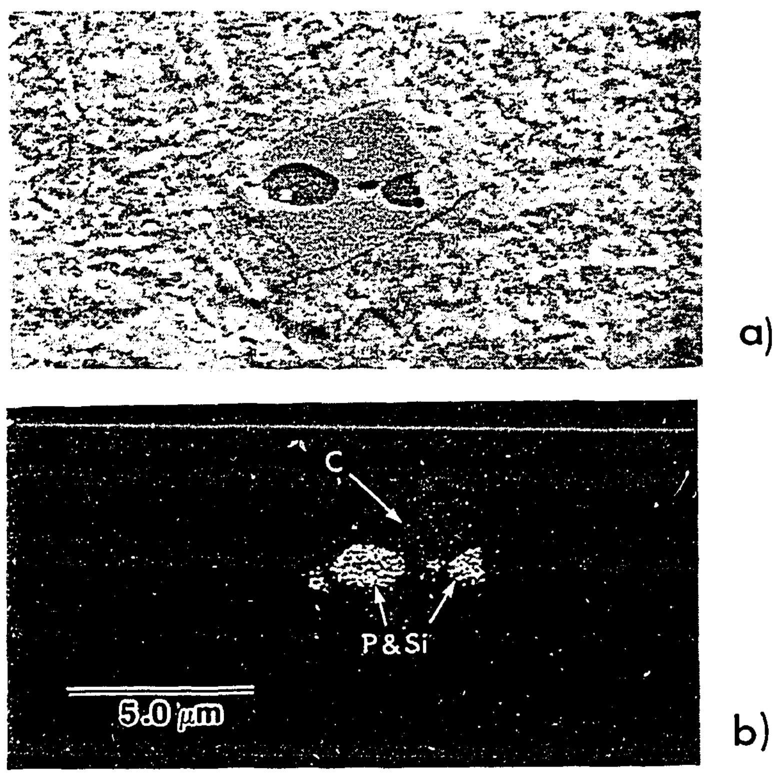

Figure 3. Secondary electron image of an inclusion (a) and an elemental map showing carbon, and silicon and phosphorous, as indicated (b).

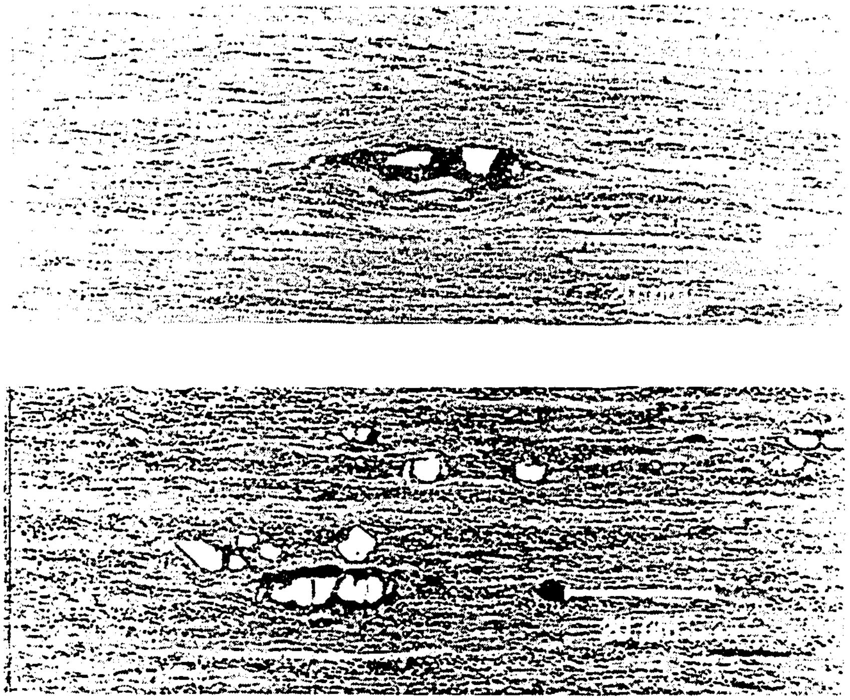

Figure 4. Inclusions prepared using acid polish (top) and caustic polish (bottom).

A quantitative analysis that compared the effect of the acid and caustic preparations on the size distribution and population of inclusions revealed that the specimen with the caustic preparation exhibited 37% more particles than the specimen with the acid preparation. Figure 5a shows the normalized distributions of inclusion size for both preparations. The distributions are similar (which is expected, as the analysis was conducted on the same sample), except that the specimen with the acid preparation has 8% fewer inclusions in the $<0.1\ \mu m^2$ size range. Figure 5b shows the normalized distributions of the number of particles observed per field for both preparations; the distributions are different. The surface prepared using the caustic preparation had a higher frequency of fields that contained more inclusions and a lower frequency of fields that contained no inclusions. The preferential etching at the interface between the inclusion and the Zr-2.5Nb interface, associated with an acid-attack polish, undermines small inclusions, allowing them to detach from the Zr-2.5Nb matrix. Conversely, the caustic preparation does not cause preferential etching; therefore, no undermining of the inclusion takes place and the presence of small inclusions is maintained.

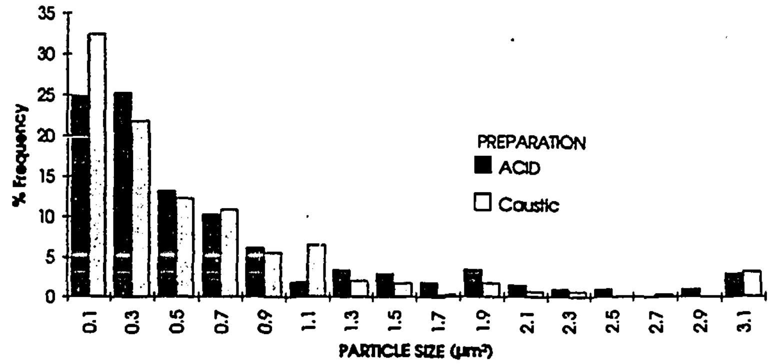

Figure 5a. Normalized distributions of inclusion size for both preparations.

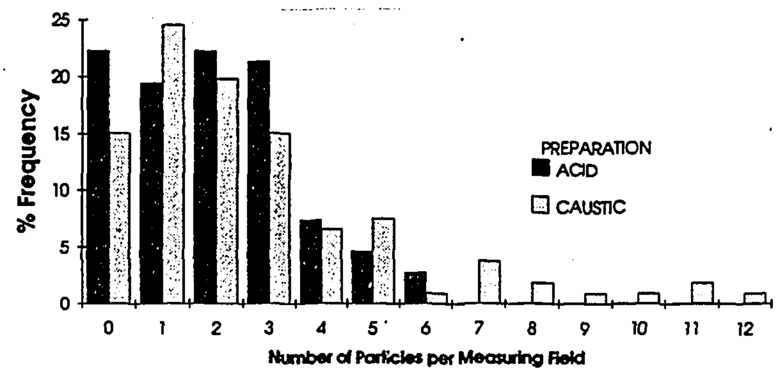

Figure 5b. Normalized distributions of the number of particles per field.

CONCLUSIONS

A new technique for preparing Zr-2.5Nb material that uses a caustic final polish has been developed. The advantages of the technique are that:

(a) the caustic slurry does not induce preferential etching at the interface between the Zr-2.5Nb matrix and the inclusions, or at cracks within the inclusions, and is well suited to the surface examination of small inclusions (less than 0.2 μm^2),
(b) no silica, which can confound SAM mapping for silicon, is used,
(c) the surface structure and the inclusions appear to be sharp, due to the lack of matrix removal adjacent to the inclusions, and
(d) it has been adapted for use with an automatic polishing apparatus, making this procedure efficient. An optimal final polish was achieved in two minutes using a synthetic velvet cloth charged with optimized caustic slurry at intervals appropriate to keep the surface wet, using an applied load of 4.5 kg per specimen.

ACKNOWLEDGMENTS

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