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FEATURE

Development of a Versatile Two-Step Etchant to Reveal Grain Boundaries in Multiple Aluminum Alloys

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Abstract

This paper describes an etching procedure to reveal grain boundaries in metallographically prepared samples from 2000, 5000, 6000, and 7000 series alloys. The etching procedure, named the Papageorge two-step etch, makes use of two established aluminum etchants with slightly modified chemistries. The first step in the etching process uses a modified Keller's reagent to attack and activate the polished surface. The second step uses a modified version of Weck's reagent to stain and develop contrast at the grain boundaries. The etching procedure is straightforward which aids in training novice users. Examples of successfully etched AA2024, AA5754, AA6061, AA7075, AA7475 and a resistance spot-welded sample of AA7075 and AA6111 are presented here. The Papageorge two-step etch offers metallographers the option to use one etch for revealing grain structures for a broad range of single alloys or joined structures fabricated with dissimilar aluminum alloys.

Keywords Aluminum alloys · Metallography · Light microscopy · Grain boundaries

Introduction

In the mid-sixth century BCE, Plato famously stated that "our need with be the real creator" which has been loosely translated over time to the more well-known English proverb: Necessity is the mother of invention [1]. The development of this etching procedure is an example of this axiom. During classes where the authors train large groups of students (up to twenty per laboratory session) in the art of metallographic sample preparation of aluminum alloys, etching the alloys to reveal grain structures has consistently been a point of failure. Multiple aluminum alloys including 2000, 5000, 6000, and 7000 series are used during processing, characterization, and corrosion laboratory sessions. The diversity of alloys required multiple etchants and techniques that were difficult for inexperienced students to master in the limited time available in the laboratory class period.

The goal of this work was to develop a single etch that reveals grain boundaries in multiple aluminum alloy series. Three important criteria were identified for a new etchant. First the technique must be easy to learn for inexperienced metallographers. Second the technique must be effective at distinguishing grain boundaries in several alloys of aluminum. Specifically, the 2000, 5000, 6000, and 7000 series alloys were targeted in this work since those are the alloys used primarily in the teaching laboratories. Third, the etch should produce a sample suitable for examination using only bright-field optical microscopy. An etchant that satisfies these criteria should be of interest and utility to industrial and quality control laboratories where limited equipment may be available. It would also be beneficial to laboratories that have a high employee turnover rate or work with student interns regularly.

There are several established etchants for revealing the grain structure in select alloys. Kroll's reagent, Keller's reagent, and Barker's reagent are a few of the popular established etchants to reveal grain structure in some aluminum alloys [2]. Kroll's reagent is composed of varying amounts of nitric acid (HNO_3) and hydrofluoric acid (HF) diluted in distilled water, and Keller's reagent is a mixed acid solution composed with a standard formulation of 5 mL HNO_3, 2 mL HF, 3 mL hydrochloric acid (HCl), and 190 mL distilled water. Both Kroll's and Keller's reagents are attack etchants that are applied using a swab or immersion technique. Neither etchant is effective for grain boundary delineation

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in many aluminum alloy series other than the 7000 series. Barker's reagent is an effective etchant to create grain boundary contrast in a variety of aluminum alloys. Barker's reagent is a dilute solution of fluoroboric acid in distilled water and is used as an electrolytic etchant (20–40 V DC) that requires a power supply. Examining the grain structure of a sample etched using Barker's reagent requires at least a polarized light optical microscope, and often a quarter wave or full wave (lambda) plate is used to add color contrast to the images. Novice metallographers often struggle to etch consistently with Barker's reagent (based on experience from multiple groups during the author's time teaching). Barker's is also not a universal etch for all alloy series and one must be careful not to over-etch which results in pitting. Another established etchant revealing grains in aluminum alloys is Graff-Sargent reagent. While it is effective for multiple series of aluminum alloys, it does not cover the four-alloy series of interests identified here. Graff-Sargent also contains hexavalent chromium which presents a dangerous and carcinogenic health risk for novice users and is more costly to dispose of the waste properly. Weck's reagent is a stain etch that has been shown effective for etching multiple aluminum alloy series [3]. The issue with Weck's reagent that prevented this as a choice in this work was that it is dependent on a high quality of surface preparation. In laboratories that rely on novice metallographers or in teaching laboratories, this is often not possible on all samples, and the results using Weck's reagent are inconsistent and do not provide the grain contrast necessary for image analysis. There are other etchants for aluminum alloys available; however, an etching procedure that is straightforward for novice metallographers, one that is safe to use, and applicable to a broad range of alloys to reveal the grain structure of aluminum

Table 1 The etching times for steps 1 and 2 for the alloys examined in this work are shown below

Alloy designation	Step 1 Modified Keller's reagent, s	Step 2 Modified Weck's reagent, s
AA2024-T3	10–15	10–15
AA5754-O	15	30
AA6061-T6	10–15	15–20
AA7075-T6	5–10	5–10
AA7475-T61	5–10	5–10

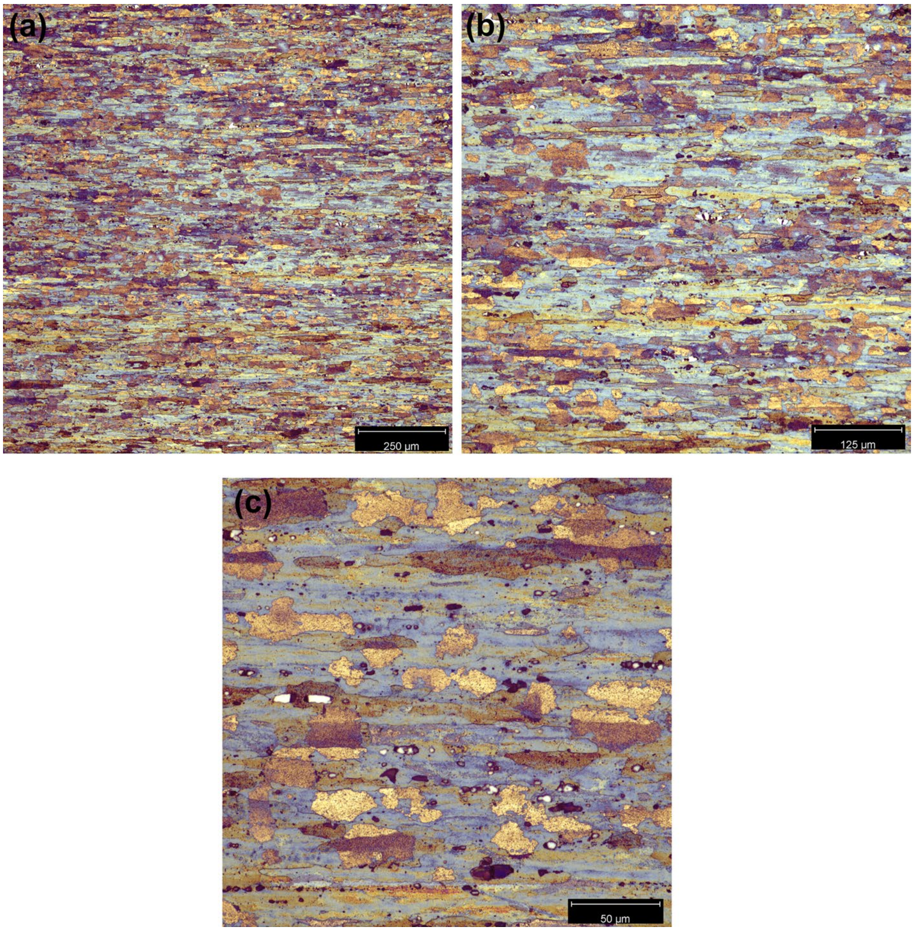

Fig. 1 Bright-field optical micrographs of a nominally 3-mm-thick sheet of AA2024-T3 in the rolling direction. Micrographs were collected at 100x original magnification (**a**), 200x original magnification (**b**), and 500x original magnification (**c**).

alloys from various series does not exist in the established etchants listed in the handbook [2].

There are examples in the technical literature of researchers exploring new and alternate etching chemicals and processes for revealing grain boundaries in aluminum alloys. Mohammadaheri et al. explored a two-step etching process similar to the method proposed here but with a different first etchant [4]. This work demonstrated effective grain etching for 2000 and 5000 series aluminum alloys; however, no other alloys were explored. During preliminary testing in the work done here, it was determined that this method did not consistently reveal grains in the 6000 series alloys. Other efforts have focused on finding an improved etchant for creating grain boundary contrast in aluminum alloys joined by welding and specifically solids-state welding processes. Tamadon et al. explored numerous combinations of two-step etching to reveal the grain structure in AA6082 joined by friction stir welding (FSW) [5]. While several processes produced excellent results, these processes were not something that could be easily transferred to a novice metallographer. Many involved three steps with an attack etch, followed by an etch to remove any Al_2O_3 on the surface, followed by a final etch to either stain or enhance grain contrast. Several procedures involved heat and ultrasonic baths to be used which adds additional variables and creates a difficult process to reproduce each time. Beach *et. al.* previously published work on a modified Barker's reagent etch for revealing grain contrast and the oxide stir line in FSW joints [6]. This etch showed limited effectiveness on the 6000 series alloys and did not produce uniform grain contrast for dissimilar welds. It also requires some experience and skill with electrolytic etching which limits consistency for novice metallographers.

The work presented in this paper presents the results of a new etching technique. The procedure is a two-step etch that combines an attack etchant with a stain etchant to reveal grain structure of 2000, 5000, 6000, and 7000 series aluminum alloys. Details of the etchant chemistry, procedures, and results are presented in this paper.

Experimental Procedures

Samples of flat-rolled aluminum sheet (3 mm in thickness) were sectioned using a Leco MSX255 sectioning machine. Samples were taken from the following aluminum alloys AA2024-T3, AA5754-O, AA6061-T6, and AA7075-T6. The cross sections were oriented in the mount so the rolling direction would be polished and etched.

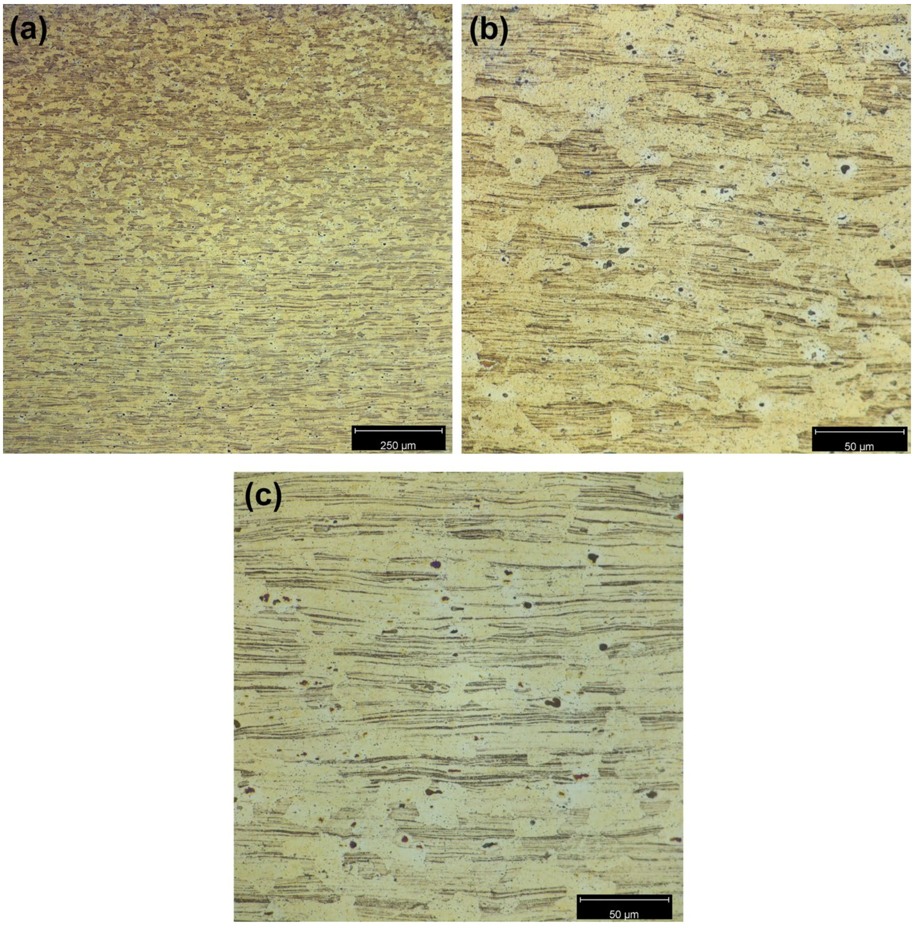

Fig. 2 Micrograph from a sheet of 3.8-mm-thick AA5754-O in the rolling direction. The image in (**a**) reveals a difference in the microstructure at the surface compared to the central region at 100x magnification. The grain structure near the surface shown here in (**b**) at 500x magnification reveals relatively equiaxed grains. The grain structure in the central region of the sample shown here in (**c**) at 500x magnification shows elongated grains indicating an incomplete through thickness anneal on this sample.

Metallographic sample preparation followed methodology specified in ASTM E3-11(17) [7]. Details of the process are provided to enable easier replication of the technique. Bakelite (phenol-formaldehyde resin) mounting compound was used to create 31.75 mm (1 ¼″) mounts. The Bakelite was heated for three minutes at 166 °C (330 °F), and a pressure of 28.3 MPa (4100 psi) was applied in a Buehler SimpliMet 4000 compression mounting machine to create the mount. Samples were ground using progressively finer silicon carbide abrasive paper with flowing water using the following sequence of grits: 240, 320, 400, and 600. Grinding time was approximately two minutes per grit with copious water rinsing to clean between each step. Polishing commenced with a 6 µm diamond paste combined with diamond extender on a Leco PAN-W cloth for three minutes. The second polishing step utilized 3 µm diamond paste with diamond extender on a Leco PAN-W cloth for three minutes. The final polishing step was completed with 0.05 µm colloidal silica (Leco) diluted with water on a Leco Imperial cloth until the samples were free of scratches (no more than five minutes to avoid precipitate pull-out). In between each step, the samples were cleaned with a cotton ball saturated with water, rinsed with ethanol, dried using warm air, and observed using an optical microscope to ensure scratches from the previous step were completely removed. All polishing was done by hand with the platen speed for all polishing steps set to 150 RPM.

The etching process developed is a two-step etch that requires applying an attack etch first followed by a stain etch. Both formulations are modified versions of established etchants. The first etching solution uses a modified version of Keller's reagent. The formula for this reagent is: 3 mL HNO_3, 2 mL HCl, 2 mL HF, and 93 mL distilled or deionized water. The second etching solution is a modified version of Weck's reagent. The second etchant mixture was: 2 g sodium hydroxide (NaOH), 3.80 g potassium permanganate (KMnO4), and 100 mL distilled or deionized water.

The etching process begins by lightly swabbing the polished surface of the sample in a circular fashion using the modified Keller's reagent. The application time for the first etchant varies by alloy series, and the etching times are listed in Table 1. Once the first etchant is washed off with water, the sample was submerged, while slowly rotating in a circular motion, in the modified Weck's reagent for the times indicated in Table 1. The samples were rinsed in flowing water, rinsed with ethanol, dried using warm air, and examined using bright-field optical microscopy.

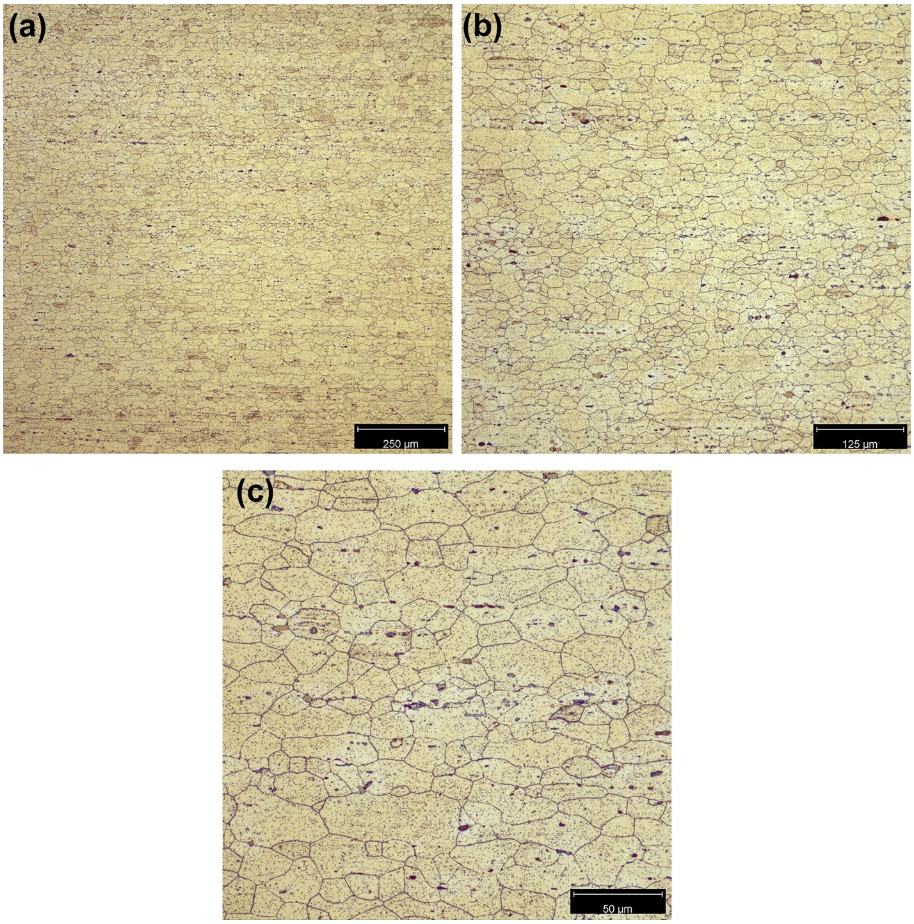

Fig. 3 Micrographs of an etched cross-section in the rolling direction through a 3 mm AA6061-T6 sample. The micrographs show the grain structure at 100x (**a**), 200x (**b**), and 500x (**c**) original magnification after etching by the Papageorge two-step process.

Optical micrographs from cross sections of samples taken from sheets of each alloy were collected using an Olympus GX53 inverted microscope. Micrographs of the etched specimens were recorded using PaxCam software at magnifications in the range of 100×–500×. All micrographs were collected in bright-field (BF) mode. A resistance spot weld (RSW) sample between a 6000 and 7000 series alloy was also prepared and etched in this work. Those images were collected using an Olympus DSX510 optical microscope with a linear motion *x*–*y* stage.

Results and Discussion

The etching procedure, which the authors refer to as the Papageorge two-step etch, was found to be effective on multiple aluminum alloys. Table 1 shows the times that were found to be optimal for creating grain contrast without creating pitting on the surface. Figure 1 shows the results for AA2024-T3 in the rolling direction at magnifications ranging from 100× up to 500×. The images in Figure 1 were collected in bright-field mode with no polarizer, quarter wave plate, or lambda plate to create the color. The AA2024 alloy was the only alloy that exhibited this type of color variation after etching. The AA2024 alloy has at least four percent by weight copper in the alloy that is distributed in the matrix and present in precipitates. The copper content is an order of magnitude (or more) higher than any other alloy investigated in this work. The Weck's stain etch appears to interact with the copper and form films on the surface of the grains that create the apparent color in this alloy. While the goal of this process is not to create a color etchant, the color helps to delineate the grain boundaries in this alloy and produces visually interesting micrographs of the grains. Additional work is required to understand this effect in more detail and that work is underway.

Figure 2 shows a cross section in the rolling direction from a sheet of AA5754-O after etching by the Papageorge two-step process. The grains are visible throughout the cross section. The etchant also revealed that the annealing (indicated by -O in the temper designation) for this 3.8-mm-thick sheet was incomplete. The grains near the surface shown in Fig. 2(b) are more equiaxed and uniform as expected in an annealed material. The grains in the central region of the sheet are deformed and show elongation in the rolling direction in Fig. 2(c). The etched cross section revealed that this sheet was not completely annealed.

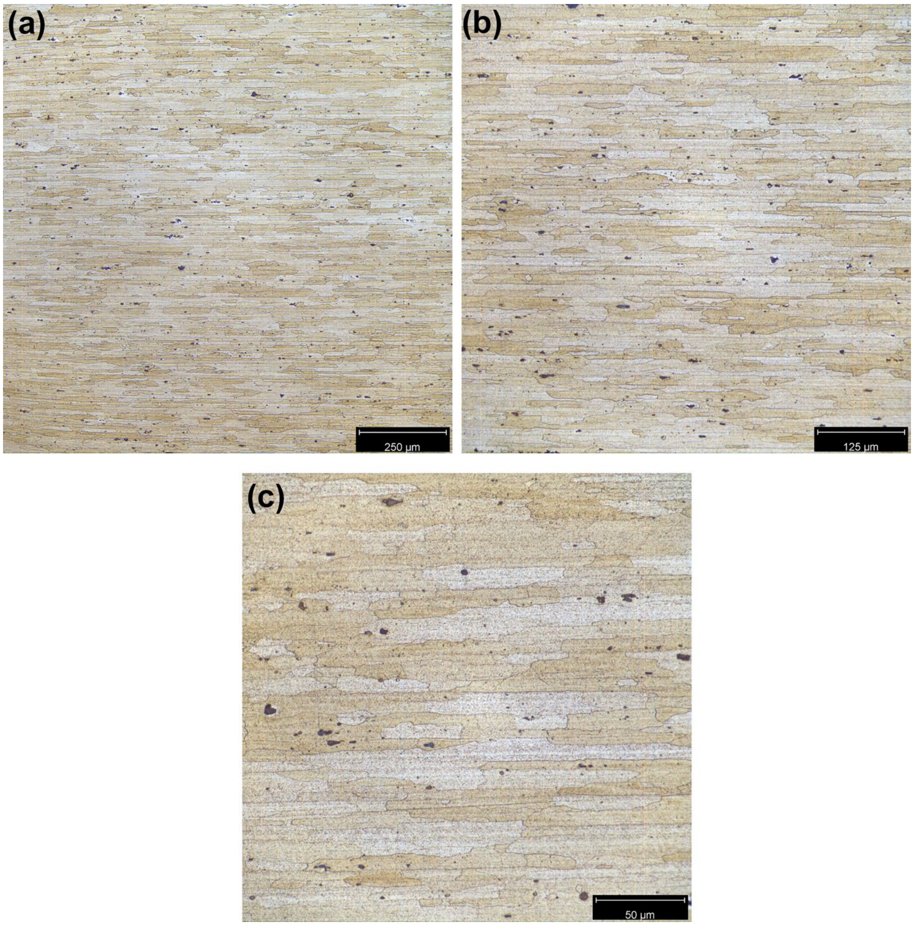

Fig. 4 Etched cross sections in the rolling direction from a nominally 3-mm-thick sheet of AA7075-T6. The micrographs reveal the grain structure at 100x (**a**), 200x (**b**), and 500x (**c**) original magnification after etching with the Papageorge two-step etching process.

Aluminum alloy 6061 is regarded as a difficult alloy to etch for grain contrast. While there are suggested etchants in ASM Handbook Volume 9 [2], none are particularly consistent or easy for novice metallographers to use to reveal the grain structure. The Papageorge two-step produced an excellent grain etch on AA6061-T6 shown in Fig. 3. The etching process creates a high level of contrast at the grains and did not create significant pitting on the polished cross section. The ability to consistently create high contrast etching at the grain boundaries of AA6061 has been the most problematic of all alloys during laboratory-based classes. The new etching procedure provides not only an improvement over other etches, but one that is easy to use and train new users to be immediately successful with.

Aluminum alloys in the 7000 series are typically etched effectively using Keller's reagent to reveal grain structure. The Papageorge two-step etch also produced effective grain contrast on these alloys as shown in Figs. 4 and 5. While there is no advantage of this etchant as compared to Keller's reagent etching, they were included in the study as having the ability to use one etching procedure across all alloys is desirable for some laboratories (including a teaching laboratory for undergraduate students). The second step in the etching process developed here does not adversely affect the contrast or quality of the images so it can be used as part of an inclusive etching process, or the second step could simply be omitted for this alloy series.

Another application where the Papageorge two-step etching procedure provides advantages for metallographers is for examining joining of dissimilar alloys. Figure 6 presents micrographs from an AA7075 (upper sheet) joined to AA6111 (lower sheet) by resistance spot weld. The low-magnification image montage shows the grain structure in both alloys; however, there is higher grain contrast in the AA7075. The etch is also effective at revealing the microstructure in the partially melted zone (PMZ) of the resistance spot weld as shown in Fig. 6(b). There are other applications including friction stir welding and explosion bonding where the Papageorge two-step etching process may provide high-quality images of dissimilar joints that were not possible using currently available etches. Work is underway currently to investigate other types of joints using this etching procedure.

There are a few practical notes to discuss when working with the Papageorge two-step etchant. The samples must be freshly polished for the etchant to work properly. Based on the experiences during this work, the samples must be etched within fifteen minutes after the final polish

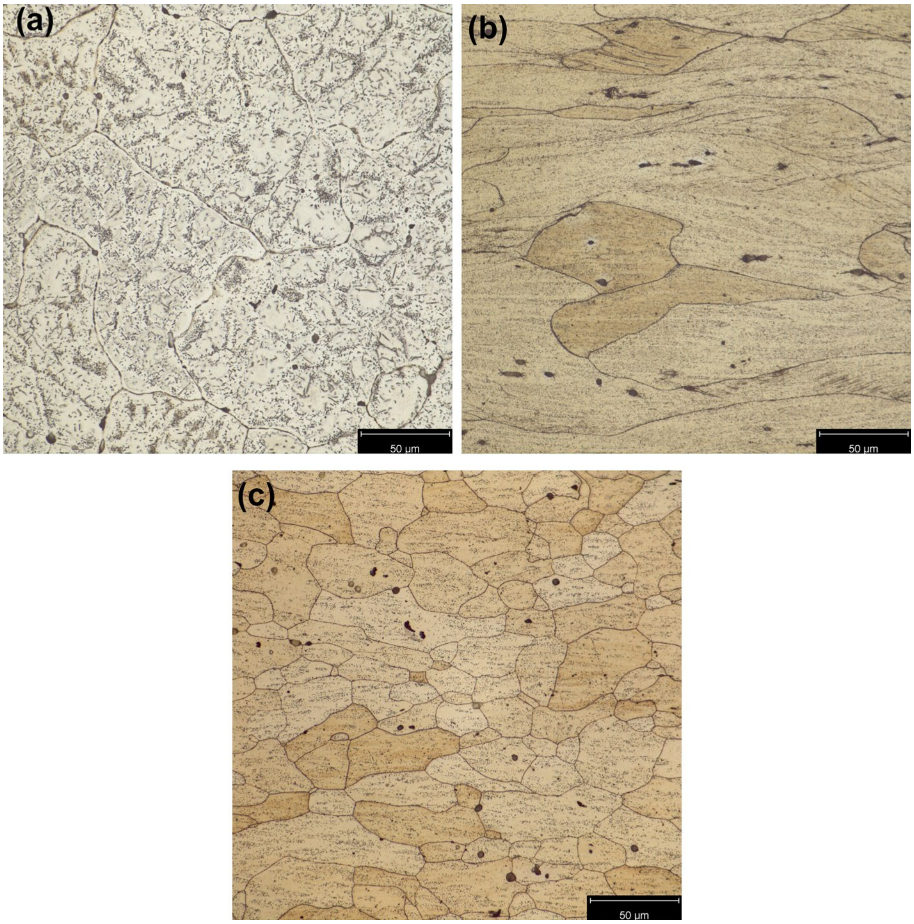

Fig. 5 Etched cross sections from a sample of AA7475. This alloy was cast and thermomechanically processed in the author's laboratory. The micrograph in (**a**) shows the microstructure after a homogenization heat treatment at 500x original magnification. The micrograph in (**b**) shows the grain structure of the AA7475 after hot rolling, and the micrograph in (**c**) shows the grain structure after solution heat treating, cold rolling and additional 1%, and artificially aging it to achieve a T61 temper designation. All samples were etched using the Papageorge two-step etching procedure.

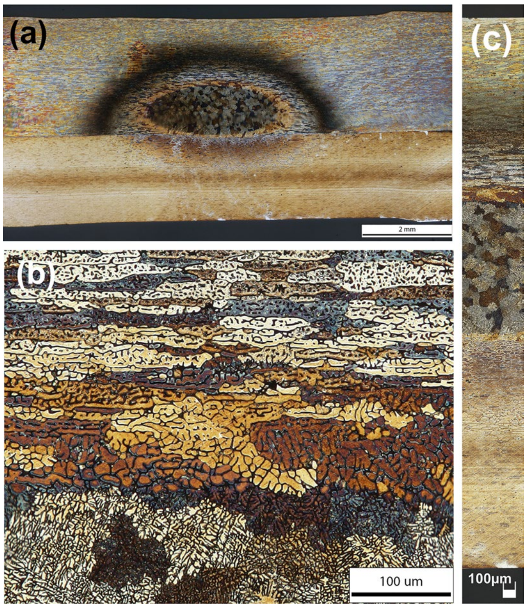

Fig. 6. Optical micrographs of a resistance spot-welded sample. The image in (**a**) is a low magnification image montage of the RSW showing the AA7075 (top sheet) and the AA6111 (bottom sheet) after etching with the Papageorge two-step etchant. The micrograph in (**b**) shows the partially melted zone in the AA7075, and the micrograph slice in (**c**) shows the grain structure in the parent metals, PMZ and weld of the dissimilar alloys.

is completed. When the samples are left to sit out for several hours before etching, the second step of staining does not produce a uniform and even contrast. It is not clear whether this is due to an inhomogeneous attack etch during step 1, as there is often insufficient contrast when inspected prior to step two of the process. It was confirmed multiple times that a more passivated (oxidized) polished surface results in a nonuniformly etched sample.

The etchants used in this work were always mixed immediately before using (e.g., not stored and reused). This is simply due to a policy in this shared teaching laboratory that no etchants are stored long term to avoid the problem of chemicals being left in the laboratory for long periods and often abandoned, creating a more work for proper disposal later. It may be possible to store these etches and reuse them more than once, but that was not the procedure followed in this work.

The last practical point that was observed during this work was that this etching process works better when the sample is swabbed only once with the modified Keller's reagent in step 1 and immersed only once in the modified Weck's reagent in step two also. It was possible to do a second immersion in the modified Weck's; however, in this work that often led to nonuniform staining of the etched surface. It is recommended to do some development work and optimize the process for the specific alloys and samples of interest to create specific times for each step of the Papageorge two-step etch for use in teaching, training, or production support work in each laboratory.

Conclusions

The results of a new etching procedure, the Papageorge two-step etch, were presented. The etching procedure was proven effective for creating grain contrast in 2000, 5000, 6000, and 7000 series alloys. The Papageorge two-step etch also worked effectively to create grain contrast on a resistance spot weld cross section from a sample fabricated from a 6000 and 7000 alloy. The etching procedure has proven straightforward for novice metallographers and offers an option to use a single etchant to simplify sample preparation in the laboratory.

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