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Explosive boiling of a metallic glass superheated by nanosecond pulse laser ablation

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We report an explosive boiling in a Zr-based (Vitreloy 1) bulk metallic glass irradiated by a nanosecond pulse laser with a single shot. This critical phenomenon is accompanied by the ejection of high-temperature matter from the target and the formation of a liquid-gas spinodal pattern on the irradiated area. An analytical model reveals that the glassy target experiences the normal heating (melting) and significant superheating, eventually culminating in explosive boiling near the spinodal limit. Furthermore, the time lag of nucleation and the critical radius of vapor bubbles are theoretically predicted, which are in agreement with the experimental observations. This study provides the investigation on the instability of a metallic glass liquid near the thermodynamic critical temperature. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4905928]

Laser ablation of solids has intriguing applications, such as film deposition,[1] surface treatment,[2] and nanostructure synthesis.[3] This technology is also of great scientific interest, since the key question of how matter removes from a laser-irradiated target remains open. In general, laser ablation involves three kinds of thermal processes: normal vaporization, normal boiling, and explosive boiling.[4] For nanosecond or shorter laser pulses, the regime of normal vaporization and boiling gives way to explosive boiling with increasing laser energy fluence.[5–10] It has been suggested that high-power laser pulses could rapidly superheat a target beyond its boiling point into a metastable liquid state; when the temperature approaches the thermodynamic critical point (TCP), the superheated liquid breaks down into a mixture of droplets and vapor. This critical process has been well understood in terms of explosive boiling or phase explosion,[11,12] which describes instantaneous homogeneous nucleation and growth of vapor bubbles in superheated liquids due to extremely large density fluctuations. Explosive boiling is considered as the most efficient thermal mechanism for laser ablation on various crystalline solids.[6,7,13–15] Metallic glasses represent a relatively novel class of non-crystalline solids that are frozen from highly viscous melts through the glass transition.[16,17] They are naturally in metastable states with intrinsic density or free-volume fluctuations.[18–21] It is therefore expected that, when a high-power laser pulse is applied, metallic glasses are prone to undergo superheating and explosive boiling, although this has never been verified so far.

In this letter, we present the experimental evidence of explosive boiling in a typical Zr-based bulk metallic glass ablated by a single nanosecond laser pulse. A thermal model is proposed to quantitatively describe the underlying mechanism.

We chose a typical $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vitreloy 1) bulk metallic glass as the target material. Target specimens ($10 \times 10 \times 2\,mm^3$) were cut by wire electrical discharge machining of the as-cast material. Then, the specimen surfaces were polished to remove oxides. The glassy nature of the targets was confirmed by X-ray diffraction and differential scanning calorimetry. Single pulse ablation experiments were performed in air by irradiation of a Q-switched Nd:YAG laser (wavelength 1064 nm, pulse width 10 ns, and pulse energy 2.3 J). The laser beam was directed along the x axis, normal to the target surface. A Photron Fastcam SA-X camera with a frame rate of 50 000 fps was used to record the ejection of matter from the target under a low-illumination condition. After irradiation, morphologies of the irradiated areas were examined by using an FEI Sirion scanning electron microscope (SEM) and a Veeco DI MultiMode atomic force microscope (AFM).

Figure 1 (Multimedia view) shows a sequence of images recorded by the camera, indicating that some bright matter was ejected from the target surface and then gradually darkened. The spatiotemporal resolution of the camera and the applied low-light condition rule out the possibility of capturing the plasma and the shock wave.[22,23] Instead, the high-temperature matter is the only capture that can be visible to the camera as bright sparks. It is well accepted that the emission of high-temperature matter provides important evidence for explosive boiling,[6,7,15,22,24] thus indicating that an explosive boiling process might have taken place in the Vitreloy 1 glass after the ns-pulse laser ablation. The glassy target should have experienced an explosion-type vaporization from its superheated liquid, resulting in a violent ejection of a high-temperature mixture of vapor and droplets. For explosive boiling, there is a certain time for a vapor bubble nucleus to grow to a critical size. This phenomenon is called the time lag of nucleation, which has been widely observed in pulse laser ablation.[6,8,10,22,25] Fig. 1(a) actually shows that

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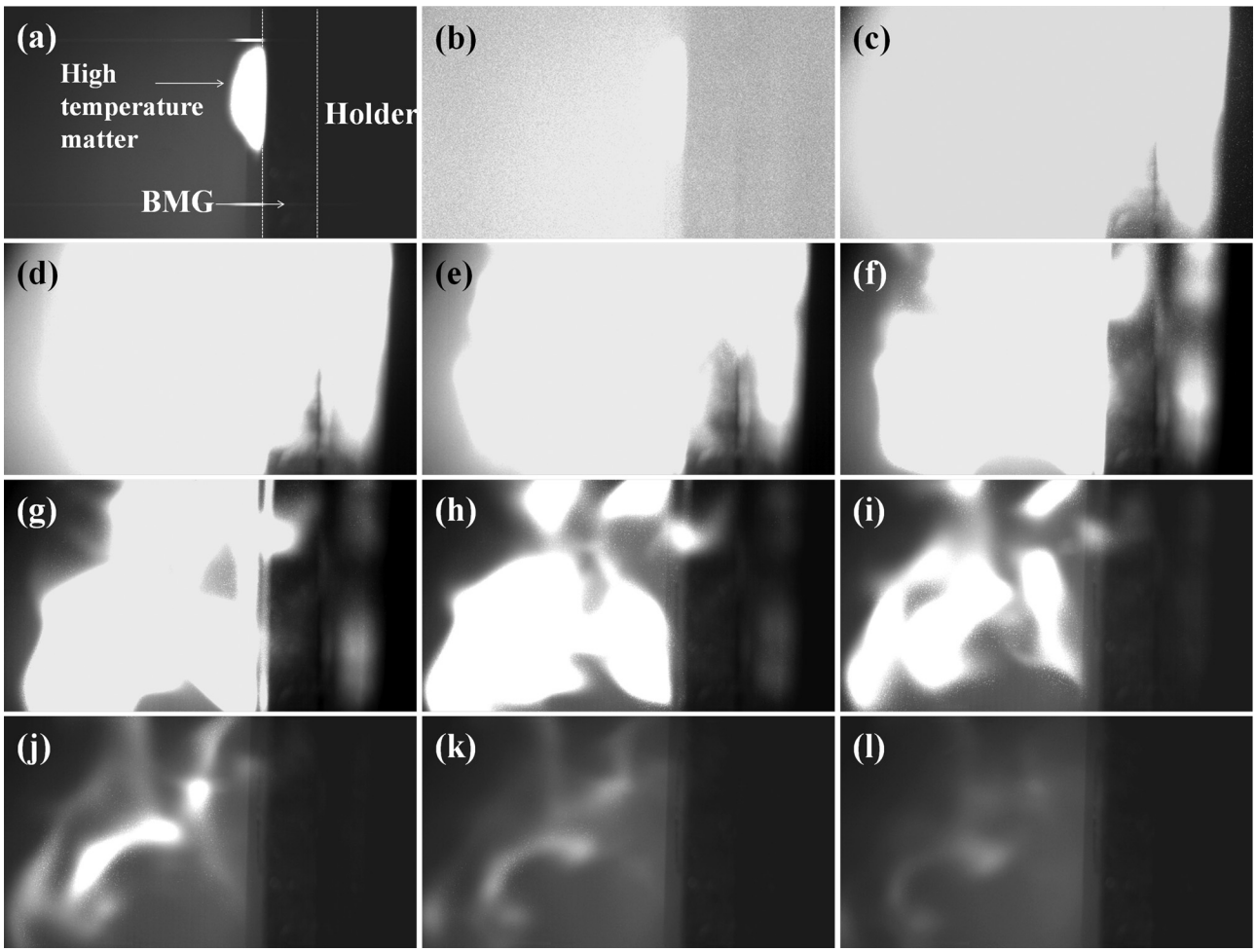

FIG. 1. Sequence of images (size: $15 \times 8.5\,mm^2$) showing the emission and cooling down of high-temperature matter from the Vitreloy 1 glass target by a nanosecond pulse laser with a single shot. (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4905928.1]

the matter ejection occurs after the extinguishing of the laser pulse, although the exact time delay is not determined here. It is also seen from Figs. 1(a) and 1(b) that the ejection of high-temperature matter lasts for several tens of microseconds, which is consistent with the observations of Yoo *et al.*[6,24] After that, the high-temperature matter ceases to erupt and gradually cools down with the recession of the thermal front (see Figs. 1(c)–1(l)).

To confirm the possibility of explosive boiling, we examined the laser-irradiated area, as shown in the inset of Fig. 2(a). By measuring the actual irradiated area, the laser fluence is estimated to be about $11\,J/cm^2$. The corresponding laser intensity is $1.1\,GW/cm^2$ that is comparable to the explosive boiling thresholds for some crystalline metals.[7,25] On the edge of the irradiated area, surface ripples can be clearly observed (see Fig. 2(a)), which most likely have been caused by resolidification of the molten Vitreloy 1.[26,27] This observation indicates that a significant thermal process occurred due to the present ns-pulse laser irradiation. Nevertheless, the entire irradiated area looks macroscopically smooth, as shown in Fig. 2(b). However, a close-up view of the smooth surface exhibits a unique porous structure, which is presented in Figs. 2(c) and 2(d) at different magnifications. It is interesting to note that the porous structure consists of 100 nm-scale voids that are homogeneously distributed. It is reasonable to assume that these voids correspond to the loci where vapor bubbles nucleated and grew in the superheated liquid. We further performed precise AFM scans on this ablation pattern, and its representative 2- and 3-D landscapes are shown in Figs. 2(e) and 2(f), respectively. Surprisingly, the porous nanostructure exhibits an interesting striated pattern, which resembles the structures formed by spinodal phenomena.[28,29] Fig. 2(e) indicates the surface profile along the marked section. We find that the spacing (about 120 nm) of the striae is on the same scale as the characteristic size of voids in Fig. 2(d).

The observations in Fig. 2 indicate the presence of a liquid-gas spinodal that is the upper boundary of a metastable liquid.[12,30] The spinodal boundary corresponds to the spontaneous and simultaneous nucleation of vapor bubbles in liquid. For most cases, explosive boiling, due to an increased nucleation rate, will prevent the liquid from approaching the spinodal.[7] However, it is possible for explosive boiling to take place at the spinodal point, if the degree of superheating is sufficiently high and/or the spinodal point is relatively low. For the multicomponent Vitreloy 1 liquid, both conditions may be at work due to its high viscosity and significant fluctuations (metastability) of free volume. In this case, a spatial separation would occur via a spinodal process between the vaporized gas and the residual liquid. We thus observed an explosive boiling phenomenon (see Fig. 1 (Multimedia view)). The ejection of the vapor bubbles leaves

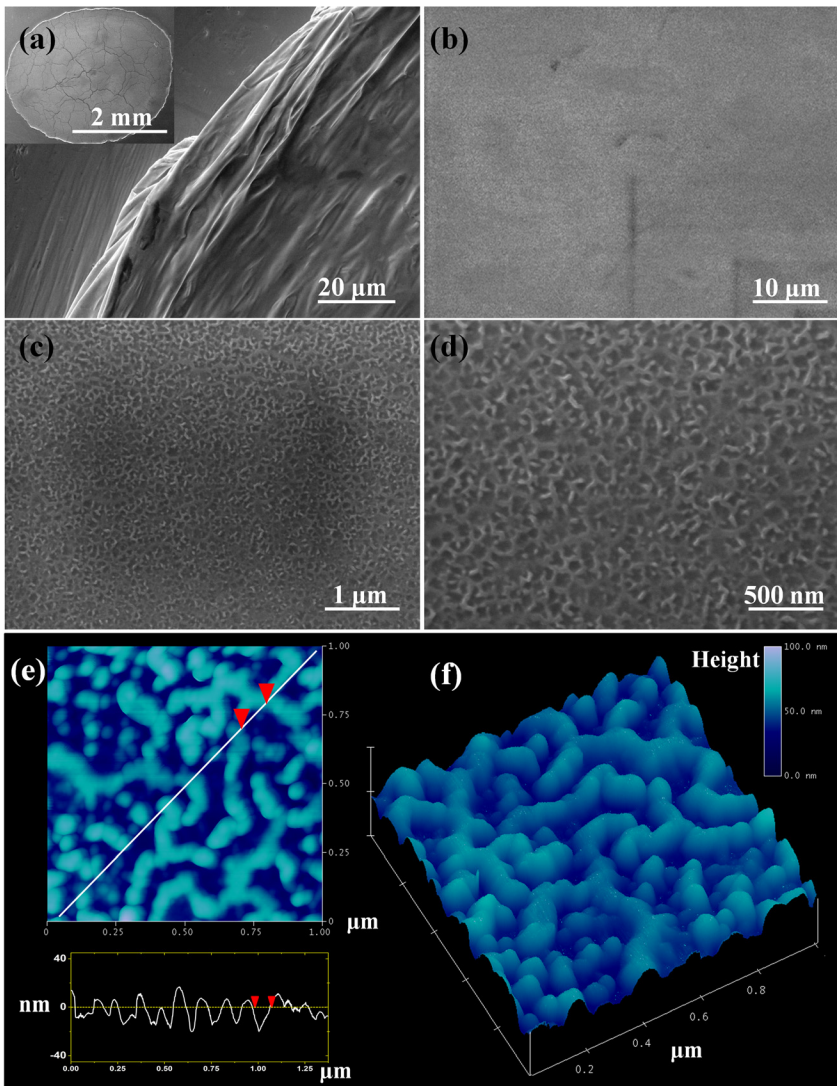

FIG. 2. The irradiated morphology of the Vitreloy 1 glass target. (a) Surface ripples on the edge of the irradiated area. Inset: full view of the irradiated area. (b)–(d) Typical ablation patterns at different magnifications. (e) and (f) AFM images showing the 2- and 3-D landscapes of the ablation pattern, respectively. Lower portion of (e): the surface profile along the marked section in (e).

homogeneous nanovoids, while the residual liquid constructs the walls of these nanovoids after resolidification (see Fig. 2(d)). Recently, a similar spinodal phenomenon has been observed in a platinum target after 15 min underwater ablation of a ns-pulse laser.[29] A possible reason for this observation is related to a strengthened superheating of platinum by the confinement of water.[31] Compared with the ablation in air, the water could result in a high confining pressure that delays the normal boiling of the target.

It is well known that whether an explosive boiling can occur or not is determined by the temperature to which the target is heated rapidly. Therefore, based on a thermal model proposed by Bulgakov and Bulgakova,[5,7] we calculated the time-dependent temperature distribution along the target depth $T(x,t)$ that is governed by the 1-D heat diffusion equation

$$\rho C_p\left[\frac{\partial T(x,t)}{\partial t}-\frac{\partial x}{\partial t}\bigg|_{x=0}\frac{\partial T}{\partial x}\right]=K\frac{\partial^2 T(x,t)}{\partial x^2}+\alpha[1-R(T_s)]I(t)\exp(-\alpha x), \tag{1}$$

where ρ, C_p, K, and α are, respectively, the density, heat capacity, thermal conductivity, and absorption coefficient of the target material; $R(T_s)$ is the reflectivity of laser pulse by the target surface that depends on the surface temperature $T_s = T(0,t)$. Considering the existence of a laser-induced plasma, the real laser intensity $I(t)$, due to the plasma absorption, can be described as[5,7]

$$I(t) = I_0 \exp\left[-\Lambda(t)\right], \tag{2}$$

where I_0 is the initial laser intensity, and $\Lambda(t)$ is the optical thickness of the plasma plume. It is postulated that during a pulse the optical thickness is proportional to the current depth of ablation $\Delta x(t)$ and the laser fluence E_a absorbed by the plasma, that is,[7] $\Lambda(t) = a\Delta x(t) + bE_a$ with two time-independent adjustable coefficients of a and b. The velocity of surface recession is determined by the Hertz-Knudsen equation[4,5,9]

$$\frac{\partial x}{\partial t}\bigg|_{x=0}=\frac{\delta}{\rho}\left(\frac{M}{2\pi RT_s}\right)^{1/2}p_s(T_s), \tag{3}$$

where δ is the vaporization coefficient, M is the molar mass, R is the gas constant, and $p_s(T_s)$ is the surface vapor pressure. Due to superheating, the surface vapor pressure is well below the saturation vapor pressure p_{sat} corresponding to the surface temperature.[8] We thus adopt a modified Clausius-Clapeyron equation to calculate

$$p_s(T_s) = \xi(T_s) p_b \exp\left[\frac{L}{R}\left(\frac{1}{T_b} - \frac{1}{T_s}\right)\right], \quad (4)$$

where a reduction coefficient $\xi(T_s)$ is introduced, L is the latent heat of evaporation, and T_b is the boiling temperature at standard atmospheric pressure p_b. The boundary conditions are: $T(x,0) = T(\infty,t) = 300\,\text{K}$ and $T(0,t) = T_s$. The relevant properties/parameters in calculations/analyses are given detailedly.[32] Two important thermodynamic temperatures: the boiling temperature T_b and TCP T_c are estimated to be about 3792 and 7196 K, respectively. The length and time of the computational domain are 5 μm and 50 ns, respectively. The spatial and time steps are, respectively, 1 nm and 1 ps.

Figure 3(a) shows the calculated temperature profiles within the target at different times. It is clearly seen that the maximum temperature is always located on the target surface, and all temperatures decrease from the surface towards the inside. This indicates that subsurface superheating is impossible in the present case. Our result is consistent with the observation that subsurface heating in metal targets is negligibly small compared with nonmetallic targets.[4,7]

The time dependences of the surface temperature and surface vapor pressure are presented in Fig. 3(b). The surface temperature increases gradually with increasing time, even beyond the boiling point T_b at 12.8 ns, and reaches its maximum T_l at 34.7 ns. Within the pulse width (10 ns), the surface temperature is less than the boiling point, implying that the target surface experiences normal heating, inducing melting without any excessive evaporation. Subsequently, the liquid will be heated beyond its boiling point with a sufficiently high heating rate of about 10^{11} K/s. Therefore, the target surface presents a highly metastable (superheated) liquid that will break down until the explosive boiling occurs. The explosive boiling, as the highest level of superheating, usually initiates at the peak temperature T_l of the superheated liquid. During the superheating process, the surface vapor pressure shows a drastic rise from p_b to a maximum p_l of about 84 p_b. The maximum pressure is about 0.51 $p_{\text{sat}}(T_l)$, which is in agreement with the common relation.[33] In addition, the current value of p_l for the Vitreloy 1 is much less than the pressure (about 600 p_b) when explosive boiling occurs in a pure Ni.[8] This implies that the Vitreloy 1 liquid underwent a much higher degree of superheating. Both surface temperature and surface vapor pressure begin to decrease as the explosive boiling develops. It is noted that both heating and cooling rates are higher than the critical values of the crystallization of Vitreloy 1,[34] implying that there is no crystallization in the present case.

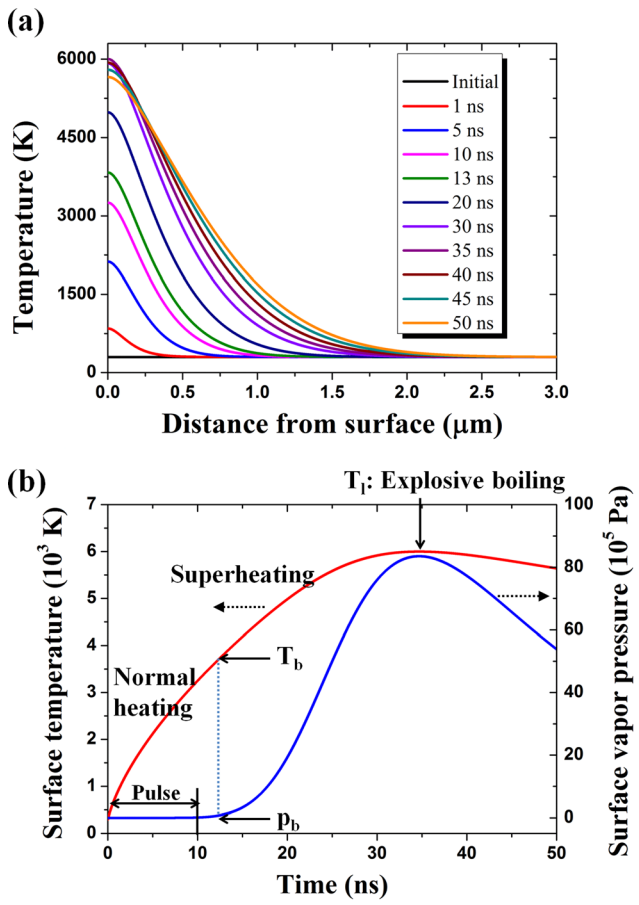

FIG. 3. The calculated time evolution of (a) the temperature profiles within the target and (b) the surface temperature and vapor pressure.

Our theoretical analysis demonstrates that the Vitreloy 1 target experienced normal heating (melting) and superheating, eventually culminating in explosive boiling at $T_l \approx 6000\,\text{K}$. We find that $T_l \approx 0.83T_c$, which lies in the temperature range of 0.80–0.85 T_c.[4,6,7] Due to the sufficiently high heating rate and the strong superheating (Fig. 3(b)), the explosive boiling temperature is close to the spinodal point of the superheated liquid (Fig. 2). Our model predicts that the surface depth where temperature can reach $0.83T_c$ is about 100 nm (see Fig. 3(a)). Thus explosive boiling can only occur in a depth of 100 nm, which is confirmed by the AFM surface profile (Fig. 2(e)). Importantly, the time lag of nucleation is determined to be about 21.9 ns (see Fig. 3(b)), which is on the same order as the pulse width.[8] This time lag actually corresponds to the critical time τ_c, at which a bubble grows to the critical radius r_c. Only if the diameter of the bubbles reaches r_c, will they grow spontaneously rather than collapse. Based on the calculated τ_c, we can further determine r_c[6,35]

$$r_c = \tau_c \sqrt{\frac{3\rho_l T_{sat}(p_l)}{2L\rho_v\left[T_l - T_{sat}(p_l)\right]}}, \quad (5)$$

where ρ_l and ρ_v are the densities of superheated liquid and vapor, and T_{sat} is the surface saturation temperature that can be obtained by the Clausius-Clapeyron equation. Using the given parameters,[32] we estimated r_c to be approximately 1–10 nm. This range is less than the characteristic size of the observed voids (Fig. 2), probably due to further growth and aggregation of bubbles. In addition, we note that either r_c or the final size of the bubbles in the present glassy target is much less than those in the crystalline target,[6] implying that spontaneous nucleation of bubbles is much easier in the glass-forming liquid.[36,37]

In summary, single pulse ablations of a Vitreloy 1 bulk metallic glass were performed in air by a nanosecond laser. Two primary observations are: the ejection of high-temperature matter from the target and the formation of a

liquid-gas spinodal pattern on the irradiated area. We, therefore, suggest that explosive boiling emerges in the initially glassy target near its spinodal point. A thermal model is proposed to describe the underlying mechanism. Calculations show that the explosive boiling occurs at $T_l \approx 0.83T_c$, with a time lag of about 21.9 ns relative to the pulse width. Finally, the critical radius for nucleation of vapor bubbles is estimated. Our results are consistent with the basic picture of explosive boiling and may be useful in understanding the structural response of metallic glasses to high-energy lasers of short duration.

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