Light emission during fracture of a Zr–Ti–Ni–Cu–Be bulk metallic glass

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(Received 11 January 1999; accepted for publication 29 April 1999)

A light emission phenomenon observed during dynamic fracture of a bulk metallic glass, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at. %), has been investigated using Charpy V-notch impact specimens. Unlike more conventional crystalline metals, these Zr-based amorphous alloys emit intense flashes of visible light when ruptured. The mechanisms for this surprising behavior are unknown and the phenomenon remains uncharacterized. Here we report spectroscopic measurements of the light emitted from specimens fractured in both room air and nitrogen gas. Spectra acquired from specimens ruptured in air exhibited a single broad peak, which could be fit to a blackbody temperature of ~3175 K. Emission from specimens fractured in nitrogen, however, was at least four orders of magnitude less intense. The spectrum was shifted to the red with an effective blackbody temperature of ~1400 K. Fracture surfaces of specimens ruptured in both air and nitrogen exhibited local melting, providing further evidence of intense heating during fracture. Based on these observations we argue that the intense light emission in air is associated with pyrolysis of fresh material exposed during rupture. © *1999 American Institute of Physics.* [S0003-6951(99)04825-1]

Amorphous metallic alloys have long represented an intriguing class of materials.[1] For many years, however, the very high cooling rates necessary to prevent crystallization ($>10^5$ K/s) limited specimen geometry to very thin ribbons or wires (~10–100 μm thick), making the measurement of many mechanical properties difficult. The recent discovery of a number of highly glass-forming alloy groups, requiring cooling rates of <10 K/s, has rekindled interest in this class of materials,[2–5] largely because the specimen geometry constraints associated with rapid quenching are far less severe. We investigate here the intense light emitted during rupture of a Zr-based bulk metallic glass. Light emission of this intensity is unprecedented in conventional crystalline metals and remains poorly understood. Although recent work on the bulk amorphous alloys $Zr_{52.5}Al_{10}Ti_5Cu_{17.9}Ni_{14.6}$ and $Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$ report qualitative observations of light accompanying tensile rupture,[6,7] the mechanistic basis of this behavior is still speculative and the emissions have yet to be characterized.

Emission of photons, electrons, ions, and neutral particles following fracture or deformation has been studied for many years in a range of materials. The phenomenon is often referred to as fractoemission; Dickinson, *et al.*[8] is a comprehensive review. Fractoemission is associated with the release of mechanical energy applied to regions at or near a crack tip over very small time scales. Fracture surfaces undergo mechanical, chemical, and electronic relaxation from the high-energy states caused by rupture. These nonequilibrium states are created by phenomena such as defects at or near freshly created surfaces, the release or interaction of excited and reactive species, charge separation across crack walls, and the production of heat and acoustic waves. There are numerous studies of fractoemission in brittle insulating solids such as ceramics, oxide glasses, semiconductors, and polymers.[8–11] Fractoemission in metals is less well studied, and emissions, particularly of light, tend to be weaker. When fractoemission is observed in metals, it is attributed to oxidation of freshly created surfaces,[8] heating during deformation (as in Ti alloys),[9,10] rupture of surface oxides,[8,11] or to recombination associated with dislocation or other defect formation.[10] To our knowledge, fractoemission in amorphous metals has not been studied quantitatively.

Fully amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (at. %)[3] was machined from as-cast plates into Charpy V-notch impact specimens (50×10×8 mm).[12] Samples were fractured dynamically in room air and nitrogen gas using a pendulum impact apparatus, with a pendulum velocity of ~3.5 m/s at impact. Tests in nitrogen were performed in a plastic tent with a positive gas pressure; gas flushed the chamber for at least 1 h prior to measurements. The optical path was oriented along a tangent of the pendulum swing, and the notch was imaged 1:1 with a 200 mm *f/4* lens onto the entrance slit of a 0.25 m spectrometer. Beam alignment was performed using a HeNe laser directed at the notch. Spectra were collected over the visible range (350–925 nm) with a liquid nitrogen cooled charge-coupled device (CCD) camera (Princeton Instruments), and in the near-infrared using a liquid nitrogen cooled HgCdTe detector (Rockwell, Inc.) equipped with a 1100–1300 nm filter. The spectral calibration was established using Hg and Ar atomic emission lines. Visible spectra collected with the CCD were corrected for variations of instrument throughput and detector quantum efficiency by normalizing the collected signal to that obtained from a NIST-traceable standard of spectral irradiance (quartz-halogen tungsten lamp operated at 39 W, Optronics Laboratories Model 245A). Spectral data were fit using

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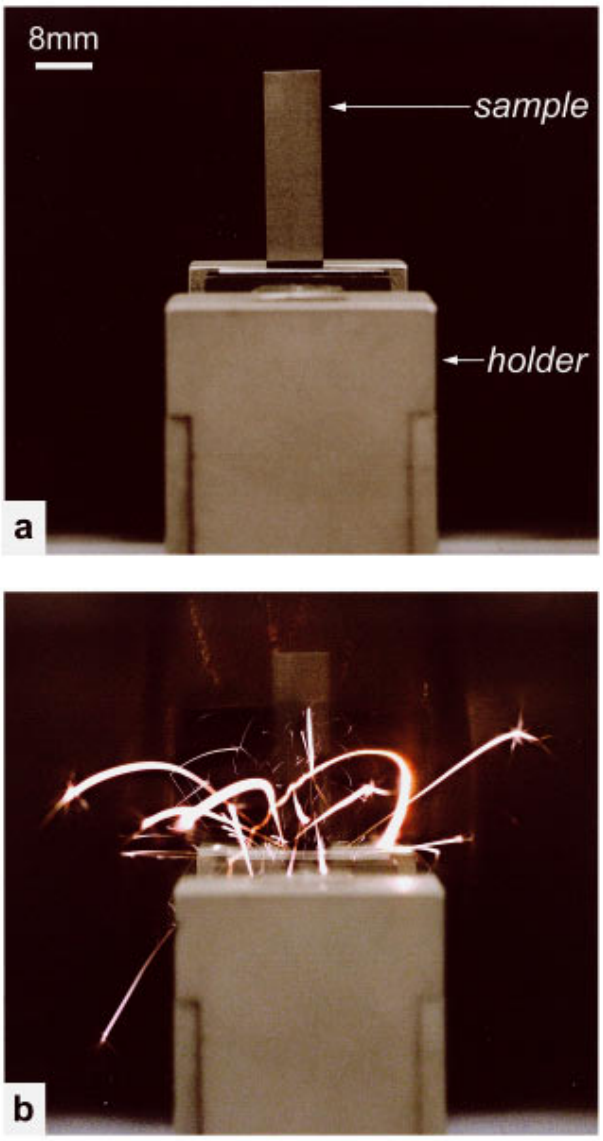

FIG. 1. In (a), a bulk metallic glass impact specimen is loaded vertically into the pendulum apparatus with the lower half clamped into the sample holder. The notch is oriented horizontally and is visible in the center of the photograph. The axis of the pendulum swing is perpendicular to the page, and strikes the sample ~10 mm below its top edge. A 1 s exposure was used to capture the light emission event in (b).

weighted nonlinear least-squares regression to determine an effective blackbody temperature.

Light emission was time resolved by splitting off a portion of the light with a 50/50 beam splitter and focusing it onto a fast photodiode with a spectral range of 200–1100 nm. The transient signal was captured with a 100 kHz data collection card triggered immediately prior to impact. On some samples, the light was also captured with a digital camera using an exposure time of 1 s, again timed to coincide with the release of the pendulum. Fracture surfaces produced in both air and nitrogen were subsequently examined in the scanning electron microscope (SEM).

Optical photographs of the light emission event in room air revealed discrete streaks of visible light emanating from the fracture plane. The light was easily visible to the eye, even in ambient light. A sample is shown loaded vertically into the pendulum apparatus prior to fracture in Fig. 1(a),

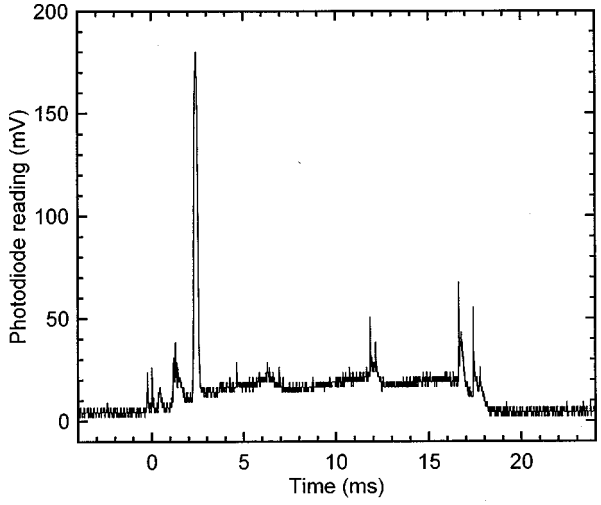

FIG. 2. A photodiode was used to collect the total optical signal from 200 to 1100 nm as a function of time during fracture in air. The sharp spikes are attributed to hot particles crossing the detector's field of view [Fig. 1(b)].

with the lower half rigidly clamped into position. The notch is oriented horizontally and is visible in the center of the photograph. The axis of the pendulum swing is perpendicular to the page, and the pendulum strikes the sample ~10 mm below its top edge. Figure 1(b) shows a continuous exposure of the fracture event. The presence of bright streaks suggests that light emission is associated with the ejection of hot particles from the fracture surface. In fact, inspection of the streaks indicates that some particles bounced off the testing apparatus. In Fig. 2, visible light was emitted over a time interval of 18 ms, during which several discrete peaks of high intensity, each lasting ~1 ms, were observed. Based on the streaks found in Fig. 1(b), these are likely associated with hot particles crossing the detector's field of view.

In room air the emitted spectrum (Fig. 3) exhibited a broad peak with no sharp features, fit to a blackbody tem-

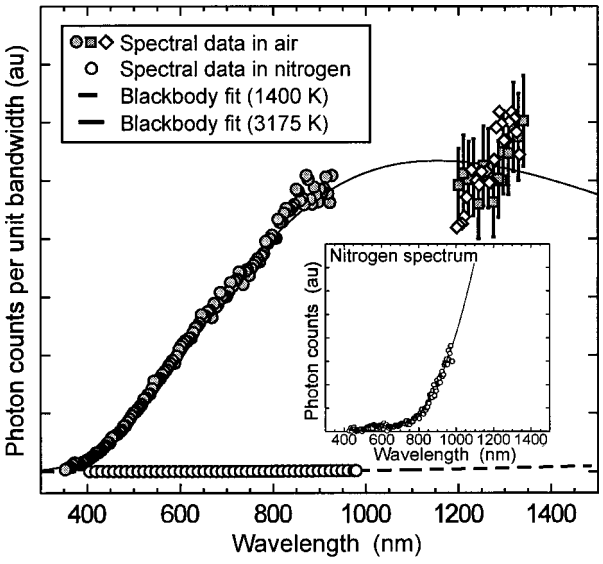

FIG. 3. Fractoemission spectra of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ from 350 to 1300 nm. Data shown for fracture in air were obtained from tests on three samples. In nitrogen, the signal was reduced by at least four orders of magnitude; the inset shows the data from fracture in nitrogen on an expanded scale. Fits to the spectral data are obtained for blackbody temperatures of 3175 and 1400 K for fracture in air and nitrogen, respectively.

FIG. 4. Scanning electron micrograph of a fracture surface after rupture in nitrogen. Droplets suggestive of local melting are visible. The crack traveled from top to bottom, and the top edge of the micrograph is ~10 μm from the root of the notch. Similar features were found on surfaces ruptured in air.

perature of 3175 K (measured using a total of three specimens, represented by different symbols in Fig. 3). In nitrogen, however, the signal intensity captured by the CCD detector was reduced by over four orders of magnitude, and a flash was no longer visible to the eye. In this case, a regression fit to the leading edge of the visible spectrum (Fig. 3) yielded a much lower blackbody temperature of 1400 K (observed on two specimens). Evidence for local melting (in the form of droplets) was observed on fracture surfaces developed in both air and nitrogen when examined in the SEM (Fig. 4). These melted features existed only near the root of the notch (within the first ~250 μm) were fracture initiated. Such apparently melted and resolidified regions have been observed previously in this and many other amorphous alloys following rupture.[7,13–17] Given that the melting temperature is ~936 K,[3] the presence of such features places a lower bound on temperatures achieved during fracture, consistent with our blackbody measurements.

Based on these experimental observations, we conclude that in air the light emission and extreme blackbody temperature of 3175 K are associated with oxidation of freshly exposed material following fracture. Indeed, Zr and Ti both possess a strong affinity for oxygen, and their oxides have particularly large heats of formation.[18] The suppression of light emission in nitrogen, along with the large drop in temperature, most likely resulted from the decrease in oxygen partial pressure.

Of particular interest is the distinction between temperature rise due to oxidation and due to deformation. Plastic deformation in these alloys is highly localized into narrow slip bands,[14] and such localization can generate intense heating associated with concentrated plastic work.[9,17] Strain and thermal localization are favored by many of the properties of this alloy, including a high flow stress (~2 GPa) which drops rapidly with temperature near the glass transition, nonexistent work hardening, and relatively low thermal conductivity (~3.5 W/mK).[14,17] Tests in oxygen-free environments should allow for the direct measurement of deformation-induced temperatures, and the temperature measured in nitrogen is presumably approaching this value. Indeed, recent estimates based on the conversion of stored elastic energy into heat suggest that a temperature rise of 900 K or more within a slip band is not unreasonable.[7] We speculate, in fact, that the severe pyrolysis observed in air may be facilitated by initial deformation-induced heating.

Work supported by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. Thanks are also due to Amorphous Technologies International, Corporation and to Howmet Corporation.

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