Annual scientific report

Microstructures and properties of materials under repeated laser irradiation

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Grant participants:

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Scientific Goals:

This research program explores the stability of alloys under pulsed laser irradiation. Two directions are under investigation: (i) phase stability during a single energetic shock wave, and (ii) phase stability under repeated laser irradiation. The first area is primarily concerned with a crystalline to amorphous phase transition as a precursor to spall in shocked materials. The second project examines the phase evolution during 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).

Accomplishments:

In this second year of the grant, we have made good progress toward our goals of elucidating the basic materials response to repeated laser pulsing. This work includes both computer simulation and experimentation, as we now describe. In addition, a major new development in the program occurred with the awarding of a NSF equipment grant to the PI's (and three others) for the purchase of an amplified (2.5 mJ/pulse) femtosecond laser system and construction of an *in situ* time-resolved electron diffraction system

a) *Molecular dynamics simulation of shear-induced mixing*

Nearly 10 years ago, the two PI's published a paper illustrating that repeated shearing of an immiscible alloy can lead to compositional patterning. This work, which employed kinetic Monte Carlo computer simulations, assumed that shear was a "high energy" event that was not influenced by chemical potentials, i.e., it was purely ballistic in nature. A problem in this work was the fact that large degrees of phase separation were

observed during low-temperature ball milling experiments in systems such as NiAg, which have large positive heats of mixing. Recently, Schuh and co-workers have performed molecular statics calculations of the shear process in amorphous alloys, in two dimensions, and concluded that the atomic mixing during shear was not entirely ballistic, but strongly influenced by thermodynamics. We have now performed in this project, fully 3-d molecular dynamic simulations of the shear process in crystalline alloys and find that mixing during repeated shear at 100 K is in fact only weakly dependent on chemical potentials and further that the lack of mixing of immiscible systems in experiments can be traced to the deflection of dislocations away from hard precipitates.

Our simulations were performed by creating model alloy systems. We first examined the effect of the heat of mixing by creating alloys in which the two components both had the elastic properties and atomic volume of pure copper but one with a large positive heat of mixing (similar to NiAg) and the other with zero heat of mixing. Then while repeatedly deforming the solid in the x, y, and z directions, successively, the solubility was measured. The solubility is characterized by an order parameter, Ω, as illustrated in Fig.1; a value of $\Omega = 1$ indicates complete ordering, $\Omega = 0$ implies a random solution; and $\Omega = -1$ means complete phase separation. Plotted below are the results for various compositions and starting configurations. Clearly evident is that all alloys, regardless of initial conditions and compositions, arrive at nearly the same final steady state, which is a random alloy. This shows that for reasonable heats of mixing, the mixing process during energetic shear is essentially ballistic. It should be noted, however, that the alloys with high heat of mixing do show a small negative order parameter, showing some indication of phase separation.

We also examined the situations when the alloys had different elastic properties by creating a precipitate with the elastic properties of Ag in a matrix of Cu and vice versa. As seen in Fig. 1, curve 4, the interdiffusion of Cu and Ag is dramatically suppressed when the elastically harder component, Cu, is the precipitate. This results from the difficulty of dislocations in the softer Ag matrix from cutting into the Cu precipitate, and thus preventing interdiffusion. We believe that this result explains why alloys like AgNi can not be mixed by mechanically alloying, and it may have important consequences for our attempts to mix Cu and Ag by laser peening, as we discuss below.

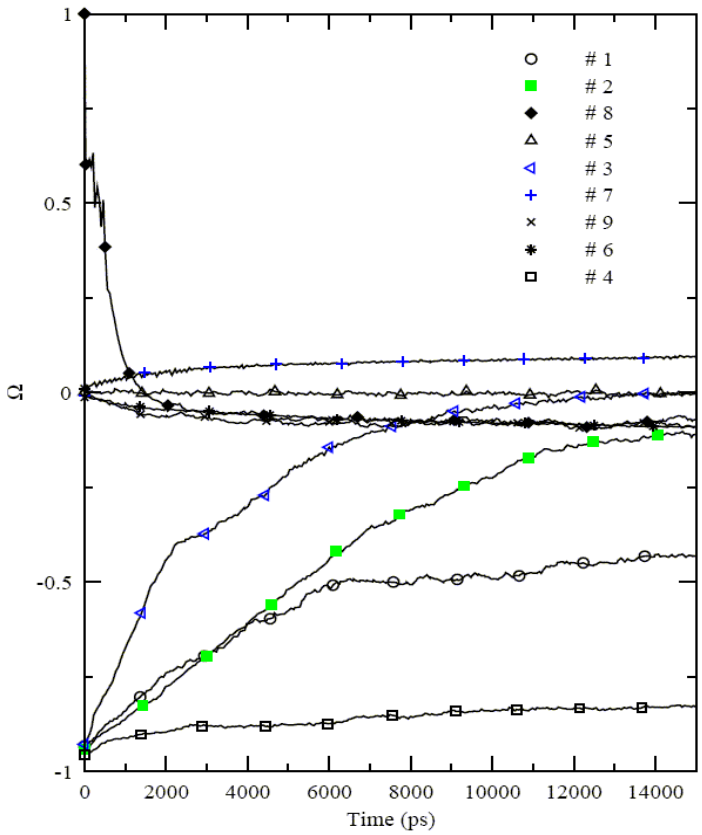

Fig. 1 Chemical short range order parameter versus time of shearing. The different symbols represent different alloys as described in Table 1.

Alloy system	Atomic concentration	Initial structure	Heat of mixing	A and B Lattice mismatch	potential
1	A-6.4%at B	B ball in A matrix	5.7 kJ/mol	12%	P1
2	A-6.4%at B	B ball in A matrix	6.4 kJ/mol	0%	P2
3	A-6.4%at B	B ball in A matrix	0.1 kJ/mol	12%	P0
4	B-6.3%at A	A ball in B matrix	6.9 kJ/mol	12%	P1
5	A-6.4%at B	Random	5.7 kJ/mol	12%	P1
6	A-50% at B	Random	23.3 kJ/mol	12%	P1
7	A-50% at B	Random	6.8 kJ/mol	12%	P0
8	A-25% at B	$L1_2$	15.8 kJ/mol	12%	P1
9	A-25% at B	Random	15.8 kJ/mol	12%	P1

Table 1. Alloy systems investigated. Systems 1-4 refer to spherical precipitates of component “i” in matrix “j”.

(b) Self-organization of alloys during (repeated) laser melting-the Kirkendall effect in liquids

One of the goals of this project is to examine self-organization during repeated melting. As we progress in this direction we first examined the effect of just a few laser

pulses. The configuration of the specimen is illustrated in Fig. 2(a), where it is seen that three alternating layers of Cu and Ag are grown on a thin film Pt layer, which in turn is grown on Cu. During the first laser pulse, the Cu and Ag layers nearly intermix completely, as expected since they form miscible liquids, Fig. 2(b). The Cu and Pt also began to mix, indicating that the Pt had also melted. After four pulses, it is observed in Fig. 2(c) that the Ag has become enriched near the Pt interface, with the Cu that had alloyed with the Ag during the first pulse, diffusing into the Pt. We believe that this peculiar phenomenon is precisely the Darken effect but observed here in liquids for the first time. Recall the original Darken experiment utilized a diffusion couple with carbon and Fe in both sections of the couple, but with a small fraction of Si added to one side. The Si raised the chemical potential of the carbon, driving it up the carbon concentration gradient into the other side. The Si is relatively immobile and therefore can diffuse into the other side only slowly. Although our geometry is somewhat more complicated, the Pt lowers the chemical potential of the Cu in the PtCu alloy, enabling the Cu to flow up its concentration gradient. Eventually the system would equilibrate, but this is not possible during the short times of a laser pulse. The experiment illustrates that kinetic pathway of a reaction can be very unusual. Accordingly, it can provide opportunities for creating new materials, but it can also result in problems in materials subjected to rapid heating.

(c) Alloys subjected to laser pulsing

We have shown that ball milling can induce compositional patterning by dislocation motion in micron size powders. Since laser peening can produce plastic deformation in metals to depths of some millimeters, it was hypothesized that compositionally patterned could be realized in bulk alloys by this method. In a collaborative effort with G. Campbell, (LLNL), R.B. Schwarz (LANL) and L. Hackel (LLNL), we laser-peened ultrafine AgCu eutectic alloys at room temperature. The laminar structure of the eutectic structure had a particularly small wavelength, ≈ 100 nm, which we desired in order to reduce the amount of mixing required to homogenize the alloy by shearing. The results for hardness are shown in Fig. 3 as a function of depth. The increase in hardness is typical of Cu-Ag alloys cold-rolled to ≈ 70% reduction, or nanocrystalline Cu samples with a grain size of just 20 nm. On the other hand, ball milled

CuAg, completely mixed to a solid solution, has approximately twice the hardness. Future work will apply the laser pulses to different directions of the sample to enhance plastic deformation and mixing.

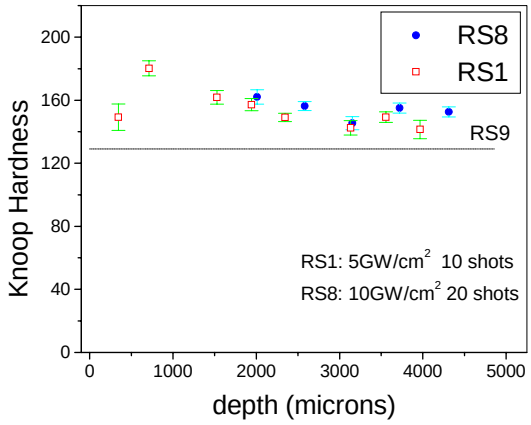

Fig. Knoop hardness as a function of depth from laser-peened surface.

(d) Femtosecond laser-solid interactions

The PI's along with two others received an NSF equipment award for the purchase of a 2.5 mJ/pulse femtosecond laser and construction of a time resolved electron diffraction system. This effort is becoming the primary focus of the research group. We have currently received the laser and are in the final stages of construction of the optical system and target chamber. First measurements using pump-probe reflectivity and post-irradiation examinations are scheduled for early March. The electron diffraction system is currently being designed. The costs for this effort are being shared by the Materials Research Laboratory at UIUC.

Interactions with National Laboratories

- Prof. Averback had discussions with Dr. Schwarz by telephone concerning the laser peening experiments. Dr. Schwarz subsequently prepared eutectic CuAg alloys for this project.
- Dr. Hackel (LLNL) laser-peened our Cu-Ag samples.
- Profs. Averback and Bellon met in San Franscisco with Dr. V. Bulatov on April 14 for discussions.
- Prof. Averback visited LLNL April15-16 to meet with Drs. T. Diaz de la Rubia, W. King and G. Campbell to discuss opportunities in building a dynamic transmission

electron microscope (DTEM) and time resolved fast electron diffraction systems (TRFED).

- Prof. Averback visited LLNL Sept. 2-3 to discuss work in this current project with T. Diaz de la Rubia, and G. Campbell. During that time he had continued discussions with W. King and G. Campbell concerning DTEM and TRFED.

Publications:

Shock-induced amorphization as the onset of spall
Yinon Ashkenazy and R.S. Averback
Appl. Phys. Lett. **86,** 051907 (2005)

Molecular dynamics simulation of shear-induced mixing
S. Odunuga, Y. Li, P. Bellon and R.S. Averback
Phys. Rev. Lett (submitted)