

## Final report

### Microstructures and properties of materials under repeated laser irradiation DOE DE-FG52-02NA00070

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#### Grant participants:

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#### Executive Summary

This research program has explored the stability of alloys under pulsed laser irradiation. Two primary directions were investigated: (i) phase transitions during a single laser pulse, and (ii) phase stability under repeated laser irradiation. The first theme was primarily concerned with both the crystalline to amorphous phase transition and the transition of liquids and glasses to crystalline matter. The second project examined the phase evolution during laser pulsing in situations where plastic deformation was prevalent (high-energy laser pulses). Both computer simulation and experimental programs were undertaken.

Our work using computer simulations had several notable successes. For the work connected with multiple pulsing, we used molecular dynamics (MD) to simulate the behavior of alloys under severe plastic deformation. We found that during high strain-rate deformation atomic mixing of chemical species is random, independent of the detailed thermochemical properties of the system. This result contrasts with recent reports. In this work, we also developed two new methods of analyzing atomic mixing, one is based on *relative* mean square displacements (RMSD) of atoms and the other, Burgers vector analysis (BVA), on nearest neighbor displacements. The RMSD analysis is valuable in that it specifies the length scales over which deformation processes take place, and we applied it to understand deformation in nanocrystalline, amorphous and large-grained systems. The BVA analysis, on the other hand, reveals if the damage is homogeneous.

Finally we showed that at elevated temperatures, the phase stability is not determined from a simple competition between shearing events and vacancy diffusion, which has long been assumed, but rather atomic mixing in the shearing events is temperature dependent. This work is significant in that it elucidates the fundamental mechanisms that underlie high strain rate deformation, and it provides computational tools for other researchers to perform related work.

Our work on MD simulation also examined shock-induced spall. We showed that as voids develop in the early stage of spall, an amorphous region forms around them and that voids coalesce via mass transfer through this amorphous medium. Finally the MD work began examining solidification at deep undercoolings; we found the surprising result that solidification was limited by *defects in the liquid* and that these defects have virtually identical properties as *interstitialcy atoms in the crystalline state*. This work is being continued in the renewal project since it offers new insight into the melting and solidification processes under extreme conditions.

The experimental work began looking at plastic deformation and liquid-state diffusion using nanosecond laser pulses, but taking advantage of an NSF equipment award, we switched to study solidification at deep undercooling using a femtosecond laser system. We have developed in this program the first application of non-linear reflectivity using third harmonic generation (THG) of light to monitor the solid-liquid/liquid-solid (or any phase transition with 10 fs time resolution). THG decreases by  $\approx$  three orders of magnitude on melting whereas the change in linear reflectivity in metals is only  $\approx$  5%. We have also showed that THG can be used as an ultrafast (sub picosecond) thermometer for systems such as Si.

#### Comparison of Initial Goals with Outcomes

This research program set out to explore the stability of alloys under laser-induced shock-wave loading. Two directions were planned for investigation: (i) phase stability during a single energetic shock wave, and (ii) phase stability under repeated laser irradiation. The first area was primarily concerned with a crystalline-to-amorphous phase transition as a precursor to spall in shocked materials. The second project planned to examine the phase evolution during repeated laser pulsing in situations where the laser either induces local

melting of the alloy (low-energy laser pulses) or plastic deformation (high-energy laser pulses). Many of the original goals were carried out in the simulation portion of this work; however, with the granting of the NSF equipment award to purchase a femtosecond laser system, we modified the experimental program. In particular, we performed molecular dynamics (MD) computer simulations to examine shock-induced spall, solidification, and phase stability under prolonged high strain-rate deformation. Our experimental program attempted to examine high-strain deformation under repeated laser shock, but the laser intensity was not sufficiently strong to much influence phase stability. We also were not able to secure time on the Omega Laser Facility for single shot experiments to validate our simulations of a crystal-to-amorphous transition in CuTi under high strain rate deformation. Using the femtosecond laser system, we investigated solidification behavior in metals under extremely deep undercoolings, which we performed in collaboration with the effort of Hector Lorenzana at LLNL. We also performed MD simulations to complement this modified experimental program; these included crystallization behavior of pure metals from the glass, and the velocity of solid-liquid interfaces at ultradeep undercoolings.

#### Major activities:

##### I. Shock-induced amorphization:

The MD simulations had several successes during grant period. Our first efforts on understanding spall under shock loading revealed that when the shock energy was just below the threshold for spall, a crystalline-to-amorphous phase transition was triggered; however, this transition was always preceded by void nucleation. This behavior is shown in Fig. 1. Since the energy was subthreshold in this example, the voids close following passage of the rarefaction waves, leaving behind the amorphized regions. This behavior was independent of system size and did not change when temperature was raised from 100 K to 300 K, clarifying that the process is not ordinary melting. The simulations also showed that above the threshold for spall, the voids coalesce by deformation through the amorphous phase. We had hoped to perform an experimental test of these simulations at the Omega laser facility; the idea being that we could find amorphous regions in the

specimen in recovery experiments. Unfortunately we were not granted time for this project.

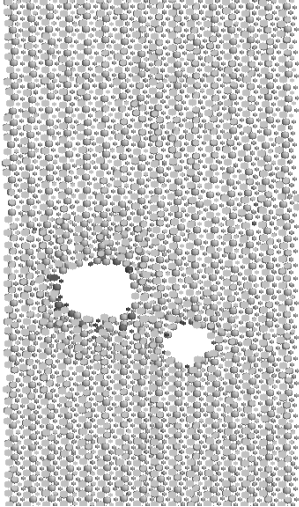


Fig. 1a. Void initiation. Tension at the void area is about 120 Kbar. Ti atoms are larger than Cu atoms. Darker atoms have relatively higher energy. Voids were visible 1-2 psec after the two release waves collided.

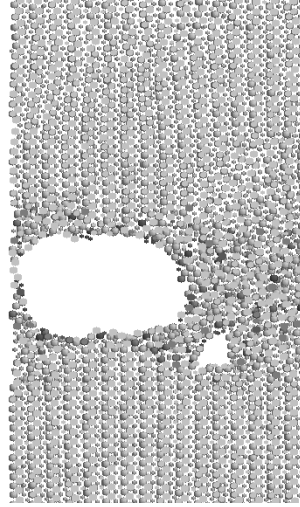


Fig. 1b. Void growth. 3 psec later.

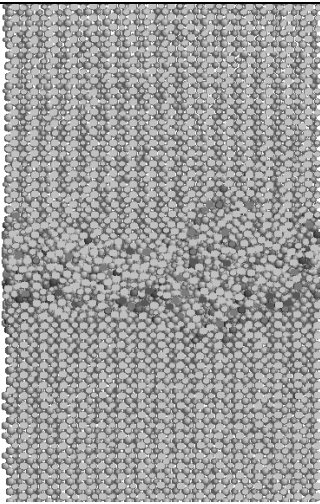


Fig. 1c Amorphized region in CuTi following the collapse of the void structure

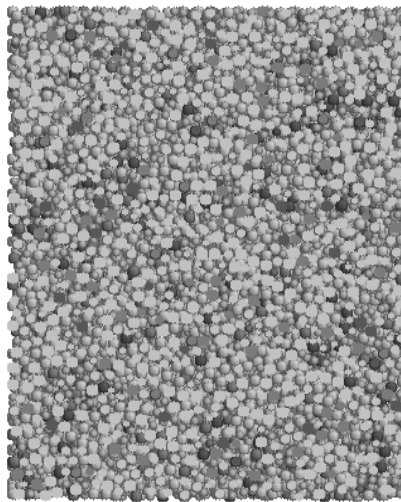


Fig. 1d Cross sectional view of the amorphous region shown in Fig. 1c.

## II. Chemical disordering under high strain-rate plastic deformation:

In this effort we employed MD to simulate the response of model crystalline binary alloy systems to sustained plastic deformation at low temperature. We showed that a large positive heat of mixing and a large lattice mismatch are not sufficient to prevent

complete mixing. This is contrary to previous reports, but in that work, 2-dimensional systems were employed, which is the probable reason that the wrong conclusion was obtained. Analysis of the mixing in our simulations demonstrated that deformation proceeds by dislocation glide. This is illustrated by Fig. 2(a) where the displacement of atoms is shown relative to nearest neighbors. The displacement distance of the first peak corresponds to the motion of partial dislocations, since the displacement distance is less than a nearest neighbor distance. We showed, also, that the atomic mixing possess during shear has the unusual property that the efficiency of moving atoms, relative to each other, increases with increasing separation distance between atom pairs. This is shown in Fig. 2(b). This discovery provides a powerful new way to analyze deformation in plastically deformed materials. We have used to method to clearly explain the mechanism leading to dynamical stabilization of compositional patterns during deformation at elevated temperatures.

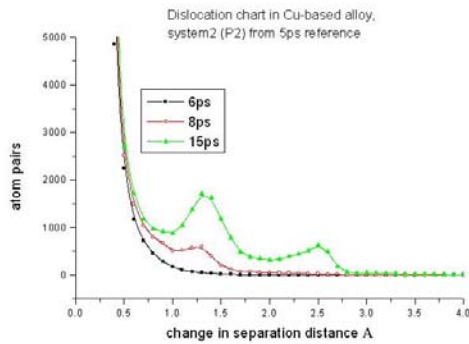


Fig. 2a Displacement distance of atoms relative to nearest neighbors illustrating that motion occurs by glide

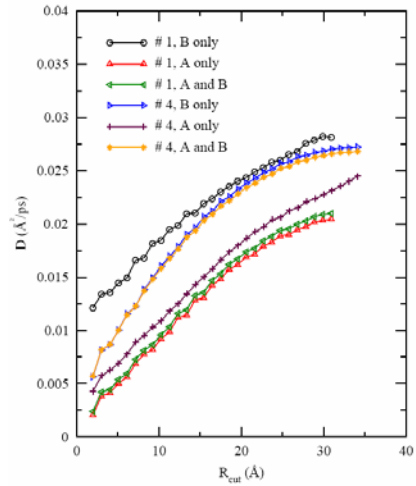


Fig. 2b Relative mean square displacement of atoms during shear.

### III. Solidification kinetics of pure metals from deeply undercooled liquids and glasses:

Toward the end of this grant, we began to examine solidification using MD simulation and made this work a centerpiece for our renewed grant. During the grant period we measured the activation energy of crystallization for pure metals that had been quenched into the glass. The method was to first quench the glass at high cooling rates and then monitor the potential energy of the system on subsequent warming. The results

are illustrated in Figs. 3(a) and 3(b) for Fe using different warming rates. The precipitous drop in potential energy at a temperature  $\approx T_0$  indicates the liquid to crystal transition. By plotting the natural logarithm of the heating rate as a function of inverse temperature,  $T_0$ , in a so-called Kissinger plot, the activation energy can be determined; this is shown in Fig. 3b for various metals. The results of this analysis are compiled in Table 1. The surprising result seen in the table is that the activation energy for crystallization is precisely the same as that for diffusion in the supercooled liquid, but most surprising is that it is the same as the activation energy of interstitial atoms in the *crystalline state*, as illustrated in Table 1. This work is being continued to better understand this astonishing correlation.

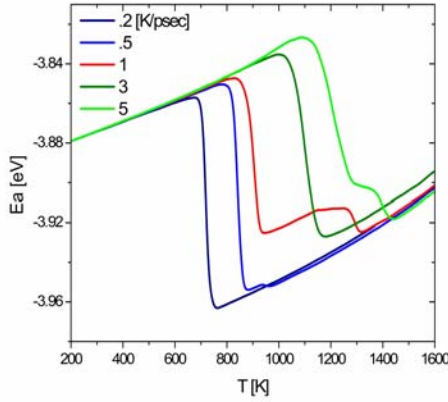


Fig. 3(a) Potential energy of Fe during warming at different rates.

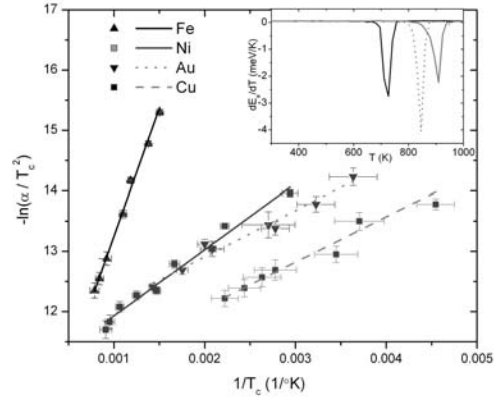


Fig. 3(b) Kissinger plot for the crystallization energies of several pure metals. Inset is the derivative curves shown in Fig. 3(a)

Material	$E_{migration}^i$	$E_{app}$	$E_{diffusion}$
Au	0.06	0.065	0.06
Cu	0.08	0.078	0.07
Ni	0.11	0.107	0.09
Fe	0.32	0.332	0.31

Table 1. Interstitial migration energies in the solid state, apparent activation energies for crystallization, and activation energies for diffusion in the liquid state for selected pure metals.

#### IV. Measurements of melting and solidification of Si and Cu

With the successful application for a NSF equipment award, we purchased a 120 femtosecond laser with 2.5 mJ per pulse and 1 kHz repetition rate. We have now installed this equipment and have started to measure solidification velocities in Si and pure metals. This work is beginning to show important results. First, we have showed that non-linear reflectivity arising from third harmonic generation (THG) of light can be used for time-resolved measurements of phase transitions, with sub-picosecond resolution. This is an important discovery since the usual method for using time resolved measurements employ linear reflectivity and these measurements do not provide sufficient sensitivity. For example, the reflectivity of metals changes  $\approx 5\%$  on melting, but the change in the THG on melting (or solidification) is over three orders of magnitude. The work is also significant because THG can also be used as an ultrafast thermometer in pump-probe experiments. Fig. 4(a) illustrates, for example, the temperature dependence of linearly and circularly polarized THG as a function of temperature. In this case the sample has been heated statically. Fig. 4(b), in contrast, shows THG for circularly polarized light as a function of time in a pump-probe experiment. Here a 135 mJ pump pulse of 800 nm light is applied to Si<100>. At early times, melting is observed by the drop in reflected light by three orders of magnitude. Resolidification occurs after a few nsec. The velocity of the solid-liquid interface was deduced to be  $\approx 5 \text{ m-s}^{-1}$ . Noteworthy is that the temperature deduced from the THG at solidification is precisely the melting temperature of Si, indicating that THG does indeed serve as an ultrafast thermometer.

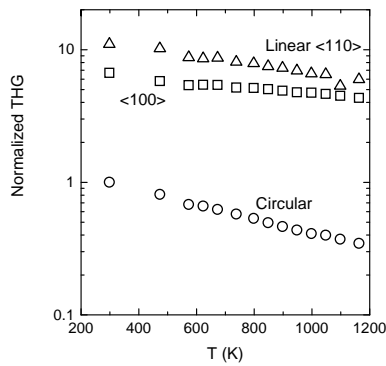


Fig. 4(a) Intensity of reflected third harmonic light from Si as a function of temperature

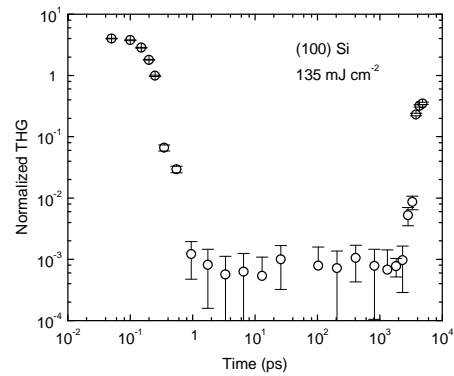


Fig. 4(b) Normalized third harmonic signal as a function of time delay from (100) Si substrate with an incident fluence of  $135 \text{ mJ cm}^{-2}$ . At 0.9 ps the signal has dropped by just over three orders of magnitude, which is the noise floor for the measurement, from the crystalline value; by 2.8 ns the sample has begun to solidify.

#### V. Personnel

- Graduate Students receiving support: Bryan Gundrum and Samson Odunuga
- Non-supported collaborators: Yinon Ashkenazy, Hebrew University of Jerusalem, Israel
- National Laboratory Collaborators: H. Lorenzana, G. Campbell, LLNL; Ricardo Schwarz, LANL

#### Publications:

Shock-induced amorphization as the onset of spall

Yinon Ashkenazy and R.S. Averback

Appl. Phys. Lett. **86**, 051907 (2005)

Forced chemical mixing in alloys driven by plastic deformation

S. Odunuga, Y. Li, P. Bellon and R.S. Averback

Phys. Rev. Lett **95**, 045901 (2005).



Atomic mechanisms controlling crystallization behavior  
Yinon Ashkenazy and R.S. Averback  
(submitted to Nature Materials)

#### Publications in Preparation

Ultrafast thermometry using third harmonic generation of light  
B. Gundrum, D.G. Cahill and R.S. Averback

Phase evolution of alloys under high strain-rate deformation at elevated temperatures  
S. Odunuga, P. Bellon, and R.S. Averback

#### Presentations

Microstructural Evolution in Nanoscale Alloys Under Plastic Deformation.  
Samson Odunuga, Pavel Krasnochtchekov, Pascal Bellon and Robert Averback  
MRS Nov. 2006, Boston (*Invited*)

Thermal Conduction of Metal-Metal interfaces  
B. Gundrum, D.G. Cahill, and R.S. Averback  
APS March meeting, Baltimore, 2006.

Liquid processing of thin metal films under repeated laser pulses,  
B. Gundrum, R.S. Averback, P. Bellon  
MRS Dec. 2004, Boston