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Abstract. Laser-induced breakdown spectroscopy (LIBS) has been used to study the surface hardness of special aluminum alloys containing zeolite. The aluminum alloy has acquired pronounced changes in its metallurgical properties due to the zeolite inclusion. The surface hardness of the samples under investigation is determined by measuring the spectral intensity ratios of the ionic to atomic spectral lines in the LIBS spectra of samples having different surface hardness values that have been conventionally measured before for comparison. The presence of aluminum silicate mineral in the studied alloys enabled material volume to expand under compression. This feature gave new results in the measurement of hardness via LIBS. It has been proven that the trend of the alloy density change complies with the increase of ionic to atomic spectral line intensity ratio.

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1 Introduction

The behavior of aluminum alloys under compressive loading does not receive the attention given to tensile properties, perhaps because the strength of structural members is so often limited by buckling.¹ For most engineering purposes, it is common to use the same design stress data for a compressive load as for the tensile one. In the testing machine, an aluminum alloy will show an apparently higher strength in compression than in tension, but this can in part be attributed to the cross-sectional areas' change of the specimens, increasing in one case and decreasing in the other, while the stress is based on the original area. It is worthwhile to mention that the mechanical, physical, and casting properties of cast aluminum alloys make them attractive for use in cost-effective, lightweight engineering components. However, to successfully use such alloys in components intended for long-life applications, it is necessary to understand their fatigue resistance.² From the metallurgical point of view, the effect of hardening by compression changes the sample total volume and consequently its density.

Most materials get compacted or fall apart under pressure, but scientists working in an international collaboration between the U.S. Department of Energy's Brookhaven National Laboratory and the School of Chemical Sciences at England's University of Birmingham have discovered that some expand. These unusual materials may have applications as "molecular sponges" for soaking up chemical pollutants or even radioactive waste.³ This material contains aluminum, silicon, and oxygen with a three-dimensional structure containing regularly spaced pores within the molecular framework, and it is named "zeolite." It is also defined by Martínez et al.⁴ as microporous aluminum silicate

minerals. These nano- or micro-pores make zeolites very useful for sucking up small molecules, ions, or gases, just like a sponge sucking up water. The pores are normally filled with positively charged ions, such as calcium or sodium, and water molecules. So zeolites are said to be hydrated. Many zeolites are currently used as water softeners and in detergents. As for laser interaction with aluminum containing zeolite, it is well known that the change in density due to zeolite inclusion in aluminum alloys affects its heat diffusivity and in turns its vulnerability to laser beam.

Shortly after the invention of the laser in 1960s, researchers found that the beam from a laser could melt and vaporize small amounts of material, especially when the beam is focused onto the surface of an absorbing material. In the early 1970s, laser processing advanced further with the development of multikilowatt CO₂ lasers, which led to deep penetration mode of operation. Almost at the same time in 1971, Peterson et al.⁵ showed that the application of laser processing increased steadily and described the current status of material processing with lasers before 1971.⁶ In 1978, Ready^{7,8} emphasized the fundamental physical phenomena behind laser material processing and discussed a broad overview of the field of operation and the effect of different types of lasers and mode of operation on the parameters of laser material processing. In 1999, Xu et al.⁹ carried out laser transformation hardening experiments on three model steel alloys of nominal composition using continuous wave laser with a near-Gaussian beam. It has been shown that it is possible to isolate the effects of alloy chemistry and beam mode on the kinetics of the hardening process.¹⁰

Laser-induced breakdown spectroscopy (LIBS) is a well-known spectrochemical elemental analysis technique. It has been found that there is a remarkable correlation between the

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ionic to atomic spectral lines' emission ratio and the surface hardness of solid targets. The relation between the target surface hardness and the ionic to atomic spectral lines' intensity ratio of Zirconium in specially prepared steel alloys treated thermally to have different surface hardnesses has been estimated via LIBS.¹¹ The simplicity and easiness of the LIBS technique in addition to its other advantages compared with other conventional elemental analysis techniques made it exploitable in the field of surface hardness measurements. Moreover, it has been shown that with compact portable LIBS systems, the technique is promising for *in situ* measurements of solid samples surface hardness of any geometrical shape.

The aim of the present work is to study the effect of inclusion of zeolite in aluminum alloy samples' on surface hardness measured by LIBS. The effect of volume expansion under compression on the relation between the surface hardness and the ionic to atomic spectral lines emission intensity ratio will be demonstrated.

2 Materials and Methods

2.1 Materials

The chemical composition of the studied special aluminum alloy (containing zeolite) resembles the 6xxx series aluminum alloys, which are frequently used in industrial applications due to their low density, favorable mechanical properties, and excellent corrosion resistance. The classical definition of a zeolite is a crystalline, porous aluminosilicate. Zeolites have unusual properties under pressure. If a fluid is introduced into the tiny pores of the material, its volume increases. This extra volume can also allow slightly larger molecules or atoms, such as pollutants, to enter the expanded pores. When the pressure is released and the material contracts, the pollutants would be trapped inside. As the pressure increases, the material first compresses, as one would expect. But as the pressure climbs between 0.8 and 1.5 GPa, the material expands along two of its three dimensions. When the pressure increases beyond 1.5 GPa, the material compresses once again. Analysis of the molecular structure revealed that, during the expansion, additional water molecules were added into the zeolite's pores.¹² A volume

increase of about 7.0% occurs at pressures near 1.0 GPa via expansions of the *a*- and *b*-axes parameters (4.0% and 4.2%, respectively) and contraction of the *c*-axis parameter (1.2%). Further increase of pressure above 1.2 GPa results in the opposite behavior; i.e., the *a*- and *b*-axes parameters contract (2.5% and 2.2%, respectively) and the *c*-axis parameter expands (1.2%), leading to an overall volume reduction of 3.9% compared with that of the intermediate phase.¹³ Three groups of aluminum alloys of highly polished small slat each of 2×2 cm² area and 3 mm thickness have been investigated. The hardness of the samples has been measured by a mechanical tester.

2.2 Method

In the experimental setup shown in Fig. 1, the laser used is a commercial Nd:YAG laser (BRIO, Quantel, Billancourt, France) delivering laser energy of 96 mJ/pulse at its fundamental wavelength $\lambda = 1064$ nm with pulse duration of 5 ns and 20-Hz repetition rate. The beam diameter before the focusing lens was 4 mm, the focused beam diameter on the sample was 547.8 μ m, and the fluence/pulse ≈ 40.75 J/cm². The laser-induced plasma was produced by focusing the laser beam by 100-mm focal length plano-convex lens onto the sample surface, and the emission from the plasma plume was collected by a fiber optic (600- μ m diameter) and fed to an echelle spectrometer (Mechelle 7500, multichannel, Stockholm, Sweden) having a spectral resolution of 0.1 nm. The spectrometer is coupled to a computer-controlled ICCD camera (DiCAM-PRO, PCO-Computer Optics, Kelheim, Germany) with its relevant software. The lens-to-sample surface distance is controlled by a micrometer translation stage, in order to achieve precise focusing just below the target surface to avoid breakdown in the air. Each LIBS spectrum is the average of 50 spectra taken as 10 spectra at 5 different positions on each aluminum alloy sample. The obtained spectra have been displayed on a PC for further processing and spectroscopic analysis adopting LIBS++ software and relevant database. The echelle was calibrated before measurements, and we compared the spectral lines identified via LIBS++ software with NIST Spectra Database to be sure that a given emission line is from the element that we think it is from.

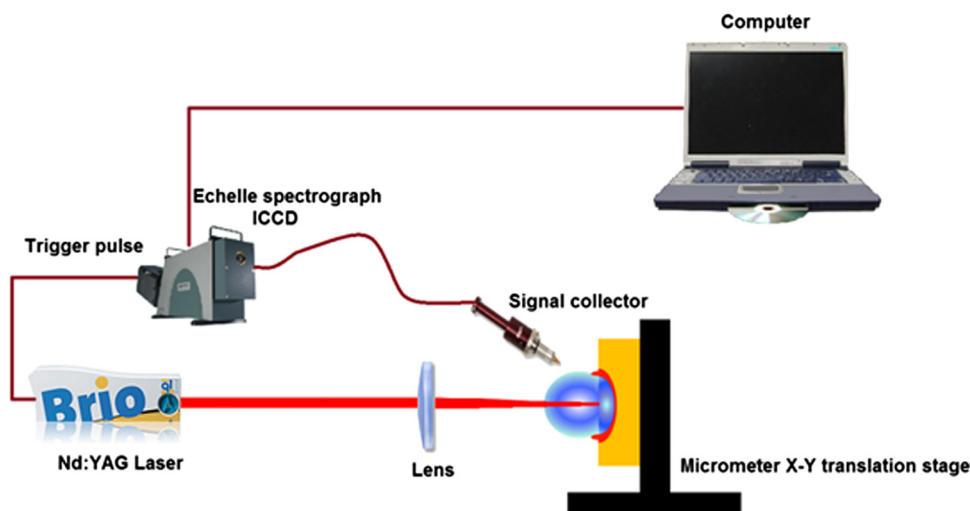


Fig. 1 Laser-induced breakdown spectroscopy (LIBS) experimental setup.

Three identical aluminum alloy samples have been used throughout the measurements. Two of the samples are compressed to different degrees of hardness, and the third has been used as prepared. The volume and weight of the samples have been determined before and after the compression process. After the compression process, the surface hardness of the three samples was determined by Vickers hardness test and via LIBS analysis.

3 Results and Discussions

3.1 LIBS and XRD Analyses

Figure 2 shows a typical LIBS spectrum of one of the aluminum alloy samples used in the recent work. Aluminum and magnesium are the major elements, whereas Ti, Si, Fe, Cr, and Co represent the existing minor elements. The inset in Fig. 2(a) demonstrates the presence of zeolite, which is represented by the silicon spectral lines. The spectrum shown in Fig. 2(b) demonstrates the well-resolved magnesium lines obtained via the high-spectral resolution (better than 0.1 nm) of the used echelle spectrometer-ICCD system.

To confirm the existence of aluminum silicate or “zeolite” in the samples, x-ray diffraction (XRD) spectra have been

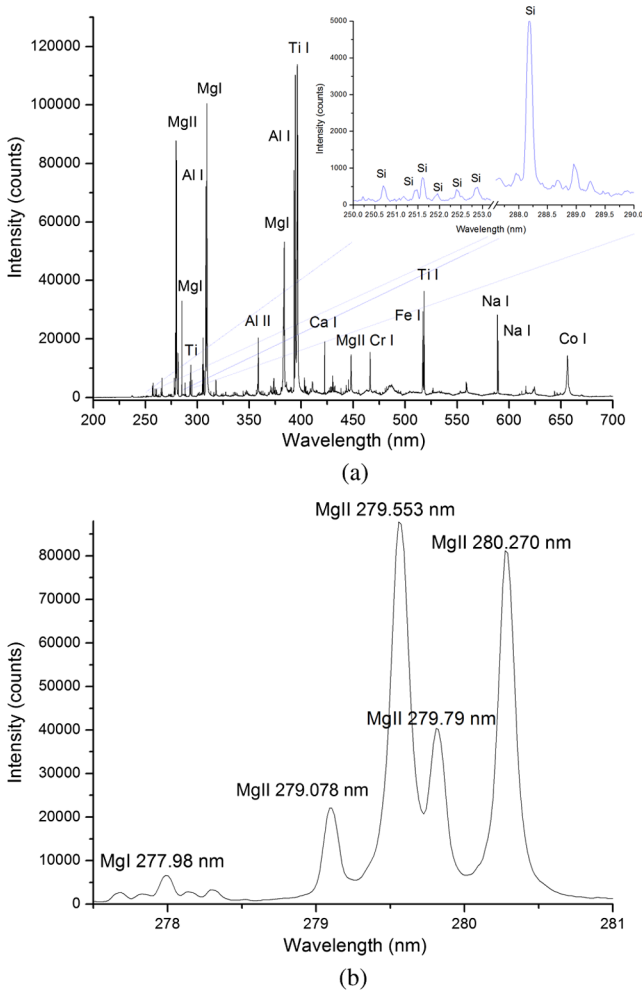


Fig. 2 (a) Typical LIBS spectrum of one of the aluminum alloy samples. The inset depicts the silicon spectral lines due to the zeolite inclusion. (b) The well-resolved magnesium spectral lines used in surface hardness determination.

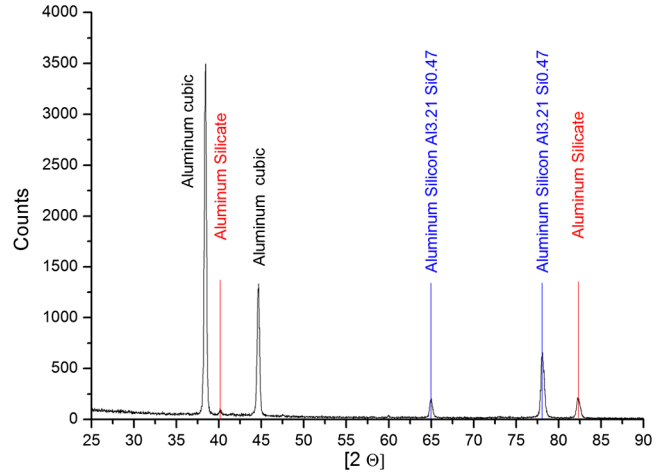


Fig. 3 X-ray diffraction (XRD) analysis for the aluminum alloy sample by X-Pert PRO, PANalytical system.

obtained for the samples under investigation. The used XRD spectrometer was an X-Pert PRO, PANalytical with fixed tube, Cu target, secondary graphite monochromator, flat-plate horizontal sample holder, X-Celerator for faster data acquisition with X-Pert Hi-Score plus software pattern analysis, and phase identification (ICDD database). The XRD results are depicted in Fig. 3, indicating the existence of the aluminum silicate (Al_2SiO_5), beside aluminum cubic and aluminum silicon ($Al_{3.21}Si_{0.47}$).

3.2 Hardness Measurement

In the compression test, two identical aluminum alloy samples that have been subjected to different degrees of compression suffered from a permanent change in its volume (density) after the compression procedure. The measured values of samples’ hardness with conventional equipment were 87.95 HV30 for normal sample (as prepared), 104.166 HV30 for medium hardening sample, and 109.25 HV30 for maximum hardening sample.

The volume and mass of each sample are measured before and after compression procedure. The results show that the volume of the medium hardening sample has been increased by about 12%, and the volume of the maximum hardening sample has been increased by about 20% after compression. This expansion in volume yields a decrease in density in the two compressed samples from ρ in the normal sample to 0.893ρ in the medium hardening sample and 0.833ρ for the maximum hardening sample (see Fig. 4).

Distinctively different from conventional analytical techniques, which are time consuming, labor intensive, and destructive, LIBS as an emerging analytical tool offers many superior advantages such as being fast, cheap, *in situ*, and a quasi-nondestructive technique. Furthermore, LIBS allows remote analysis without direct contact with the sample surface, because it requires only optical access. This would be very useful in this case, especially for analyzing difficult places or surfaces of buildings structures, where otherwise they cannot be reached by other conventional tools.¹⁴ Recently, optical emission in LIBS was found to be influenced significantly by the compressive strength (hardness) of the sample, offering an opportunity for determining material hardness using LIBS technique. Accordingly, by means of

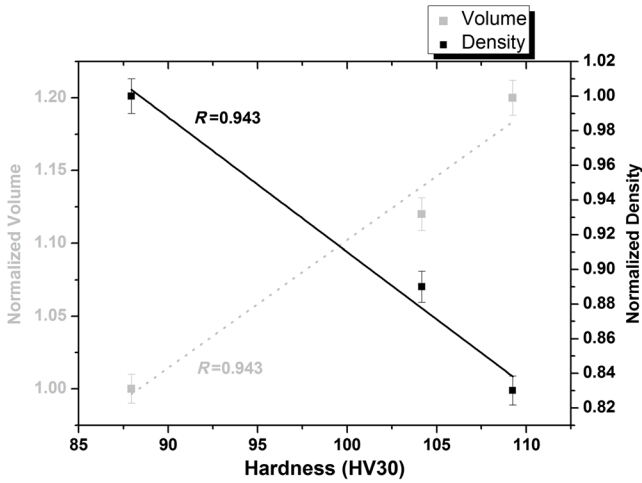


Fig. 4 Relation between sample hardness, volume, and density, demonstrating that the ratio of volume expansion with hardness increases under compression.

some specific ionic to atomic line emission ratio from the produced plasma, LIBS technique has been successfully used for measuring a specific physical property of solid, namely compressive strength of concrete.¹⁵ The developed technique was then used to measure the hardness of samples of a biological nature¹⁶ and natural minerals and stones.¹⁷

To avoid a strong self-absorption effect on the lines' intensity, the partial self-absorption coefficient $KR(\lambda)$ (in $m^2 s^{-1}$) for a spectral line can be obtained by multiplying the self-absorption cross-section of such line (S_L) with the lower energy level population (C)

$$KR(\lambda) = S_L \cdot C,$$

where

$$S_L = 0.330\lambda_0^3 \sqrt{\frac{M}{T}} \frac{g_j}{g_i} A_{ji},$$

and C is given by

$$C = (g_j A_{ji} / U) e^{-E_i / kT},$$

where λ_0 is the wavelength of the spectral line (in m), T is the temperature (in K), and A_{ji} is the transition probability (in s^{-1}). M is the atomic mass of the element, g_i and g_j are the statistical weights of the lower and upper levels, respectively, U is the partition function, E_i is the energy of the lower energy level, and k is the Boltzmann's constant. In principal, it is easy to calculate both parameters S_L and C , so a partial self-absorption coefficient has been calculated for each line.¹⁸ Since A_{ji} and g_j are in the numerator of both S_L and C , they have the most effect on the partial self-absorption coefficient $KR(\lambda)$ final value. On the other hand, g_i must not equal zero.

For the two magnesium spectral lines chosen in our measurements, Mg I $\lambda = 277.983$ nm ($A_{ji} = 1.36e + 08 s^{-1}$, $g_j = 57833.40 cm^{-1}$, $g_i = 21870.464$) and Mg II $\lambda = 279.078$ nm ($A_{ji} = 4.01e + 08 s^{-1}$, $g_j = 71491.06 cm^{-1}$, $g_i = 35669.31$), they have relatively low-partial self-absorption coefficient $KR(\lambda)$.

Figure 5(a) shows that the relation between the hardness and the emission intensity ratio of the aluminum alloy samples is an inverse proportionality. This result confirms that the ionic to atomic spectral lines' emission intensity ratio could be an effective measurement tool for the surface hardness. However, the relation obtained for the investigated special aluminum alloy samples demonstrates that the relation between the hardness and the emission intensity ratio of Mg II/Mg I is not as obtained in previous works for other materials,^{14,16} i.e., direct proportionality.

Figure 5(b) shows the relation between the ionic to neutral spectral lines intensity ratio and the density instead of hardness. The relation in this case is direct proportionality. So, it can be said that for these very special aluminum alloy samples, the emission intensity ratio is directly proportional to the sample density and not to its surface hardness.

The repulsive force of the laser-induced shockwaves depends clearly on the target density and laser irradiance and leads to an appreciable increase in the ionic species on the account of the neutral ones, and consequently raises the ratio of Mg II/Mg I. For low-density sample, the speed of the shockwave would be slowed down in comparison to the case of a high-density target, resulting in a reduction of the

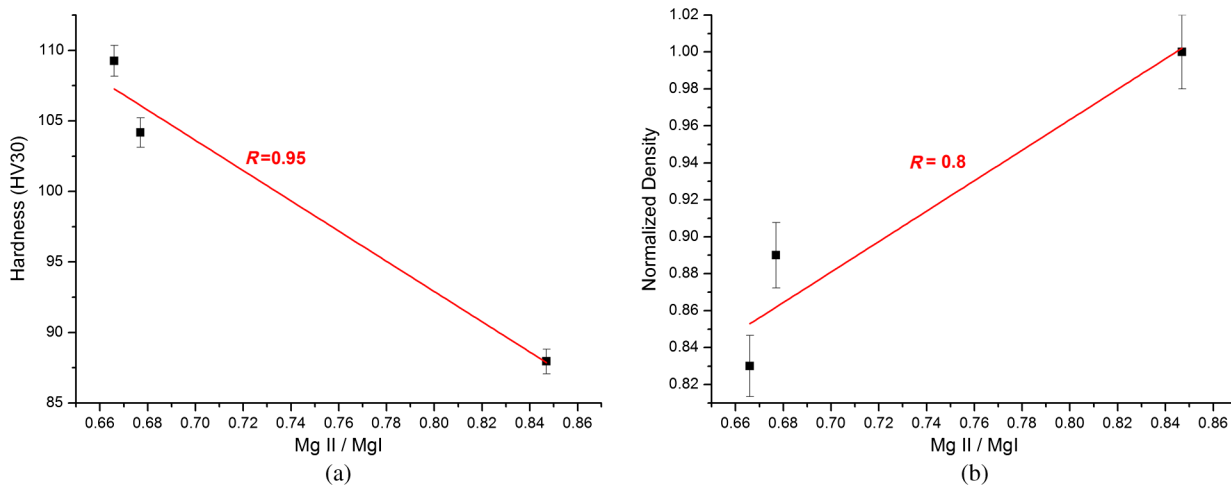


Fig. 5 (a) Correlation between hardness of aluminum alloy and the emission intensity ratio of Mg II 279.078 nm/Mg I 277.983 nm. (b) Correlation between density of aluminum alloy and the emission intensity ratio of Mg II 279.078 nm/Mg I 277.983 nm.

ionization effectiveness and then of the ionic to neutral intensity ratio. In fact, higher target density would lead to higher plasma density and consequently to higher collision frequency (which is proportional to the plasma electron density). The electrons gain energy as they oscillate in the laser field and collide with the ions, causing further ionization to the next ionic state. It is well known that this is the dominant ionization mechanism in case of nanosecond LIBS.

4 Conclusion

It has been demonstrated that LIBS is a powerful technique that can be used easily in the determination of the surface hardness of a metallic alloy. In the present work, special aluminum alloy samples containing zeolite have been used to determine their hardness by adopting LIBS. The idea was to relate the ionic to neutral spectral lines intensity ratio in the LIBS spectrum of the samples under study to the surface hardness of such samples. Contrary to the previously published results, the relation was inverse proportionality for such a special aluminum alloy with special metallurgical properties due to the inclusion of zeolite. However, direct proportionality between the target material density and the ionic to neutral magnesium spectral lines' intensity ratio has been obtained. This new result is relevant to the special properties acquired by the aluminum alloy due to the inclusion of zeolite.

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