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Rapid nondestructive assessment of degrees of sensitization of 5456 aluminum alloys using laser-induced breakdown spectroscopy (LIBS) with multivariate analysis

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The 5xxx series aluminum (Al) – magnesium (Mg) alloys are extensively used in marine transportation and naval ships due to their high strength-to-weight ratios and great corrosion resistance properties. However, material degradation of the 5xxx alloys occurs over time after exposure to environments at elevated temperatures, referred as sensitization. Sensitization is characterized by β-phase (Mg_2Al_3) precipitates along the grain boundaries, which increase the susceptibility to intergranular corrosion (IGC) and stress corrosion cracking (SCC). Therefore, it is important to assess the degree of sensitization (DoS) in modern naval ships, whose structures are primarily made of Al-Mg alloys, to determine whether they have reached a DoS threshold that may require maintenance or repair activities. In this study, laser-induced breakdown spectroscopy (LIBS) with statistical multivariate analysis methods was successfully developed to assess the DoS levels of the 5xxx alloys. LIBS measurements were conducted after chemical etching on 5456 Al-Mg alloy samples with DoS values of 7.1 (unsensitized), 20.2 (indeterminate), and 47.3 (sensitized) mg/cm^2, respectively. The statistical multivariate analysis method of principal component and discriminant function analysis (PC-DFA) was used to process the LIBS spectra to establish a calibration model used for prediction of Al alloys with unknown DoS values. For each alloy sample, a total of 400 LIBS spectra were acquired. 350 of them were used to establish the calibration model by PC-DFA and the rest 50 of them used as unknown spectra for external validation of the model established. External validation of the established classification model shows accuracies of 100%, 100%, and 82%, respectively, for predicting tested Al alloy samples with unsensitized, indeterminate, and sensitized DoS values. Successful external validation of the classification model established by PC-DFA indicates the ability for sensitization assessment of 5456 Al alloys with unknown DoS values. The technology developed has the capability for rapid and non-destructive sensitization assessment on site.

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1. Introduction

Aluminum (Al) alloys are extensively used in marine transportation and naval applications due to their high strength-to-weight ratio, formability, cold workability as well as weldability. The 5xxx series aluminum-magnesium (Al-Mg) alloys possess the combined properties of high strength-to-weight ratio and excellent corrosion resistance; therefore, they are widely used as the primary structural materials for building high-speed ships and vessels in marine transportation or naval applications. The alloying element of magnesium (Mg) is used to strengthen the original Al for different 5xxx series Al-Mg alloys containing varying amounts of Mg, up to ~ 5 wt% in 5456 by solid solution strengthening. Although the 5xxx alloys present excellent corrosion resistance, they are susceptible to sensitization over time after exposure to elevated temperatures. Sensitization of 5xxx alloys is characterized by the formation of magnesium rich β-phase (Mg_2Al_3) precipitates primarily along grain boundaries due to the super-saturated Mg (> 3.5 wt%) diffusion and precipitates out of solid solutions at elevated temperatures (50-200 ºC) for extended time periods.[1-3] The β-phase is anodic to the matrix and preferably dissolved in corrosion environments.[4-5] Therefore, sensitization significantly increases the material's susceptibility to intergranular corrosion (IGC) and stress corrosion cracking (SCC).[1]

The 5xxx Al alloys are used as the critical materials in the design and construction of state-of-the-art naval ships.[6] Sensitization-caused material degradation is currently one of the most important problems that is costly and needs to be taken care of. With the expected extension of the service life of naval ships to 30-50 years and beyond, it is critical to develop a technology to assess Al sensitization to reduce total ownership cost.[6] Nondestructive methods for assessment of the degree of sensitization (DoS) will significantly reduce the costs associated with maintenance, modernization, and repair activities.[6] The current standard method for quantification of DoS is the ASTM G67-13 Nitric Acid Mass Loss Testing (NAMLT) technology which uses the mass loss of the materials after immersed in concentrated nitric acid (70%) for 24 h as the DoS values.[7] This method is quantitative and accurate but is a laborious technology, costly, destructive and time consuming, taking a two- or ten-day turnaround for field ship sensitization measurement with the total cost up to several thousand dollars per test.[8] Therefore, technologies for rapid and nondestructive onsite assessment of Al alloy sensitization are highly desired to improve the work efficiency and reduce the total cost of ownership. Based on this requirement, a few technologies have been reported for quantitative assessment of DoS in the Al alloys, including electromagnetic acoustic transducer (EMAT) ultrasonic technology, metallographic imaging, X-ray diffraction (XRD), eddy-current test (ECT), and electrochemical method.[6-7, 9-13] However, most of them are either laboratory-based or unreliable enough for onsite applications.[9-13] Among them, the electrochemical method (also referred as the DoS probe) is the one currently available for onsite non-destructive DoS assessment on naval ships. It is used for modernization planning, third party repair planning, real-time ship repair and maintenance activities. Technically, the DoS probe utilizes electrochemical measurements of the relationship curves between the current and time to establish calibrated models to quantify the DoS values. Specifically, a few steps are contained in DoS probe measurements, including cleaning the test surface (4" diameter to 1200 grit), heating the test area up to 50 ºC, and electrochemical measurement of the relationship curves.[6] A typical time consumed per measurement by the DoS probe is around 75 min, much reduced compared with the two to ten-day turnaround

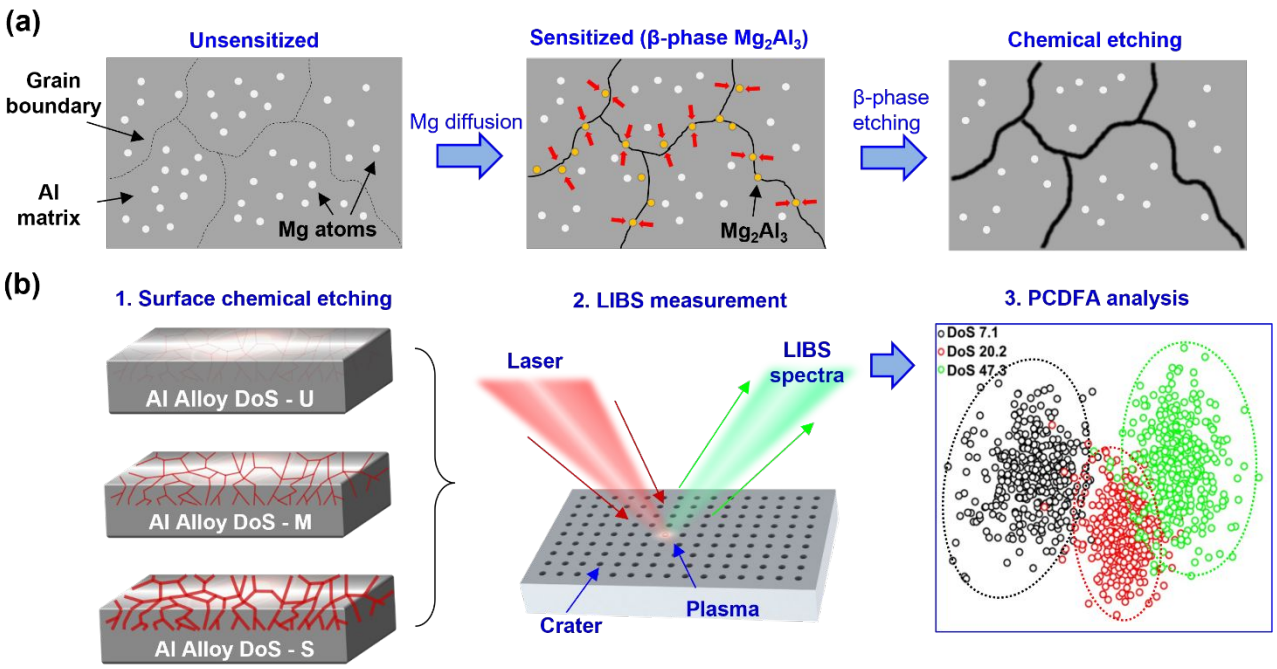

Figure 1. (a) Schematic of the microstructures and spatial concentration variations of Mg in unsensitized, sensitized (β-phase precipitates), and chemically etched (preferred β-phase etching) in an Al-Mg alloy; (b) Overview of the proposed technology for sensitization assessment, including chemical etching of Al-Mg alloy with different DoS values, to induce Mg concentration variation correlated with the DoS values, subsequent LIBS measurements to probe the Mg concentration variations, and LIBS spectra processing by PC-DFA for DoS classification and prediction.

required by the ASTM G67 laboratory measurement for field sensitization assessment. The total cost by DoS probe is over one thousand dollar per measurement, only around one-fifth of the total amount required by the ASTM G67 destructive laboratory measurements. Although the DoS probe is currently used for onsite nondestructive assessment of Al alloy sensitization, there are still needs to develop faster, more cost-effective, and more flexible technologies to further improve the work efficiency and reduce the total costs.

Laser-induced breakdown spectroscopy (LIBS) with multivariate analysis was proposed as a rapid and nondestructive approach to onsite sensitization assessment with rapid in situ measurement, maintenance free, high spatial resolution, economic as well as flexible calibration which can be extended for other alloys. LIBS is an optical emission spectroscopy technique used for chemical composition analysis of materials. In LIBS, a pulsed laser beam is focused and delivered to material surfaces to locally ablate alloy materials and induce a plasma via breakdown of the ablated materials, with the laser-induced crater sizes in a micrometer scale. The optical emission spectroscopy of the laser-induced plasma is measured to semi-quantitatively provide the chemical composition information of the materials with the limit of detection (LoD) down to a few ppm. LIBS has the characteristics of real-time in-situ analysis, nearly non-destruction, multi-element analysis, and remote detection.[14-18] Multivariate analysis has been applied in the field of spectroscopy for decades to establish calibration models for classification, pattern recognition, clustering, regression etc., to predict properties interested. [19-23]

In this study, LIBS with multivariate analysis was used to establish calibration models for sensitization assessment and to predict 5456 Al alloys (one typical Al alloy in 5xxx Al alloy family) with the DoS levels unknown to the model. Mg concentration variations after chemical etching were detected by LIBS and then correlated with the DoS values. To our best knowledge, there is little research effort working on this area, while sensitization is a unique corrosion issue in many models of 5xxx Al-Mg alloys that can lead to the formation of magnesium-rich β-phase precipitates along grain boundaries. This is a major cause of Al-Mg alloy corrosion in marine environments, particularly for naval ships. This research aims to fill this gap. The schematic of the proposed technology using LIBS with multivariate analysis for Al alloy sensitization assessment is shown in **Figure 1**. As shown in **Figure 1(a)**, β-phase precipitates preferably along the grain boundaries due to the super-saturated Mg atom diffusion out of the solid solution during sensitization. Therefore, alloys with higher DoS values have more β-phase (Mg_2Al_3) precipitates which contain much higher Mg contents (~ 38 wt%) than that in the Al matrix (~ 5 wt%). For sensitized materials, chemical etching preferably dissolves and removes the β-phase precipitates. Therefore, as shown in **Figure 1(b)**, alloys with higher DoS values suffer from more Mg loss after chemical etching due to more Mg-rich β-phase precipitates dissolved, which were probed by LIBS. The LIBS spectra were analyzed by the multivariate analysis method of principal component and discriminant function analysis (PC-DFA) to establish a calibration model for sensitization assessment. Generally, the Al-Mg alloys are considered as unsensitized with DoS values of 15 mg/cm^2 or less, indeterminate with DoS values within the range of 15 - 25 mg/cm^2, and sensitized with DoS values greater than 25 mg/cm^2.[1-2] Determination of the alloy DoS levels as unsensitized, indeterminate, or sensitized is extremely important to support repairing and maintenance. Therefore, Al alloys with DoS levels as unsensitized (DoS-U), indeterminate (DoS-M), and sensitized (DoS-S) were chosen for LIBS measurements and sensitization assessment in this study.

2. Experimental methods

2.1 Sensitization and chemical etching

Industrial 5456 H116 Al-Mg alloy plates with a thickness of 3/8 inch purchased from Pierce Aluminum were used in this study. Large 5456 Al alloy plates were cut into small ones and placed into an oven at a temperature of 100 ℃ for 0, 5, and 79 days to reach DoS values of 7.1, 20.2, and 47.3 mg/cm^2, respectively. The DoS values were certified by the ASTM G67 nitric acid mass loss test. The unit mg/cm^2 indicates the mass loss per unit after ASTM G67 test. The sensitized plates were further cut into bars with a size of 2×0.25×0.375 inch^3 as samples. Before chemical etching, the sample surfaces were polished by sandpapers to 800-grit. In the chemical etching, samples with different DoS values were immersed into nitric acid (70%) for 2 h at room temperature. There are a few other chemical etchants able to rapidly reveal the grain boundaries by preferred β-phase dissolution with the etching times reduced down to sub-minutes.[24-25] However, this study focused on demonstrating the feasibility of using LIBS with multivariate analysis for sensitization assessment. Hence, the effects of different etchants on LIBS and sensitization assessment were beyond the scope of this study. After the chemical etching, a laser microscope (Keyence laser scanning microscope VK-X200K) was used to image the sample surfaces with the DoS values of 7.1, 20.2 , and 47.3 mg/cm^2, respectively, as shown in **Figure 2**.

2.2 LIBS setup

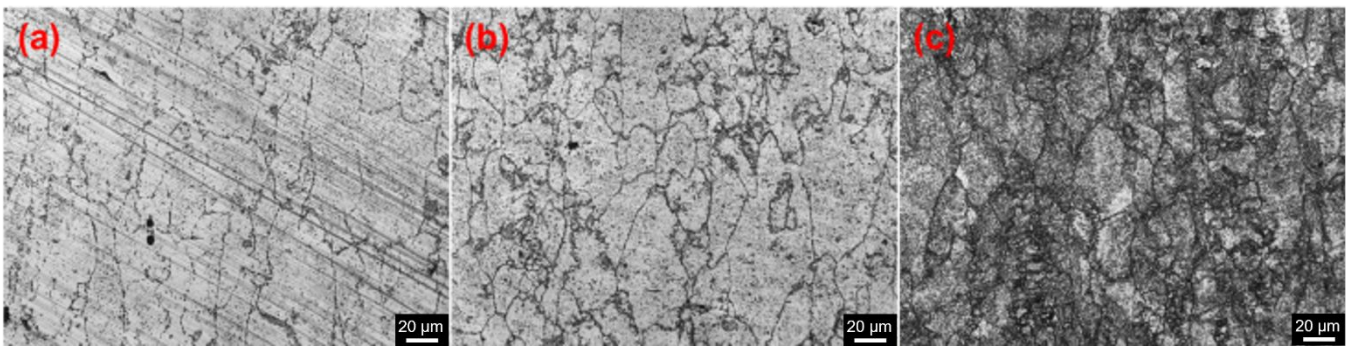

Figure 2. Laser microscope images of the sample surfaces with the DoS value of (a) 7.1; (b) 20.2; and (c) 47.3 mg/cm^2, respectively, after immersed into nitric acid (70%) for 2 hours at room temperature by chemical etching. The scale bar is 20 μm.

After the chemical etching, the samples were used for LIBS to probe the Mg concentration variation. **Figure 3** shows the schematic of the LIBS system used. A Q-switched Nd:YAG laser (Continuum, Powerlite Precision II 8010, 1064 nm, 6 ns, 10 Hz) was used as the laser source to induce plasmas on the sample surfaces. The laser beam was focused by an objective lens (5×) to a spot size of 20 μm in diameter on the sample surfaces. The samples were horizontally moved with a speed of 1 mm/s by a three-dimensional automatic stage platform. A laser displacement sensor was fixed above the sample surfaces to track the position of sample surfaces to assure consistent focal distance for all samples. A neutral-density filter with the optical density of 1.5 was inserted before the objective lens to

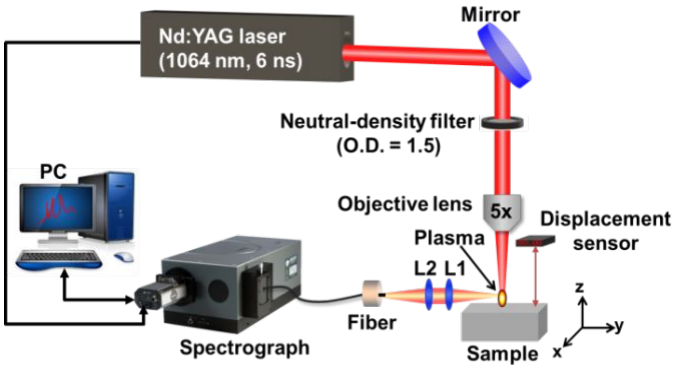

Figure 3. Schematic of the LIBS system.

attenuate the laser pulse energy to 1.5 mJ/pulse. The laser-induced plasma emission was collected by a pair of convex lenses (f1 = 10 cm, f2 = 6 cm) before coupled into a spectrometer (Andor Technology, Shamrock 505i, ICCD DT-334T) via an optical fiber for spectroscopy measurements. Three gratings (150, 600, and 1200 l/mm) are installed in the spectrometer. The 150 l/mm grating blazed at 500 nm was used for all LIBS measurements. An intensified charge-coupled device (ICCD) was externally triggered by the Nd:YAG laser. A gate delay of 300 ns and a gate width of 5 μs were used.

3. Results and Discussion

3.1 LIBS measurements

Each LIBS spectrum (raw data) used for multivariate analysis was averaged from 5 laser pulses in line scanning on the sample surface to improve the signal stability, as shown in **Figure S1**. All LIBS raw data from the samples with different DoS values were pre-processed by the standard normal variate technique (SNV) for intensity normalization. The LIBS spectra averaged from 400 raw data for each sample with the DoS values of 7.1, 20.2, and 47.3 mg/cm², respectively, were shown in **Figure 4**. Figure 4 shows that peak intensity of the Mg I 383.5 nm emission line (a combination from the Mg I 382.9, 383.2, and 383.8 nm lines) gradually decreases for samples with increased DoS values, indicating decreased Mg concentrations on the sample surfaces after the chemical etching. This is consistent with the material properties that more Mg-rich β-phase (Mg_2Al_3) precipitations were removed from samples with higher DoS values after the chemical etching, resulting in decreased Mg concentrations. Since all the samples were from the same Al-Mg alloy plate, the original chemical composition of all the samples before sensitization can be treated as the same and all the Mg concentration variation after the chemical etching can be attributed to the DoS difference.

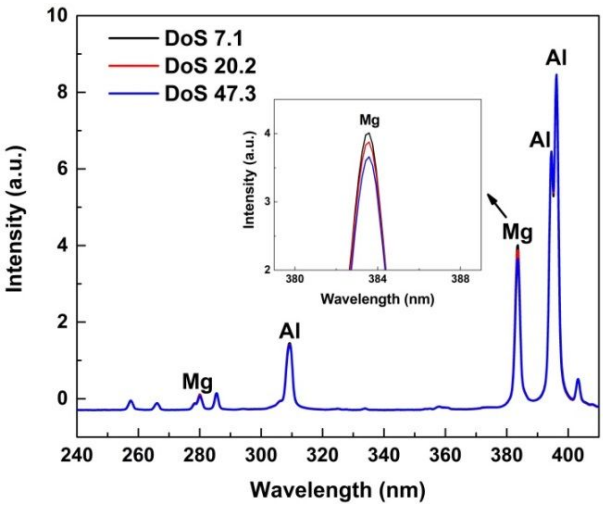

Figure 4. The LIBS spectra averaged from 400 raw data for each sample with the DoS values of 7.1, 20.2, and 47.3 mg/cm², respectively.

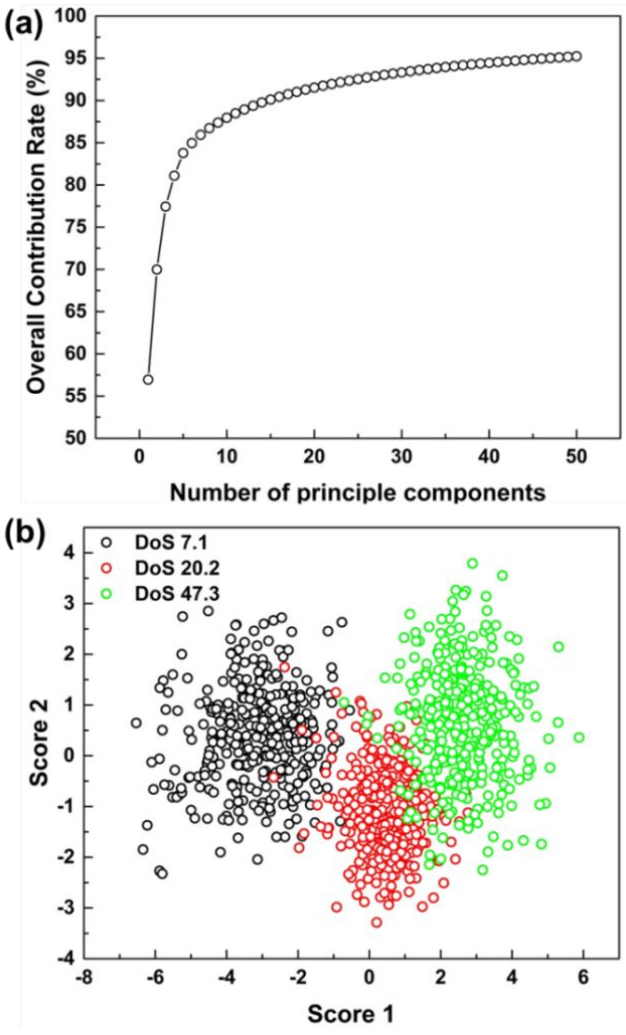

Figure 5 (a) The overall contribution rate of the number of PCs used; (b) Plot of PC-DFA scores of the total 350 training spectra for each DoS value of 7.1 (black circular symbol), 20.2 (red circular symbol), and 47.3 (green circular symbol) mg/cm², respectively.

3.2 PC-DFA analysis

Although peak intensities of Mg emission lines in the LIBS spectra are correlated with the alloy DoS values, it is nearly impossible to use only one peak to make comparisons between different samples. Therefore, statistical multivariate analysis method of PC-DFA was used for full spectrum analysis to correlate the LIBS spectra with the DoS values. PC-DFA has been proven to be efficient for Raman spectroscopy analysis to establish classification models for disease prediction in our previous studies.[19-21] In this study, LIBS spectra from alloy samples with different DoS values were classified by PC-DFA to establish a calibration model. DoS prediction for testing LIBS spectra unknown to the established model was also performed by the external validation method. Before the PC-DFA, all the raw LIBS spectra were pre-processed by the standard normal variate technique without background removal to minimize multiplicative error. For each sample, 400 raw spectra were acquired with 350 of them used as the training data to establish the classification model and the rest 50 used as testing spectra (unknown to the model) for external validation in PC-DFA. The 400 raw spectra were locally measured from four different areas on each sample surface.

LIBS spectra in the wavelength range of 250 - 410 nm were used for the PC-DFA analysis. In PC-DFA, principal component analysis (PCA) was first performed on the LIBS spectra to reduce the data dimensions (wavelengths in a spectrum) into fewer principal components (PCs) which were then used as inputs for the discriminant function analysis (DFA). The number of 10 PCs was used in PC-DFA, which carries 87.95 % of the most important information of the dataset. **Figure 5(a)** shows the accumulated contribution ratio by the number of PCs used, which shows that PC #1 carries the most important data information with 57.0% of the total variance and PC #2 carries the next important information with 13.0% of the total variance. The scores and loadings of PC 1 and PC 2 are shown in **Figure S2**. PC scores are the sequentially listed values of PCs after PCA transformation of the LIBS spectra. PC loadings can be considered as the weights for each original variable (wavelength in spectrum) when calculating the PCs in PCA. Therefore, the LIBS spectra were reduced from 1024 variables to 10 PCs by PCA. **Figure 5(b)** shows the plot of the PC-DFA scores for all the training LIBS spectra.

3.3 External validation of the multivariate-calibrated model for DoS prediction

In the earlier discussion, LIBS training spectra from samples with different DoS levels were accurately classified by PC-DFA using the cross-validation method. Here, the prediction on testing LIBS spectra, which are unknown to the model established, also need to be evaluated. Therefore, external validation of the established model for DoS prediction was performed using the 50 testing spectra from each alloy sample. The PC-DFA scores of both the training (open circular symbols, 350 spectra from each sample) and testing data (closed square symbols, 50 spectra from each sample) are plotted in **Figure 6**. Accurate prediction of the testing data into correspondingly correlated DoS levels were achieved with accuracies of 100%, 100% and 82%, respectively, as shown in **Table 1.** The testing spectra correlated with the DoS values of 7.1, 20.2, and 47.3 mg/cm^2, respectively, were predicted as unsensitized, indeterminate, and sensitized.

Using the classification model established from the data training in PC-DFA, the test data correlated to the DoS values within the unsensitized and transitional range, respectively, were predicted into their corresponding DoS levels with an accuracy of 100% for both cases. Testing spectra correlated to the sensitized DoS range was predicted into the corresponding sensitized DoS level with an accuracy of 82%, with the rest 18%

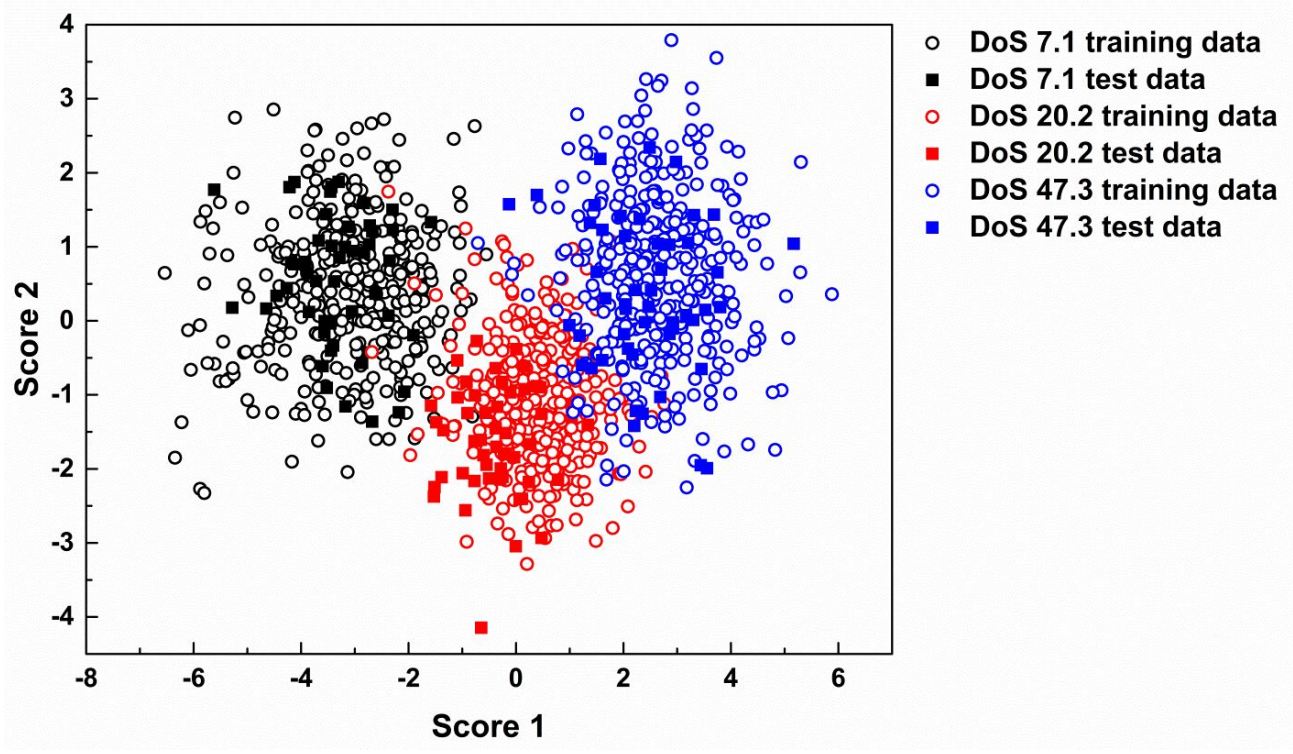

Figure 6. Plot of PC-DFA scores of the 350 training spectra (open circular symbols) and 50 test spectra (open square symbols) for the DoS value of 7.1 (black circular symbol), 20.2 (red circular symbol), and 47.3 (blue circular symbol) mg/cm^2, respectively.

Table 1. Results of external validation of multivariate-calibrated model for DoS prediction

DoS levels (mg/cm^2)	Number of testing spectra	Prediction results		
		Unsensitized	Indeterminate	Sensitized
Unsensitized (7.1)	50	100% (50)	0	0
Indeterminate (20.2)	50	0	100% (50)	0
Sensitized (47.3)	50	0	18% (9)	82% (41)

inaccurately predicted into the indeterminate DoS level. If an 5xxx alloy suffers from serious sensitization, it indicates that more Mg-rich β-phase (Mg_2Al_3) precipitates accumulate along the grain boundaries as well as discrete precipitates inside the grains. Thus, after chemical etching, more Mg-rich β-phase (Mg_2Al_3) precipitates will be removed from the grain boundaries, resulting in decreased Mg concentrations. Since the laser spot size is about 20 μm, there is a possibility that each laser shot covers a different number of grain boundaries during scanning. Thus, if one laser shot covers a smaller number of grain boundaries, it shows as less sensitized from the spectrum measurement than it really is. As shown in Figure 2 (b) and (c), the densities of grain boundaries vary on the surface, which may make the algorithm classify the LIBS spectra obtained from the 20-um laser spot as an indeterminate DoS level, even if it is measuring a sensitized alloy sample. We believe this is the main reason for the inaccuracies in predicting the sensitized DoS level. Even so, the 82% accuracy can still support the identification of the material as the sensitized DoS level with confidence. The external validation of the multivariate-calibrated model for DoS prediction has been demonstrated with success. This study shows that LIBS with multivariate analysis after chemical etching can be successfully used for sensitization assessment of Al-Mg alloys, which demonstrates the feasibility for rapid and nondestructive onsite measurements.

4. Conclusions

LIBS with the statistical multivariate analysis method of PC-DFA was used for rapid non-destructive onsite assessment of sensitization on 5456 Al-Mg alloys. Industrial 5456 H116 Al-Mg alloy plates with the DoS values of 7.1 (unsensitized), 20.2 (indeterminate), and 47.3 (sensitized) mg/cm^2, respectively, were used as samples. Chemical etching was used to preferably remove the Mg-rich β-phase precipitations along grain boundaries before the LIBS measurements. Al-Mg alloys with higher DoS values have more β-phase precipitates which is anodic to the Al matrix and dissolvable during the chemical etching. Therefore, after the chemical etching, Mg concentration on the surfaces of higher DoS value alloy samples is expected to be much reduced due to more loss of the Mg-rich β-phase. This DoS-value-correlated Mg concentration variation can be probed by LIBS for DoS prediction using the multivariate analysis methodology. In this study, 400 LIBS spectra for each sample with different DoS values were used for PC-DFA analysis, with 350 and 50 of them used as the training and testing data, respectively. This classification model established was then evaluated for DoS prediction using the external validation method. The prediction accuracies achieved for test data correlated with the unsensitized, indeterminate, and sensitized DoS levels are 100%, 100%, and 82%, respectively. LIBS with PC-DFA is demonstrated to be feasible for material sensitization assessment.

Therefore, the technology of LIBS combined with statistical analysis methods after chemical etching is capable of rapid and onsite nondestructive sensitization assessment. Combining a portable LIBS system, this approach possesses the advantages of rapid *in-situ* characterization and non-contact flexible measurement with high spatial resolution on ships. With an established spectral database, the LIBS spectra obtained from onsite measurement can be rapidly determined by artificial intelligence methods, which is free of calibration. Moreover, because most models of 5xxx Al alloys have same sensitization issues and our method assesses the Mg loss in grain boundaries after chemical etching, the technology has potential to be extended to other Al alloys suffering similar sensitization issues.

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Note and References

A patent titled "Artificial intelligence methods for correlating laser-induced breakdown spectroscopy (LIBS) measurements with degree of sensitization (DoS) values to determine the sensitization of an alloy" was published based on this research work. Publication Number is WO/2021/173963 and International Application Number is PCT/US2021/019860.

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