Improvements in the metallography of as-cast AZ91 alloy

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Abstract

Evaluation of the grain structure and grain size of cast magnesium–aluminum alloys is usually performed after grain-boundary-enhancing treatments which involve tedious heat treatment at high temperature. In this work, a rapid and simple etching method is described for metallographic preparation of AZ91 alloy, revealing grains without altering the as-cast dendritic microstructure and the presence of secondary phases. The etching reagent, composed of acetic acid, alcohol and water, has not been reported previously. After etching and drying, a crackled film containing fine stripes is found at the surface of the substrate. The optical contrast between grains under polarized light is attributed to form birefringence induced by the stripes, preferentially aligned according to the orientation of underlying grains. The composition of the crackled film was evaluated and its characteristics are presented. It was found that a minimum concentration of aluminum is necessary in the magnesium-rich matrix for the formation of the crackled film. Likewise, beyond a maximum concentration of aluminum, the surface film does not crack.

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1. Introduction

The development of light structural applications is continuously pushing for magnesium components with higher performance and overall quality at the lowest cost. The mechanical properties and corrosion resistance of cast magnesium components are generally improved by microstructural refinement: castings having fine grains usually show a more uniform distribution of solute and a better dispersion of secondary phases within their structure [1]. They are stronger and more ductile, exhibit enhanced fatigue resistance and machinability [2]. The thin interdendritic network formed between fine grains also reduces the negative consequences of microsegregation on corrosion resistance [1]. In that perspective, many researchers have focused their efforts during the last 50 years at reducing the grain size of magnesium alloys, in particular, Mg–Al-based alloys, which are widely used by industry, and many literature reviews were published about grain refinement mechanisms [2–5].

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Different means have been developed and published to reveal the grain boundaries and texture of cast Mg–Al-based alloys [5–14]. Most of them involve a tedious first step consisting in solution heat treatment and homogenization to reduce microsegregation (coring), followed by rapid cooling. These heat treatments are sometimes followed by precipitation at 200 °C for a short period of time to enhance the delineation of grain boundaries [6,8,10]. In the case of cast AZ91 alloy, a modified T4 heat treatment is frequently recommended to reduce microsegregation and to reveal the granular microstructure [15]. It consists in solution treatment at 413 °C for 6 h followed by a rapid cooling to 352 °C for 2 h, then reheating for about 10 h at 413 °C, and finally rapid cooling to room temperature. Following this heat treatment, etching of grain boundaries is carried out with appropriate reagents [5–8,13,14,16]. Such indirect heat treatments are time consuming and they modify the as-cast substructure.

An alternative and more rapid method to reveal the microstructure of cast alloys consists in color etching which is performed for a great variety of alloys with specially designed reagents [17,18]. For magnesium alloys, Ernst and Laves [19] published the composition of etchants containing perchloric acid whereas many etchants containing glacial acetic acid and picral were developed by George [11]. Observations were usually performed under polarized light for revealing the distinctly colored grains. However, all these etchants are not frequently reported in micrographic studies about grains in magnesium alloys. The unstable characteristic of mixtures containing perchloric acid or picric acid (trinitro-phenol) and their toxicity render many of them somewhat less attractive.

More recently, an electrolytic color etching method has been published for examination of the granular microstructure of as-cast high-purity AZ91 [20] and it has been applied to thixocast Mg–Al alloys of other composition as well [21,22]. The authors indicate this anodic etching creates a color contrast between grains when viewed under polarized light due to the formation of an anisotropic surface film. However, this method involves special electrolytes (composition not given) and it is sensitive to process parameters, such as electrolyte composition, flow rate, applied voltage, and etching time [20]. Authors specify that observation and measurements cannot be delayed due to the reactive nature of the etched surface of their specimens. Electrolytic attack of the polished surface can occur although it can be reduced by appropriate pre-etching treatments [20].

These inconveniences pushed for an improved solution to metallographic preparation of as-cast Mg–Al alloys. In our laboratory, an applied research project has been undertaken recently with the purpose of refining the microstructure of magnesium alloys cast in permanent molds by using low-frequency mechanical vibrations [23,24]. During this project, a new etching method has been developed to avoid the modified T4 heat treatment and to facilitate metallographic preparation while revealing simultaneously the grains and general microstructure of cast Mg–Al-based alloys. This method, firstly developed for AZ91D alloys, was presented in the International Metallographic Contest in 2002 by Maltais [25] and is detailed in the present paper. It is based on the formation of a crackled surface film, similar to that described by George [11], creating a remarkable color contrast between grains under polarized light. The surface film has been characterized and the grain size was compared to that obtained with the usual method for metallographic preparation. A mechanism is proposed to explain the enhanced color contrast between grains obtained with this new and simple etchant.

2. Experimental procedure

2.1. Preparation of cast specimens

The specimens prepared for this metallographic study were composed of magnesium–aluminum-based alloy AZ91D (Mg–9Al–0.5Zn) in the as-cast condition. Ingots of AZ91D were melted in 430 stainless steel crucibles, the melt being protected under a CO₂–0.5%SF₆ gas mixture. After melting, they were cast in permanent steel molds coated with a protective ceramic compound. The thickness of castings varied between 6 and 25 mm, producing a wide range of grain size and texture [23,24].

2.2. Metallographic preparation of specimens

Specimens of AZ91D castings were cut, ground, and polished according to usual procedures developed
for magnesium alloys [13]. Grinding of specimens was carried out on silicon carbide papers wet with water, down to grit size 1200. It was followed by fine polishing with diamond, particle size from 6 to 1 μm, on Texmet cloth, rinsing with water and ethyl alcohol. Aluminum polishing discs were used to minimize stray currents. For best results, the polished surface must be mirror like, i.e., free from any residual tarnishing layer.

Specimens were etched at room temperature in diluted acetic acid solutions containing ethyl alcohol and water. The concentration of each component in the etchant was systematically studied to obtain optimum solution for Mg–Al alloys. It was found that the best solution for AZ91D alloy is composed of:

- distilled water (50 ml)
- anhydrous ethyl alcohol (150 ml)
- glacial acetic acid (1 ml).

Polished specimens were immersed in the etching solution and gently agitated for about 45 to 120 s. They were then rinsed in anhydrous ethyl alcohol and dried in a blast of air. The visual contrast between grains is not obtained during etching but during the drying step.

It was found by repeated experiments that an appropriate concentration of water in the etchant is essential. Too much water promotes the formation of an opaque whitish layer at the specimen surface. Too little water will not produce grain contrast at all. It was found that a draft of warm and humid air following the drying step improves grain contrast. However, the reaction between the etched surface of specimens and ambient air (50% relative humidity and 20 °C) is slow and does not reduce the contrast between grains following etching. Consequently, the delay between etching and light optical microscope observation is not critical and long periods of observation are possible without degradation of surface quality.

2.3. Light microscopy, scanning electron microscopy, and atomic force microscopy

The etched specimens were examined using a light microscope with polarized light; the polarizer and analyser being perpendicular to each other. Color contrast between adjacent grains was enhanced by using a retardation wave plate.

The microstructure was also examined at higher magnifications with a JEOL 8500 scanning electron microscope (SEM) to study the etched surface and to clarify the mechanism by which the grain contrast is created. Following observations with the SEM, electron microanalysis at the surface of specimens was performed using energy-dispersive spectroscopy (EDX). An incident-beam energy varying between 3 and 15 keV was selected for analyses. Reduced incident energy was necessary to generate X-rays only from elements present close to the surface. The electron beam current was set to approximately 6 nA for microanalyses.

Surface texture was characterized using an atomic force microscope (AFM). AFM imaging was performed in the tapping mode on a Dimension 3100 Atomic Force Microscope from Digital Instruments using an ULTRASHARP etched silicon probe model NSC15 from Silicon-MDT (≤10-nm nominal tip radius of curvature, aspect ratio of approximately 2.6:1).

2.4. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS)

The etched surface was further characterized by using FTIR and XPS. Mid-infrared spectra of the etched surface of AZ91D specimens were recorded using a Nicolet Magna-550 FTIR spectrometer (Thermo-Nicolet, Madison, WI) equipped with a DTGS detector in the attenuated total reflectance (ATR) mode with a Split-Pea attachment (Harrick Scientific, Ossining, NY). One hundred scans with an optical retardation of 0.25 cm were routinely coadded, triangularly apodized, and Fourier transformed to yield a 4 cm⁻¹ spectral resolution.

XPS measurements were performed on a PHI 5600 ESCA System from Physical Electronics. Survey spectra and depth profiles were acquired at low-energy resolution, using the Kα line of a standard Al X-ray source. For elemental peak shape and shift analyses, high-resolution (approximately 0.5 eV FWHM) spectra were acquired using the Kα line of a standard Mg X-ray source. Detection angle was 45° except where otherwise noted. Sputtering for the depth profiles was done with a beam of Ar⁺ ions of
4 keV energy and 2.5 μA/cm² density, scanned at an angle of 45° over a surface of approximately 0.2 cm². Base pressure was always kept below 5 × 10⁻⁹ mbar and low-energy electrons were always used for charge compensation of the poorly conducting surfaces.

For comparison purposes, model molecules were purchased and analysed by SEM and XPS: hydrated magnesium acetate (CH₃CO₂)₂Mg·4H₂O and aluminium subacetate Al(CH₃CO₂)₂OH, both in powdered form, were obtained from Laboratoire Mat (Quebec City, Canada).

2.5. Grain size evaluation

As mentioned above, in most of past research works, the grain size of cast Mg–Al alloys was determined by indirect methods that include solution heat treatment to reduce microsegregation, to enhance the grain boundary delineation by etchants, and to facilitate grain observation. Here, the grain size has been determined (1) in as-cast specimens of AZ91D alloy etched with the new reagent and (2) by the indirect method that involves the modified T4 treatment [15] followed by etching to show grain boundaries. Average grain size and grain size distribution obtained from these two methods were then compared.

As-cast specimens of AZ91D alloy were polished and microhardness indentations were carefully marked at the surface to facilitate the positioning of sample. The surface was first etched using the new etchant to produce color etching. Average grain size and grain size distribution were evaluated near indentations and following this series of measurements, the microstructure was photographed. The specimen was then heat treated according to the modified T4 treatment [15], lightly polished, and etched using the following etchant which was used to enhance grain boundaries after the T4 heat treatment:

- glacial acetic acid (1 ml)
- nitric acid (1 ml)
- anhydrous ethyl alcohol (75 ml)
- distilled water (25 ml).

The grain size was determined and photomicrographs were taken from the surface near the hardness indentations. These microstructures were then compared. The grain size has been evaluated using the intercept method described in ASTM E-112 with a semiautomatic approach [26,27]. The grain boundaries were marked manually and evaluated statistically with a programmed subroutine of the Clemex Vision System to obtain the grain size distribution. About 400 grains were counted for each series of measurement.

3. Results and discussion

3.1. Optical micrograph of as-cast AZ91D alloy after etching

Fig. 1 shows a typical microstructure of AZ91D specimen in the as-cast condition after etching with the new reagent (glacial acetic acid–water–ethyl alcohol). The granular structure is made visible by the color contrast between adjacent grains. The dendritic structure enclosed within grains is also revealed by etching.

3.2. SEM micrograph of AZ91D after etching

Fig. 2a shows a SEM micrograph of as-cast AZ91D alloy after etching with the new reagent. Within each grain, most of the surface is crackled into a network of fine and oriented stripes, each grain having stripes oriented in a preferential and different direction. The network of stripes inside each grain is not continuous but fragmented. At higher magnification (Fig. 2b), four different zones are clearly distinguished. In the vicinity of grain boundaries (see arrows) and near intermetallics, a dense and continuous film is visible (Zone A). Above the intermetallic phase Mg₁₇Al₁₂ (labeled as Zone B), no cracking is visible. Within grains, areas where extensive cracking occurred were labeled as Zone C. The microstructure of the crackled network observed in Zone C consists of approximately 1-μm-wide stripes, distant from each other by a varying gap, usually about 1 μm wide. Within grains, some areas are found where cracking is limited (Zone D). The thickness of stripes within Zone C is approximately 0.5 μm, as determined by using the AFM (Fig. 3).

Fig. 4a shows the different aspects of the film in areas containing stripes (Zone C) and partially crack-
led film (Zone D). In this figure, there is a continuously varying film texture between Zones C and D: both zones have experienced cracking but in a different way. At high magnification (Fig. 4b), the partially crackled surface film (Zone D) appears to be very porous. It contains angular grains and somewhat more fibrous and smaller particles suggesting the presence of two distinct phases. The film texture in Zone D indicates a uniform microcracking between its fine constituent grains. By contrast, Fig. 4c shows that discrete cracking occurred in Zone C where stripes, sometimes straight and with parallel sides, have a dense microstructure composed of rather angular grains. The composition of these individual grains will not be determined by SEM due to their small size, although a more global analysis will be carried out to obtain information about constituting elements.

The linear contraction necessary to create the gap between stripes in Zone C (Fig. 4c) is sometimes more than 50%. The textured surface of the film and optical contrast is observed immediately after air drying of the specimen. Because the thermal expansion of the magnesium–aluminum substrate is negligible during drying, it is concluded that tensile stresses generated within the film during drying have induced the cracking of the film and formation of surface stripes. Dehydration of the surface film during drying and more compact rearrangement of atoms could explain the shrinking.

The sides of stripes sometimes show two types of surface (Fig. 4d and e): a straight side suggesting cleavage and a stretched bound at the base of stripes near the substrate where evidence of cleavage is less visible. The straight side of stripes is indicative of some sort of long-range order within the film in Zone C. The
soft surface at the base of stripes probably results from delayed drying of the film, a portion of the stripe near
the interface being still ductile at the beginning of tearing and formation of stripes. This morphology reveals that a large contraction of the film occurred and crackling took place suddenly upon drying of a significant portion of the film. This phenomena was not uniform, the resulting film morphology being stripes where the film is dense (Zone C), and uniform microcracking elsewhere (Zone D).
3.3. Structure of surface film

The preferential alignment of stripes within each grain and the contrast between adjacent grains indicate that some sort of epitaxial relationship exists between the underlying crystalline substrate and the surface film from which the stripes formed (the internal structure of the film being related with that of the substrate). The straight side of stripes and frequently parallel sides also suggest that significant portions of the film are crystalline. However, X-ray diffraction with a grazing angle failed to reveal a crystalline structure for the thin surface film, probably due to the low density of this surface layer or imperfect degree of crystallization. In contrast, George [11] mentioned that an amorphous film was formed at the surface of magnesium alloys upon etching with acetic–picral etchants.

3.4. Composition of surface film

The semiquantitative microanalysis of the surface film has been performed using the SEM. Reducing the incident beam energy from 15 to 5 keV resulted in a decrease of the magnesium/aluminum signal ratio which confirms that magnesium X-rays emitted from the substrate were detected at high incident energy. Working at 3 keV prevented the underlying substrate from being excited by the incident electron beam and provided sufficient overvoltage for practical analytical conditions.

Carbon, oxygen, magnesium, and aluminum were detected in stripes and at different places where the surface film has formed. However, no precise stoichiometry was calculated for the surface film due to the low atomic weight of elements and because hydrogen, which is probably present in the film, cannot be detected by this microanalytical method. Moreover, the presence of submicron grains within the surface film prevents quantitative phase determination using SEM.

Fig. 5 gives the signal of each element detected in each Zone (A to D) and within the two reference acetate compounds, the count rate from the detector being fairly reproducible. Usually, the X-ray counts for oxygen is much stronger than the counts for carbon in various zones of surface film. Relatively more aluminum is present in the film formed above substrate areas where aluminum has segregated (Zone A) and less aluminum was found in films formed above the dendrite core where no tearing occurred (Zone D). Above the intermetallic phase Mg17Al12 (Zone B), the X-ray signal for carbon and oxygen are very low, suggesting that, if any film formed above
Fig. 4. (a) Detailed SEM micrograph of the film in Zones C and D; (b) magnification of Zone D showing the microstructure of film and porosities; (c) magnification of Zone C showing the granular and dense structure of stripes, the higher density enabling cracking; (d) side view of the crackled film showing the fractured surface; (e) detailed view of the stripes: the arrows show stretching at the interface of the crackled film with the substrate.
intermetallic phases, it is very thin. In stripes (Zone C), the X-ray signal for aluminum and magnesium is comparable. Most analysis revealed somewhat more aluminum in aligned stripes and less in stripes with a more irregular shape.

Microanalysis has shown that the presence of aluminum in the magnesium substrate is essential to obtain stripes and that only a narrow range of concentration is favourable to the formation of stripes. A uniform but limited tearing occurred in Zone D, above the core of primary and secondary arms where the concentration of aluminum due to microsegregation of solute is less than about 3–4 wt.% (confirmed by microanalysis). The maximum aluminum concentration in the primary magnesium-rich phase (in the vicinity of intermetallics and grain boundaries) where tearing took place is close to 10 wt.%. Consequently, between 3 and 10 wt.% aluminum is necessary in the magnesium-based substrate for tearing of the film (Zone C). In locations where well-aligned stripes were found, the local concentration of aluminum in the magnesium substrate was between 4 and 8 wt.%. The X-ray signals measured in the two reference materials are given in Fig. 5 for comparison purposes. In pure
acetates, the signal for carbon is dominant, being comparable to the signals for aluminum or magnesium. The relatively higher concentration of oxygen in the surface film could be ascribed to a more important degree of hydration compared to the reference acetates or to the presence of another oxygen-rich phase within the film.

Ernst and Laves [19] mentioned that organometallic films are produced during etching of magnesium by various acids. As revealed by EDS microanalyses with the SEM, the presence of carbon and oxygen (and probably hydrogen) in the surface film also suggests formation of such organometallic compounds following etching with dilute acetic acid. More information about such organic compounds was obtained by infrared spectroscopy.

Fig. 6 shows the infrared spectrum of the surface of an AZ91D alloy etched with the reagent developed during the present work. Spectra recorded in the mid-infrared are particularly useful to detect and identify organometallic compounds that could potentially be formed between the metals of the alloy and the chemicals contained in the etching media. As an example, the infrared spectrum of a protonated acetate, such as acetic acid, displays two characteristic peaks assigned to CO and C–OH stretching mode vibrations near 1709 and 1276 cm$^{-1}$, respectively (Fig. 7). On the other hand, the infrared spectrum of the noncoordinated ion displays two strong bands near 1553 and 1415 cm$^{-1}$ because the negative charge born by one of the oxygen atoms is delocalized over the entire ester group, therefore leading to the equivalence of both C–O bonds. The aforementioned infrared features are thus assigned to asymmetric and symmetric stretching mode vibrations of the (O–C–O)$^-$ chemical bond, respectively. The infrared spectrum presented in Fig. 6 indicates that two types of metallic acetates are present on the etched surface. First, the infrared feature observed at 1421 cm$^{-1}$ can be assigned to the symmetric (O–C–O)$^-$ stretch of acetate moieties coordinated with magnesium as previously published by Quilès and Burneau [28]. Second, the 1464 cm$^{-1}$ infrared band is likely due to the symmetric (O–C–O)$^-$ stretching mode vibration of an acetate group coordinated with aluminum as demonstrated by Persson et al. [29]. The asymmetric (O–C–O)$^-$ stretching mode vibrations of these two types of acetate seems to lie behind the wide feature centered at 1578 cm$^{-1}$ as the bandwidth at half maximum of this band is 107 cm$^{-1}$, well above the value reported by Quilès and Burneau [28] of 54–59 cm$^{-1}$ for pure alkaline–earth and copper acetates. It is therefore obvious that two spectral components that pertain to the aluminum-containing acetate and mag-

![Fig. 6. FTIR-ATR spectrum of an etched AZ91D sample (solid line). The dotted lines and dashed lines were obtained from the curve fitting of the feature located at 1578 cm\(^{-1}\).](image-url)
nesium-containing acetate are superimposed in this region, the former compound giving rise to the higher frequency spectral component. On the basis of the infrared results, it is difficult to conclude if the surface film formed upon etching is made of two distinct acetate compounds (e.g., an aluminum-containing acetate and a magnesium-containing acetate or an acetate containing both aluminum and magnesium). However, the infrared frequencies of both asymmetric and symmetric (O–C–O) stretching mode vibration point toward the formation of a bidendate acetate. Therefore, this observation allows the two precited hypotheses. It does not rule out the presence in the surface film of other compounds hardly detected by FTIR spectroscopy because of the possible overlap of their infrared features with those of the acetates.

Fig. 8 shows the XPS survey spectra of an etched AZ91D sample acquired at grazing (15°) and normal (90°) angles to the surface. Evidently, the substrate portion of the surface that is partially exposed produces a signal contributing to the recorded spectra, although less importantly at an incident angle of 15°. Hydrogen is not taken into account in the calculated concentrations, being practically undetectable with XPS. Fig. 8 also shows the spectra of aluminum subacetate and hydrated magnesium acetate for comparison.

Considering the presence of a thin layer of carbon due to the commonly observed organic surface contamination, these spectra confirm that the surface film contains more oxygen than carbon. From the variation between the concentrations measured at the two different acquisition angles, it can be noticed that, in the range of the first few nanometers from the surface, carbon is more concentrated near the surface. Oxygen and aluminum vary less significantly. Aluminum being much in excess of magnesium in both cases, it seems that relatively more aluminum than magnesium is present in the surface film.

Compared to the stochiometric ratios, the elemental concentration ratios of the hydrated magnesium acetate show a small excess of carbon (C/Mg = 5.3, instead of 4), which can probably be attributed to the usual surface contaminants, but also a large deficit of oxygen (O/Mg = 4.6, instead of 8) which could be explained by a desorption of the hydrating water under the vacuum and/or X-ray bombardment. For the aluminum subacetate, there is only a small excess of both carbon and oxygen (C/Mg = 4.6, instead of 4; O/Mg = 6.4, instead of 5) attributable to surface contaminants.

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<tr>
<th>Acetate type</th>
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<td>Protonated acetate</td>
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<td>H₃C=C=O</td>
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<td>v C=O = 1709 cm⁻¹</td>
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<td>Noncoordinated acetate</td>
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<td>H₃C=C=O</td>
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<td>v asym O-C=O = 1553 cm⁻¹</td>
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<td>Monodentate coordination complex with a metal</td>
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<td>H₃C=C=O</td>
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<td>Δ between v asym O-C=O and v sym O-C=O &gt; 200 cm⁻¹</td>
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<td>Bidentate coordination complex with a metal</td>
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<td>Δ between v asym O-C=O and v sym O-C=O &lt; 150 cm⁻¹</td>
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Fig. 7. Variation of the infrared vibrational frequencies assigned to the asymmetric and symmetric stretching modes of acetate groups as a function of their coordination state.
A high-resolution spectrum of the C1s peak is shown in the insert of Fig. 8 for the two reference acetates and for etched AZ91D. The same component peaks appear for the three cases, at almost exactly the same energies, with similar areal ratios. The first component at 285 eV is generally attributed to carbon atoms linked only to carbon and/or hydrogen atoms while the component at 289 eV are attributed to carbon atoms which are part of carboxyls, carbonates, or esters groups. Thus, for the two model molecules, the two components of the C1s peak can be attributed mainly to the methyl and ester parts of the acetate. A
small percentage of the 285-eV component can be attributed to surface contaminants. The same attribu-
tions would be compatible with the C1s peak of the AZ91D sample. The carbon detected at the surface of
AZ91D could be part of the acetates, with the usual contaminants.

The depth profile of etched AZ91D is shown in Fig. 9. Carbon as well as oxygen decrease with
sputtering time, but initially, carbon decreases more rapidly, in agreement with a surface contamination by
carbonaceous species. After the removal of these contaminants, carbon, oxygen, and aluminum
decreases slowly, oxygen and carbon steadily dimin-
ishing to a negligible concentration. On the larger
scale, magnesium increases almost linearly and then
reach a maximum concentration, while the aluminum
concentration decreases regularly to a minimum con-
centration corresponding to the substrate concentra-
tion (approximately 10 wt.%). It is noticeable from the
insert that the O/C ratio is approximately constant
during sputtering, although their concentration relative to metals is decreasing. The O/C ratio of about
12, however, suggests that the discontinuous surface film is possibly hydrated to account for all the oxygen.
The presence of hydroxides in the film is another possibility. Unfortunately, the high-resolution spectra
for oxygen (not shown) could not permit the different-
ation of hydroxides, or hydrates from acetates, due
to the very similar energy shifts.

3.5. Grain size evaluation

The grain size of the AZ91D alloy cast in a
permanent mold has been compared using two
approaches: (a) the new etching solution presented
in the present work (dilute acetic acid in a water–ethyl
alcohol mixture) and (b) the modified T4 heat treat-
ment followed by grain boundary etching using the
acetic acid–nitric acid in alcohol–water solution. The
average grain size and statistics are given in Table 1
and the grain size distribution is given in Fig. 10. It
was found that the average grain sizes obtained with
the two methods are similar. As shown in Fig. 11, the
grain boundaries obtained after modified T4 heat
treatment and delineated by etching with the acetic–
nitric–alcohol–water are in coincidence with bound-
aries of grains in the as-cast condition, as revealed
with the acetic–alcohol–water reagent. However, the
contrast in a few grains may be sometimes difficult to
observe. For this reason, an adjustable retardation
wave plate is used to change the grain’s color, which
facilitates grain boundary identification.

![Fig. 9. Depth profile of etched AZ91D. Also shown in the insert is the O/C composition ratio.](image-url)
3.6. Mechanism creating optical contrast

At the surface of as-polished magnesium alloys, the optical contrast between grains is rather weak under polarized light and not sufficient for observation of grains [30]. However, etching solutions can produce thin surface films with anisotropic properties, allowing observation of underlying grains of magnesium alloys [11,19,31]. To obtain optical contrast between grains, the incident polarized beam and the reflected beam must be out of phase to enable the reflected beam to go through the analyzer. In addition, the phase shifting must vary between adjacent grains to obtain intergranular contrast.

Anodic oxidation of metals and alloys frequently produces an epitaxial surface layer leading to color contrast between grains [17,18,21]. The thickness of these layers is determined by the crystallographic orientation of grains in the metallic substrate. Such is the case with galvanic fluorination of Mg–Zr alloys [31]. As shown in Fig. 12, the optical path difference (δ) between the beam reflected at the metal–film interface and the beam reflected at the free surface of the layer creates interference and contrast between adjacent grains [18]. Polarized light is not necessary but coloration can be intensified by using crossed, or nearly crossed, polarized light [17].

An epitaxial layer of uniform thickness but optically anisotropic material can also produce grain contrast under polarized light due to “birefringence,” or two different indices of refraction (n₁, n₂) of the material. Accordingly, the interference intensity varies between zero and a maximum value according to the crystallographic orientation of the film. Thus, if the orientation of the granular substrate and the film is related, optical contrast between grains will occur under polarized light. As shown in Fig. 13, the incident beam splits in two when entering the film.

| Average grain size and statistics in AZ91D specimen in as-cast condition (see Fig. 11a) and after modified T4 heat treatment (see Fig. 11b) |
|----------------------------------|-----------------|-----------------|
| Mean grain size (μm)            | 472             | 481             |
| Minimum/maximum size (μm)       | 43/1448         | 381/728         |
| Standard deviation (μm)         | 310             | 314             |
| Counted grains                   | 408             | 384             |
| Total measured length (mm)      | 193             | 185             |

Fig. 10. Grain size distribution of AZ91D cast in a permanent mold. Measurements were performed using two methods: (1) in the as-cast condition and using the new acetic acid–alcohol–water reagent and (2) after the modified T4 heat treatment and using the acetic–nitric–alcohol–water reagent.
and recombine phase shifted due to the interference phenomena.

The birefringent crackled film produced by using the reagent developed in the present study is not attributed to intrinsic or natural birefringence of the film but to its texture. Birefringent layers of this type have been obtained with aluminum by electrolytic etching [32]. This phenomenon is known as “shape double refraction” or “form birefringence” [33]. Form birefringence occurs with periodic structures satisfying several conditions related to shape, periodicity, size with respect to wavelength, etc. [34]. For surface gratings satisfying these conditions, the contrast produced by birefringence depends on parameters, such as incident wavelength (\(\lambda\)), grating period (\(A\)) and its duty cycle (\(F\)), index of refraction of the surface layer (\(n_1\)), and index of refraction of the gaps (\(n_2\)) [34]. As noted using optical and electron microscopy, the orientation of stripes in the crackled film produced by using the new reagent is dependent on the orientation of underlying grains. This phenomenon was first observed by Jones [35]. Because optical properties under polarized light vary with the orientation of stripes, they are causing optical contrast between grains as shown in Fig. 14.

By rotating the surface of etched AZ91D alloy under cross-polarized light, the coloration of grains varies with a period of 180°, a variation that would not be induced if contrast was dependant only on film thickness. The natural birefringence of the film is excluded as a cause of the contrast: by using a wetting liquid, such as water or ethyl alcohol, at the etched surface of specimen during rotation, the contrast

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Fig. 11. (a) Microstructure of as-cast AZ91D etched with the dilute acetic–alcohol–water reagent (as viewed under polarized light); (b) microstructure of AZ91D etched with the dilute acetic–nitric–alcohol–water reagent after the modified T4 heat treatment.

Fig. 12. Optical contrast caused by a layer having a thickness which depends on the crystallographic orientation of the substrate. Polarized light is not necessary to obtain the contrast between grains because the optical path difference does not depend on the crystallographic orientation of the layer.

Fig. 13. Optical contrast obtained under polarized light and caused by a naturally birefringent layer. The orientation of the layer depends on the crystallographic orientation of the substrate.

Fig. 14. Optical contrast caused by a layer having a thickness which depends on the crystallographic orientation of the substrate. Polarized light is not necessary to obtain the contrast between grains because the optical path difference does not depend on the crystallographic orientation of the layer.
variation disappears. A more detailed study on this matter has been made by Huber [36] showing a parabolic relation between the index of refraction of the liquid and phase shifting.

4. Conclusion

In the present study, a new and simple etching method was developed for quickly revealing the granular structure of the AZ91D magnesium–aluminum alloy in the as-cast condition. A tedious heat treatment is not necessary with the new etchant which can be prepared with simple chemicals.

Under polarized light, the color contrast created by the new etchant is remarkable; it facilitates grain observations and evaluations of grain size without changing the as-cast microstructure.

The crackled film deposited at the surface of the AZ91D magnesium alloy upon etching with the diluted alcohol–water–acetic acid solution developed in the present work contains acetate groups, probably aluminum and magnesium subacetates. The aluminum is present in the film in a proportion depending on the local concentration of aluminum in the underlying grains. It is not possible to confirm if compounds different from acetates are present in the film. The precise stoichiometry of the surface film could not be determined owing to the fact that it is likely composed of submicron phases; and, it likely contains hydrogen which could not detected by the methods used in the present study.

It was observed that the film crackles into stripes where the local composition of the magnesium substrate is between 3 and 10 wt.% aluminum, the stripe texture depending on the local concentration of aluminum in magnesium.

The grain contrast produced by the crackled film is explained by form birefringence. It is different from intrinsic birefringence and from interference produced by grain-dependant film thickness.

Average grain size and grain size distribution obtained with the new etching method are comparable to that obtained by the conventional etching method (using modified T4), and it is faster.

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