Laboratory Name: LLNL
B&R Code: KC0201010

FWP and possible subtask under FWP:
Advanced Positron Materials Characterization (A. Kumar)
FWP Number: SCW0289

Program Scope:
This is a new program to develop and use the experimental non-destructive materials evaluation capabilities of positrons to determine the details of the size, concentration and elemental composition of nanostructural features and their response to changes in composition, to stress or to other modifications. By analyzing the annihilation radiation of positrons attracted to negative sites we can determine their size and concentration by positron lifetimes and the elemental composition of the surrounding atoms by electron momenta determined from the Doppler broadening of the annihilation radiation. These determinations can now be theoretically related to detailed descriptions of atomic structure in metals. The current focus takes advantage of the MeV Pelletron positron beam and related 100MeV positron beam experiments to analyze the structure of bulk metallic glassy alloys.

Major Program Achievements (over duration of support):
The beam was first used to measure annihilation radiation during positron channeling at MeV levels with G. Golovchenko (Harvard). After these initial experiments we concentrated on bulk metallic glasses. Using Doppler broadening positron annihilation spectroscopy significant information about the atomic structure was obtained in the complicated yet useful metallic glass, $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$. Experimental evidence was provided that the atomic arrangement is not random, but the Ti content around open-volume regions is significantly enhanced over the Ni and Cu. It appears that the Ni and Cu atoms closely occupy the volume bounded by the neighboring atoms while Al, Ti, and Zr are less closely packed and more likely to be associated with the open volume regions. Defect analysis was performed on selected materials using new positron spectrometers installed at the MeV beam source. The first experiment with A. Denison and D. Akers at INEEL uniquely identified the carbon decoration of fatigued stainless steel. Theory performed in collaboration by P. Sterne, UC Davis and LLNL, has been used to relate vacancy cluster size and carbon decoration to the experimental results.

Program impact:
Understanding the details of nanostructural features such as precipitates, defects and local order in disordered systems is increasingly important in modern materials development and the advent of materials by design. Metallic glasses have been found to possess many mechanical advantages over traditional metals. In many cases they are found to have superior strength, toughness and tribological properties. The atomic arrangement in the non-stoichiometric matrix is generally not known or understood. In particular questions of randomness and the existence of open volume regions are of interest. The positron is a unique and sensitive probe of materials providing information not amenable to other more standard techniques such as x-ray or neutron spectroscopies.

Interactions:
University of California at Santa Barbara
University of California at Davis
University of Texas at Arlington

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:
Asoka-Kumar (0.3%), R. Howell (0.1%), Mech. Tech. (0.1%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $282K **FY01 BA** $304K **FY02 BA** $249K

Laboratory Name: LLNL
B&R Code: KC0201010

FWP and possible subtask under FWP:
Adhesion and Bonding at Internal Interfaces (W. King, G. Campbell)

FWP Number: SCW0289

Program Scope:
The objectives of this work are to ascertain what factors determine interfacial structure and mechanical properties and how impurities, flaws, and inclusions modify those properties. Theory and modeling validated by experiment will enable a predictive capability for materials properties that are affected by the presence of interfaces in the microstructure.

Major Program Achievements (over duration of support):
We discovered Cu occupying interstitial sites within the $\Sigma 5(310)/[001]$ symmetric tilt grain boundary in Al doped with 1 at.% Cu. Previous predictions and knowledge about metal-metal segregation did not suggest this possibility. The discovery was enabled by the availability of bicrystals produced using diffusion bonding and through close coupling of theory and experiment. We have also found that the procedure of focal series reconstruction (FSR) is absolutely necessary for the correct interpretation of HREM images from such microscopes. To unambiguously assign the site occupancy to Cu it required the acquisition of an atomic resolution z-contrast image. Atomistic modeling based on the Local Density Approximation was carried out and confirmed that the interstitial site was energetically favorable.

Program impact:
Of particular interest is this work is the discovery that copper atoms squeeze in between aluminum atoms of the aluminum matrix rather than substituting for the host aluminum sites as previously assumed. Knowledge of the location and function of copper atoms in aluminum grain boundaries is of particular technological importance as it has been known since the 1960s that small amounts of copper added to interconnects in computer chips extended the lifetime of the device.

Interactions:
Sandia National Laboratory - Albuquerque

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:
W. King (0.1%), G. Campbell (0.2%), Foils (SNLA) (0.2), Other (0.1)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $331K **FY01 BA $**275K **FY02 BA $**274K

Laboratory Name: LLNL
B&R Code: KC0201050

FWP and possible subtask under FWP:
Metallurgy and Ceramics, subtask on the Kinetics of Phase Transformation in Welds
(J. Elmer, J. Wong)

FWP Number: SCW0289

Program Scope:
Space resolved (SRXRD) and time resolved (TRXRD) X-ray diffraction techniques based on synchrotron experiments are being developed and used for in-situ investigations of phase transformation dynamics in the heat-affected zone (HAZ) and fusion zone (FZ) of welds. Data being acquired here will be used to aid in the development of models to predict microstructural evolution in welds.

Major Program Achievements (over duration of support):
Highlights include (i) the first complete mapping of phases in the HAZ during welding in CP titanium, 1005 C-Mn steel and 2205 duplex stainless steel, (ii) measurement of the interface velocity for the $\beta \rightarrow \alpha$ transformation in titanium welds, (iii) the first direct observation of primary δ-ferrite solidification in a type 304 austenitic stainless steel weld, (iv) the discovery of non-equilibrium primary austenite solidification in a C-Mn steel welding consumable containing aluminum, (v) the discovery of an unexpected low temperature phase transformation in duplex stainless steel welds and (vi) real time dynamics of the ferrite $\leftrightarrow$ austenite transformations in both the HAZ and FZ in 1005 C-Mn steel weldments.

Program impact:
Using a unique synchrotron radiation-based x-ray diffraction technique. we are able to study previously unobserved phase transformations, in-situ. In combination with other experimental and modeling tools, we have expanded the understanding of both general phase transformation theory and the kinetics of phase transformations in technologically important materials.

Interactions:
Stanford Synchrotron Radiation Laboratory: X-ray staff for novel instrumentation development
The Pennsylvania State University: Professor T. DebRoy for numerical modeling
Oak Ridge National Laboratory: Dr. S. A. David, Dr. S. S. Babu for consumable systems

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Chunky Bullet award received from DOE/OBES (2002)
Davis Silver Medal Award (2002) from the American Welding Society, to J. W. Elmer
William Spraragen Award (2001) from the American Welding Society, to Z. Yang, J. W. Elmer, Joe Wong and T. DebRoy
Fellow of the American Welding Society (2000), to J. W. Elmer

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. W. Elmer (33%), Joe Wong (33%), T. A. Palmer (33%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $547K **FY01 BA** $445K **FY02 BA** $495K

Laboratory Name: LLNL

B&R Code: KC0201050

FWP and possible subtask under FWP:
Superplasticity in Metals and Ceramics (T. G. Nieh)

FWP Number: SCW0289

Program Scope:
This work addresses the roles of boundary structure, chemistry and interphases on the sliding and rotational behavior of a boundary, in order to improve the general understanding of deformation in micro-, and nano-structured, and amorphous materials. A systematic theoretical/experimental study of the relationship between sliding and grain boundary dislocation, structure/morphology, composition, and the presence of impurities was carried out.

Major Program Achievements (over duration of support):
We investigated the plastic behavior in the supercooled liquid region of a bulk metallic glass, Zr–10Al–5Ti–17.9Cu–14.6Ni. The alloy has excellent mechanical formability in the supercooled liquid region. The alloy exhibited Newtonian behavior at low strain rates, but became non-Newtonian as the strain rate increases. Microstructural examinations showed that even though tests were carried out in the supercooled liquid region, nanocrystallization still took place. The observed non-Newtonian behavior can be attributed to glass instability during deformation. A composite model to explain the measured strain rate sensitivity values was developed. Non-superplastic behavior is caused by the difficulty of strain accommodation at grain triple junctions.

Program impact:
As the microstructure of materials, both metallic and ceramic, becomes smaller the mechanical properties can no longer be described in the classical manner. This work particularly in the amorphous and metallic glass materials showed non-Newtonian behavior. The standard Hall-Petch behavior of strain depending on $1/d^2$, where d is the diameter of a grain, is violated. The amorphous and glassy materials have many beneficial properties for technological and applied uses. It is important to understand the fundamental mechanisms of plasticity and superplasticity as these materials become more useful in future applications, in order to develop stronger, more ductile, and tougher materials.

Interactions:
MIT – Prof. Shuh
Pennsylvania State University
UC-Irvine

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Associate Editor Journal of Intermetallics
International Advisory Board of Superplasticity
International Advisory Board of Intermetallics

Personnel Commitments for FY2002 to Nearest +/- 10%:
T.G. Nieh (0.1%), Prof. Shuh (MIT) (0.1%), Graduate Student (1.0 %)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $574K **FY01 BA** $421K **FY02 BA** $422K

Laboratory Name: LLNL
B&R Code: KC0202020

FWP and possible subtask under FWP:
Fundamental Physics and Chemistry of Optical Materials: (S. Payne)

FWP Number: SCW0289

Program Scope:
Our objective is to discover and develop useful new optical materials on the basis of fundamental physics and chemistry. The purpose of this effort is to pursue novel materials and their functionalities, in order to enable next-generation laser technologies.

Major Program Achievements (over duration of support):
Earlier our effort was to understand the neutron-induced changes experienced by fused silica (SiO_2) for low-doses of neutrons (~1 Mrad of 1 MeV). We have extended this work by examining samples irradiated to very high doses (~10^5 Mrad). On the basis of our new data, we conclude that the neutron-induced defects saturate when the Collisional cascades begin to overlap. We have interpreted the experiments in terms of the volume of the collisional cascade, found to be 200 nm^3 per keV of atomic recoil energy. We proved that the neutrons concurrently produce E' centers (unbound Si atoms) in equal numbers with non-bridging oxygen hole centers (NBOHCs, or Si – O species), and that all of these defects recombine at elevated temperature. A steady state concentration of defects is created at high radiation dose, where each collisional cascade creates and anneals an equal number of defects in the saturated regime.

We have learned a great deal about the rare earth doped bromide crystal, Nd:KPb_2Br_5, a unique host material that offers the lowest phonon frequency of any viable laser crystal. We have studied the emission from the $^4F_{5/2}$ excited state of Nd^{3+}, finding that it has a surprisingly high emission yield of 50%, which is only possible in bromide crystals. We have evaluated the radiative lifetimes, branching ratios, and cross sections for the potentially new $^4F_{5/2} \rightarrow {}^4I_J$ laser transitions at 0.96 and 1.20 □m. Higher purity starting materials will be employed in the future to improve crystalline quality.

We have completed our characterization of the nonlinear optical and electro-optic properties of the $YCa_4O(BO_3)_3$, $GdCa_4O(BO_3)_3$, and $LaCa_4O(BO_3)_3$ family of crystals. Coupled with previous measurements of optical absorption and thermo-optic coefficients, these materials are thought to be suitable candidates for high power electro-optic switches.

Program impact:
Lasers and their applications play an obvious role in today's world with a wide variety of applications. There is a continued need for new and better laser materials as well as an understanding of damage and aging mechanisms in existing systems. This program has contributed to the development of three new laser inventions, which have resulted in SBIR's. In addition, the effect of neutron irradiation has been studied and the resulting defects identified.

Interactions:
University of Hamburg, Hamburg, Germany

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:
Spem (0.2%), Payne (0.1%), Rademaker (Postdoc) (0.2%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $276K **FY01 BA $**186 **FY02 BA $**215

Laboratory Name: LLNL
B&R Code: KC0203010

FWP and possible subtask under FWP:
Growth and Formation of Advanced Interfaces (L. Terminello)

FWP Number: SCW0289

Program Scope:
The goal of this project on Advanced Heterointerfaces characterization is to determine the atomic and electronic structure of reduced dimensional and nanostructured materials using synchrotron radiation core and valence level spectroscopies. In many cases, these measurements are compared directly with first principles calculations in order to synergistically interpret structural measurements with greater precision and to reveal the structure – property relationship for many nanoscale materials.

Major Program Achievements (over duration of support):
We have performed core and valence level photoemission, near-edge core level photoabsorption, and soft x-ray fluorescence experiments on a number of nanocluster, thin film, and buried interface systems at the Advanced Light Source (ALS). Many of these experiments would not have been possible without the high brightness of the ALS.

We have characterized the effect of substrate morphology, surface termination, and quantum confinement on the properties of 1 – 10 nm semiconductors nanoclusters using core level photoabsorption, soft x-ray fluorescence and photoemission. These experiments include determining the band-gap increase for nanoclusters terminated with longer chained hydrocarbons when compared to bare or short chain terminated clusters. We have made significant advancements in the characterization of diamond nanoclustering and comparing these results to our work on Si and Ge nanoclusters. This part of our effort was enabled by the use of the state-of-the-art tools available at the ALS for the characterization of nanoscale materials.

Program impact:
As technological advances in nano-structures and nano-electronics advances it is important that the electronic and band structure of these devices be understood. Of importance is the behavior at interfaces particularly interfaces of differing materials (heterointerfaces). The Advanced Light Source and X-ray spectroscopy has contributed to the fundamental understanding of electronic structure and its modification for a variety of materials as a function of size in the quantum limit and the presence of underlying matrices and junctions.

Interactions:
We have attracted several fellowship students and postdocs from prestigious European institutions and facilities. Our collaborations include some of the best nanoscience practitioners

UC – Berkeley, P. A. Alivisatos
UC – Santa Barbara, G. F. Strouse
SNL-A J. Wilcoxson

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:
L. Terminello (0.1%), T. van Buuren (0.3%), Grad. Student (0.1%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $305 **FY01 BA $**325K **FY02 BA $**232K

Laboratory Name: LLNL
B&R Code: KC0203010

FWP and possible subtask under FWP:
Nanoscale Magnets (J. Tobin)

FWP Number: SCW0289

Program Scope:
A series of investigations of complex materials, using synchrotron -radiation -based probes at the Advanced Light Source, have been performed. Particular emphasis has been placed upon the utilization of dichroic and spin-resolving experiments, founded upon photoelectron spectroscopy and x-ray absorption. This unprecedented level of scientific investigation will improve our understanding of 3d, 4f and 5f magnetism as well as the exploitation of technological advances, such as spin-valve and GMR read heads and sensors and spintronic devices. We are also participating in other exploratory investigations of complex materials such as liquids, specifically water and aqueous solutions.

Major Program Achievements (over duration of support):
Spin-Resolving/Dichroic Photoelectron Spectroscopy: We have continued our investigation of nanomagnetic alloy films, reporting the observation of internal component features and the development of a simple picture to explain our observations. Exploratory work on Liquid Water: Here, we were very successful, with the first report of Hydrogen EXAFS in water and the observation of surface effects in liquid water. f electron Systems: We have been pursuing studies of 4f and 5f electron systems . In the study of 5f systems, the expertise in spin-resolving work and the development of the spectral simulation picture including both spin-orbit and exchange splittings has proven to be essential to our advances in understanding Pu and the other actinides. Potential Half-Metallic Ferromagnets (HMFM): Of particular importance has been our investigations of potential half-metallic ferromagnetic materials, which hold out the promise of serving as pure spin sources for spintronic devices. Here, two disparate systems have been examined. Spin resolved photoelectron spectroscopy was used to measure the spin polarization of the valence bands and, especially, the near Fermi energy regime of Fe3O4 samples. In the case of the Zintl compound, Yb14Mn Sb11, X-ray Magnetic Circular Dichroism, performed on the Elliptically Polarizing Undulator (EPU), was used to demonstrate that the Mn was the dominant contributor to the magnetic moment, possessing a magnetic moment on the scale of 5 Bohr-Magnetons.

Program impact:
New families of nano-scale magnetic materials are being actively explored with a wide range of potential applications. Examples include Giant Magneto-Resistive materials; half-metallic ferromagnets and other electronic spin dependent devices. Dr. Tobin has developed a unique and powerful technique using spin dependent photo-electron spectroscopy to understand the fundamental processes responsible for the behavior of these materials.

Interactions:
LBNL Advanced Light Source
We are working with Tony Young and Elke Arenholz (ALS) on the commissioning of the EPU
University of Missouri, Prof. G. Waddill
Boyd Technologies, Dr. P. Boyd
IBM, Dr. A. Gupta
We are also working with other DOE investigators through the DOE Centers of Excellence Program on NanoComposite Magnetism, headed by Sam Bader of ANL.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. Tobin (0.3%), D. Waddill (Univ. of Mo-Rolla) (0.5%), Postdoc (1.5%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $463K **FY01 BA** $351K **FY02 BA** $395K