Laser ablation characteristics of metallic materials: Role of Debye-Waller thermal parameter

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Abstract. The interaction of a high intensity laser pulse with a solid target results in the formation of a crater and a plasma plume. The characteristics of both depend on physical properties of target material, environmental conditions, and laser parameters (e.g. wavelength, pulse duration, energy, beam diameter) etc. It has been shown for numerous metals and their alloys that plasma threshold fluence, plasma threshold energy, ablation efficiency, ablation yield, angular distribution of laser produced plasma (LPP) ions, etc. are a unique function of the Debye-Waller thermal parameter $B$ or the mean-square amplitude of atomic vibration $\langle u^2 \rangle$ of the target material for given experimental conditions. The FWHM of the angular distribution of LPP ions, ablation yield, and ablation efficiency increase whereas plasma threshold fluence and plasma threshold energy decrease as $B$-factor of the target material increases.

1. Introduction
In 1993 Butt et al [1] published a report on the correlations of macroscopic or bulk properties of cubic elements with their microscopic parameter Debye – Waller factor $B$ measured at room temperature. They found that several general, thermal, mechanical and crystal defect properties of 20 cubic elements were a unique function of their room temperature $B$-factor. This motivated Butt and Chaudhary [2] to extend this study to the deformation behavior of cubic metals. They showed that for metals of a given cubic structure, the yield stress at a given temperature between 0 and 298K was a function of their room temperature $B$-factor; smaller the $B$-factor, higher is the yield stress. Similarly, temperature dependence of the yield stress of metals with a given cubic structure was also dependent on the room temperature $B$-factor; lower the $B$-factor, weaker is the temperature dependence of yield stress.

As far as solubility limit (SL) of one metal into another to form binary substitutional solid-solution is concerned, Butt and Kaloom [3] observed that SL (wt. %) of different cubic metals in copper lattice is 100% if their $B$-factor is either equal to or less than that of copper. However, if $B_{\text{solute}} > B_{\text{Cu}}$, SL decreases progressively with the increase in $B$-value of solute metals. Greater the difference between the $B$-factors of solute and solvent metal, smaller is the solubility limit. The extremely small SL of Ag into Cu (0.1 wt. %), which is not explicable in terms of the well-known Hume-Rothery rules, can be attributed to the large difference (38.6%) in the $B$-factors of Ag and Cu.

In addition to several other correlations of bulk properties of cubic elements and cubic compounds with their $B$-factors in solid phase [4-13], it was interesting to find that solid→liquid and liquid→vapor phase transformations, characterized by melting and boiling temperatures ($T_m$ and $T_b$) of crystalline materials, were also a unique function of room temperature $B$-factor. Butt and Jabeen [7], therefore,
Inferred that cubic elements and compounds possess lattice-vibration memory in the liquid → vapor phase transformation as well.

In laser – solid interaction experiments, the laser fluence and laser energy should have a critical minimum or threshold value to generate plasma from the target solid by irradiation with laser of a given wavelength. Both plasma threshold fluence \(F_{th}\) and plasma threshold energy \(E_{th}\) of the target solids for a laser of a given wavelength depends on the nature of the target. The laser produced plasma (LPP) plume, which may consist of electrons, ions, atoms, molecules and micro-sized particles, is formed as a result of the ablation of material from the target surface [14]. The angular distribution of LPP particles, whether ions or neutrals, has been studied for several metals, and their alloys [15–29]. The commonality in these investigations is that the angular distribution of LPP particles can be described either by the cosine power-law \(F = F_o \cos^2 \theta\), where \(F\) is the flux measured in a direction making an angle \(\theta\) with the normal to the target surface or by the full width at half maximum (FWHM) of the emission profile fitted by Gauss function. Under given experimental conditions, the value of exponent \(n\) or FWHM depends on the nature of the target. A number of researchers have attempted to correlate the exponent \(n\) and the FWHM of the angular distribution of particles in the LPP plume in terms of sublimation energy, atomic mass and melting temperature of the target solids. However, no consistent picture emerged from these attempts.

In this presentation, we will analyze the laser – solid interaction parameters, namely plasma threshold fluence and plasma threshold energy necessary for solid → plasma phase transformation, together with ablation efficiency, as a function of the Debye-Waller thermal parameter \(B\) or the mean-square amplitude of atomic vibration \(<u^2>\) of the target materials under identical experimental conditions. Whether metallic materials possess lattice-vibration memory in the plasma state as well or not will also be reviewed.

2. Role of Debye-Waller thermal parameter

When radiations (X-rays, neutrons, electrons, and \(\gamma\)-rays) of wavelength \(\lambda\) are diffracted from a crystal, the intensity \(I\) of the diffracted beam at a Bragg angle \(\theta_B\) is found to be less than that of the incident beam \(I_o\) due to lattice vibrations in the crystal by an exponential factor, \(\exp\left(\frac{-2Bs\sin^2\theta_B}{\lambda^2}\right)\), known as the Debye-Waller factor, i.e. \(I = I_o \exp\left(\frac{-2Bs\sin^2\theta_B}{\lambda^2}\right)\). In a mono atomic cubic crystal, the atomic vibrations are isotropic and the mean-square amplitude of atomic vibrations \(<u^2>\) is related to \(B\) through the relation: \(\frac{9\pi^2<u^2>}{3}\). However, for non-cubic crystal structures, e.g. hexagonal close-packed, in which atomic vibrations are anisotropic, an average value of \(B_s\) and \(B_is\) is taken. Moreover, the \(B\)-factor value of a binary alloy is taken as mass weighted average of \(B_1\) and \(B_2\) of the constituent elements [17].

2.1. Laser thresholds for plasma generation

The effect of laser irradiation wavelength on plasma threshold of nine metals (Zn, Al, Ag, Cu, Ni, Fe, Cr, Mo, W) was studied by Cabalin and Laserna [30]. A nanosecond Q-switched pulsed Nd:YAG laser was operated at infrared (1064 nm), visible (532 nm), and ultraviolet (266 nm) wavelengths, and focused on the target in air at atmospheric pressure to generate plasma. They measured plasma threshold fluence \(F_{th}\) and plasma threshold energy \(E_{th}\) for these metals for each laser wavelength \(\lambda\) cited above. For each laser wavelength, they tried to correlate the plasma threshold fluence \(F_{th}\) of target metals with their melting point \(T_m\) and boiling point \(T_b\). Although plasma thresholds show an increasing trend with \(T_m\) and \(T_b\) yet considerable scatter in each case (Figures 4 and 5 in [30]) clearly points to poor correlation.

Therefore, we will now re-analyze their data in terms of the Debye-Waller thermal parameter \(B\) of target metals. The data points in figure 1 denote the experimental values of plasma threshold fluence \(F_{th}\), taken from [30], and displayed here as a function of \(B\)-factor of target metals for three different laser irradiation wavelengths. The \(B\)-values were taken from [31–33]. One can readily note from figure
Figure 1. Correlation between the measured plasma threshold fluence and the room temperature $B$-factor of nine target metals for three different laser wavelengths: (a) 266 nm, (b) 532 nm, (c) 1064 nm.

Figure 2. Correlation between the measured plasma threshold energy and the room temperature $B$-factor of nine target metals for three different laser wavelengths: (a) 266 nm, (b) 532 nm, (c) 1064 nm.

1 (a) and (b) for 266 and 532 nm wavelengths that the data points can be divided into two groups: One for body-centered cubic (bcc) metals (W, Mo, Cr, Fe) and the other for close-packed structure metals (Ni, Cu, Ag, Al, Zn). In each case, the data points are encompassed by a straight line obtained by least-squares fit method. However, figure 1(c) for 1064 nm wavelength indicates a further sub-division in close-packed structure metals; hexagonal closed-packed (hcp) Zn separates itself from face-centered cubic (fcc) metals (Ni, Cu, Ag, Al). Nevertheless, one can again note quite good linear fit to the data points for bcc and fcc metals, setting aside single hcp Zn data point.
Similarly, the data points in figure 2 depicts the experimental values of plasma threshold energy ($E_{th}$) of nine metals reported by Cabalin and Laserna [30], for infrared (1064 nm), visible (532 nm) and ultraviolet (266 nm) wavelengths and displayed here as a function of $B$-factor of these metals. As far as the dependence of $E_{th}$ on $B$ is concerned (figure 2), it is a replica of that for $F_{th}$ (figure 1).

2.2. Ablation Efficiency

In figure 3, ablation efficiency of pure Mo, Fe, Ni, Cu, Al and Pb metals in terms of ablated volume per unit of energy have been depicted as a function of the Debye-Waller thermal parameters $B$. The data points denote the measured values obtained by Semerok et al [34] in laser ablation experiments conducted in air at atmospheric pressure with sharply focused ns, ps, and fs laser pulses. The values of $B$ were taken from [31‒33]. Using least-squares fit method, a straight line is found to fit the data points in each case. The linear correlation coefficient values (0.909 – 0.999) being close to 1 points to an excellent linear dependence of ablation efficiency on the $B$-factor of target metals. Thus, under identical irradiation conditions, a metal with larger $B$-factor or higher mean-square amplitude of atomic vibrations $<u^2>$ will ablate more as compared to a metal with smaller $B$-factor and vice versa.

Similarly figure 4 illustrates the correlation between the ablation yield of several metallic targets in terms of atoms/shot and the room temperature Debye-Waller factor $B$. The data points denote the experimental values obtained by Thestrub et al [35] in laser ablation investigations carried out in a vacuum of 10$^{-7}$ mbar operating the laser at 355 nm with pulse width of 6ns and fluence of 2.0 J/cm$^2$. Using least-squares fit method, Ali et al [16] passed a straight line through the data points (figure 4) with a linear correlation coefficient $r = 0.94$. This shows that a metal with higher $B$-factor or larger mean-square amplitude of atomic vibrations $<u^2>$ will ablate more under given irradiation conditions, and hence the number of ablated atoms per shot will be larger.
2.3. Angular distribution of LPP ions

Now we will review the angular distribution of LPP ions emitted from the metallic targets as a function of their room temperature $B$-factor.

Referring to figure 5, taken from [16], the data points denote the values of exponent $n$ of $\cos^n \theta$ distribution of LPP ions for six target metals (Mo, Ni, Ti, Cu, Mg and Zn) as a function of their room temperature Debye-Waller thermal parameter $B$. The straight line fitted to the data points by least-squares fit method shows that as $B$ increases $n$ decreases. This shows that the plasma plume is broader for a metal with larger $B$-factor or higher mean-square amplitude of atomic vibrations $\langle u^2 \rangle$ and is narrower for a metal with smaller $\langle u^2 \rangle$.

Similarly, a linear $n-B$ correlation is also observed [17] for metallic targets Ti, Al, and their binary alloys Ti$_{1-x}$Al$_x$ and Ti$_x$Al$_{1-x}$, as shown in figure 6(a). Moreover, figure 6(b) shows that the maximum average charge $(q_{av})_{\text{max}}$ of LPP ions emitted from these targets in a direction normal to the target surface also correlates well with their room temperature Debye-Waller thermal parameter $B[17]$. Greater the $B$-factor, higher is the value of $(q_{av})_{\text{max}}$. It means that atoms are ejected to a greater extent from the target with higher $B$-factor or $\langle u^2 \rangle$-value, leading to higher value of $(q_{av})_{\text{max}}$ in the plasma plume.

As far as the angular distribution of various ionization states of ions is concerned, it can be seen from figure 7(a) and (b), that both the parameters $n$ and FWHM for ions of a given state ($q_{av}^{-1}$ to $q_{av}^{-4}$) also show a linear dependence on the $B$-factor of Ti$_{1-x}$Al$_{1-x}$ metallic targets with $x = 0$ to 1. For larger value of $B$-factor, the exponent $n$ of $\cos^n \theta$ distribution of ions of a given state is smaller, and the FWHM is larger. This means that not only the angular distribution of overall LPP ion flux (accumulative charge) but also that of the individual ionization states are controlled by the $B$-factor of target material.

The observed increase in the value of exponent with the increase in ionization state of LPP ions emitted from a given target(figure 7) means that the angular distribution of LPP ions becomes narrower as the ionization state increase from $+1$ to $+4$. It is because ions with higher ionization state possess more energy than lower ionization state since the acceleration of ions is proportional to their charge.
Figure 6. Dependence of (a) exponent $n$ of $\cos^n \theta$ distribution and (b) maximum average charge of LPP ions of metals Ti, Al, and their alloys Ti$_{50}$Al$_{50}$, Ti$_{75}$Al$_{25}$ on their room temperature Debye-Waller thermal parameter $B$ [17].

Figure 7. Dependence of (a) the exponent $n$ of $\cos^n \theta$ distribution and (b) the FWHM of Gaussian distribution of various ionization states on the room temperature Debye-Waller thermal parameter $B$ of metals Ti, Al, and their alloys Ti$_{50}$Al$_{50}$, Ti$_{75}$Al$_{25}$[17].

Finally, figure 8 depicts the FWHM of Gaussian distribution of laser-ablated particles from Ti$_x$Al$_{1-x}$ ($x = 0, 0.25, 0.34, 0.5, 0.75, 1$), W$_x$Cu$_{1-x}$ ($x = 0, 0.6, 0.8, 0.9$ and $1$), and Mo$_x$Cu$_{1-x}$ ($x = 0, 0.7$, and $1$) metallic targets as a function of their room-temperature $B$-factors [17]. A single straight line fitted to the entire data points shows that whatever the nature or composition of the target, the angular distribution of particles in the plasma plume is uniquely related to the $B$-factor. Thus, under given irradiation conditions, two metallic alloy targets of any composition but with identical $B$-factor value will give rise to identical angular distribution of ions in laser ablation plumes. In other words, angular distribution of LPP ions emitted from alloy targets, irrespective of the nature and composition of constituent metals, is $B$-equivalent.
3. Conclusions

- The laser ablation parameters, namely plasma threshold fluence, plasma threshold energy, ablation efficiency, ablation yield, angular distribution of LPP ions, etc. are a unique function of the Debye-Waller thermal parameter $B$ or the mean-square amplitude of atomic vibrations $<u^2>$ of the target material under given experimental conditions.
- Crystalline materials, whether metals or alloys, possess lattice-vibration memory not only in their solid → liquid and liquid → vapor phase transformations but also in the solid → plasma phase transformation as well as in the plasma state.
- Keeping in view the observed excellent correlations of the room temperature $B$-factor with laser ablation parameters as well as with numerous other properties of crystalline materials reported in the literature, one can speculate that $B$-factor of crystals is “equivalent” to the DNA of living organisms controlling their behavior in all respects.

4. References

[1] Butt N M, Bashir J and Khan M N 1993 J. Mater. Sci. 28 1595
[2] Butt M Z and Chaudhary S A 1993 Physical Review (B) 47 8418
[3] Butt M Z and Kalsoom U 1999 Fizika A 875
[4] Niaz J, Anwar M, Nadeem A H and Butt M Z 1993 J. Nat. Sci. Math. 3689
[5] Butt M Z and Hameed T 1993 Science International (Lahore) 5 313
[6] Butt N M, Bashir J, Khan M N and Willis B T M 1994 J. Mater. Sci. Lett. 13 1440
[7] Butt M Z and Jabeen S 1996 J. Mater. Sci. Lett. 15 412
[8] Kalsoom U, Butt M Z, and Khaleeq ur Rahman M 1998 J. Nat. Sci. Math. 38 261
[9] Butt M Z and Ahmad I 1999 Czech. J. Phys. 49 49509
[10] Butt M Z 1999 Czech. J. Phys. 49 1177
[11] Butt M Z and Chaudhary S A 2000 Czech. J. Phys. 50 645
[12] Sirdeshmukh D B, Krishna P G and Subhadra K G 2003 J. Mater. Sci. 38 2001
[13] Ali D, Butt M Z and Naseem S 2013 Rad. Eff. Def. Solids 168 1
[14] Ali D 2010 M.Phil. Thesis, University of Engineering and Technology, Lahore, Pakistan
[15] Khaleeq-ur-Rahman M, Ali D and Butt M Z 2010 Vacuum 85 170
[16] Ali D, Butt M Z, and Khaleeq-ur-Rahman M 2011 App. Surf. Sci. 2854

Figure 8. Dependence of the FWHM of Gaussian distribution of laser-ablated particle masses from Al, Ti, Cu, Mo, W and their alloys Ti25Al75, Ti34Al66, Ti50Al50, Ti75Al25, W60Cu40, W80Cu20, W90Cu10 and Mo70Cu30 on the room temperature Debye-Waller thermal parameter $B$ [17].
[17] Ali D, Butt M Z and Butt S 2012 *Mater. Chem. Phys.* 137 147
[18] Ali D, Butt M Z, and Khaleeq-ur-Rahman M 2010 *J. Nat. Sci. Math.* 50 1
[19] Buttini E, Thum-Jager A and Rohr K 1998 *J. Phys. D: Appl. Phys.* 31 2165
[20] Thum-Jager A and Rohr K 1999 *J. Phys. D: Appl. Phys.* 32 2827
[21] Srivastava S N and Rohr K 2005 *Nuclear Instrum. Methods B* 237 497
[22] Muller-Th, Sinha B K and Rohr K P 2003 *Phys. Rev. E* 67 026415
[23] Laska L, Krasa J, Pfeiffer M, RohlenaK, Gammino S, Torrisi L, Ando L and Ciavola, G 2002 *Rev. Sci. Instrum.* 73 654
[24] KonomiI, Motohiro T, and Asaoka T 2009 *J. Appl. Phys.* 106 013107
[25] KonomiI, Motohiro T, KobayashiT, and Asaoka T 2010 *Appl. Surf. Sci.* 256 4959
[26] Srivastava S N, Sinha B K and Rohr K P 2006 *J. Phys. B: At. Mol. Opt. Phys.* 39 3073
[27] Torrisi L, AndoL, Ciavola G, GamminoS andBarna A 2001 *Rev. Sci. Instrum.* 72 68
[28] Antoni F, Fuchs C and Fogarassy E 1996 *Appl. Surf. Sci.* 96-9850
[29] Torrisi L 2002 *Appl. Surf. Sci.* 195 8
[30] Cabalin L M and Laserna J J 1998 *Spectrochimica Acta Part B* 53 723
[31] Butt N M , Bashir J, Willis B T M and Heger G 1988 *Acta Crystallographica A* 44 396
[32] Fox AG and Fisher R M 1988 *Aust. J. Phys.* 41 461
[33] International Tables for X-rays Crystallography, vol. 3, Kynoch Press, Birmingham, 1968, pp. 238–239.
[34] Semerok A , Chaleard C, Detalle V, Lacour J L, Mauchien P, Meynadier P, NouvellonC, Salle B, Palianov P, Perdrix M and Petite G 1999 *Appl. Surf. Sci.* 138–139 311
[35] Thestrup B, Toftmann B, Schou J, Doggett B and Lunney J G 2002 *Appl. Surf. Sci.* 197-198 175