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Title: Summary Report of Summer Work: High Purity Single Crystal Growth & Microstructure of Ferritic-Martensitic Steels

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SUMMARY REPORT OF SUMMER WORK: HIGH PURITY SINGLE CRYSTAL GROWTH & MICROSTRUCTURE OF FERRITIC-MARTENSITIC STEELS

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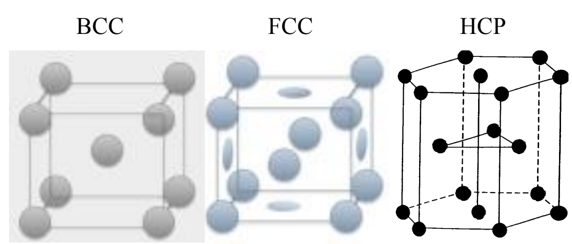
Introduction

Harnessing the power of the nuclear sciences for national security and to benefit others is one of Los Alamos National Laboratory's missions. MST-8 focuses on manipulating and studying how the structure, processing, properties, and performance of materials interact at the atomic level under nuclear conditions. Within this group, single crystal scintillators contribute to the safety and reliability of weapons, provide global security safeguards, and build on scientific principles that carry over to medical fields for cancer detection. Improved cladding materials made of ferritic-martensitic alloys support the mission of DOE-NE's Fuel Cycle Research and Development program to close the nuclear fuel cycle, aiming to solve nuclear waste management challenges and thereby increase the performance and safety of current and future reactors.

I. Basic Science

Crystal Structures

The crystal structure of a material is made of an arrangement of atoms into a unit cell, which is repeated throughout the structure to form a three-dimensional physical lattice. Most metals have solid unit cell Body Centered Cubic (BCC), Face Centered Cubic (FCC), or Hexagonal Close Packed (HCP) structures. Materials with a BCC structure have atoms at each of the eight corners of a cube and one atom in the center of the cube. Each corner atom is the corner of eight other cubes, so corner atoms are shared among 8 unit cells. This structure has a net total of 2 atoms, one from the center atom and one from the corner atoms. BCC does not allow for atoms to pack together closely, and it is often the high temperature form of metals that are close packed at lower temperatures. This structural characteristic typically decreases malleability.



FFC structures have atoms located at each corner of a cube and at the centers of each face. Each corner and each face atom is shared with the adjacent cubes, so each cube has a net total of 4 atoms. It allows atoms to pack together tightly, since atoms of one layer will nest in the empty spaces between the atoms of the next layer. A material with HCP structure consists of alternating layers shifted so that the atoms of one layer nestle into the gaps of the adjacent layers. The structure as a whole is hexagonal. It has 6 atoms in the top and bottom layers at each corner of the hexagon and 1 atom in the center of each layer. There are 3 atoms in a triangular plane in the middle layer. Applied temperature, pressure, and other factors can distort a material's crystal structure, thus altering its properties. For example, quenching steel produces specific volumes of martensite, which has a distorted crystal lattice due to its supersaturated C solution. The distorted lattice is tetragonal in shape. Distortion increases with the amount of dissolved carbon. This distortion gives martensite extreme hardness. Tempering martensite can relieve hardness by relaxing the lattice back into an undistorted BCC structure.

Microscopes

Transmission Electron Microscopes (TEM) and Scanning Electron Microscopes (SEM) offer insight into a material's microstructure. Electron microscopes consist of an electron optical column, a vacuum system, and corresponding electronics to image the sample. The TEM operates using a broad static beam with low accelerating voltages to image the surface of the sample. In the SEM, the column is shorter, the chamber is larger, and the electron beam is focused to a fine point to scan line by line over the sample, penetrating the surface. Scanning transmission electron microscopy combines these principles.

Backscattered electrons (BSE) result from elastic interactions between incident electrons and the sample. BSE emission is useful in detecting composition differences, showing topography, showing crystal orientation, and showing grain boundaries, phase boundaries, and other crystal features.

Optical Microscopes offer less magnification than electron microscopes described above, though they can provide clear images of a sample surface and prove useful during sample preparation. They use visible light and a system of lenses to produce magnified images of the sample.

Electromagnetic Spectrum

The electromagnetic spectrum includes types of electromagnetic waves organized by wavelength. Understanding the electromagnetic spectrum is useful in many areas of science, such as microscopy and scintillator research. All electromagnetic waves travel at the speed of light. Visible light is between 400 nm, violet, and 700 nm, red. In this range, scintillators can be used to detect nuclear materials. Each material emits characteristic gamma rays that the scintillator converts into visible, detectable light. The detected visible light can be matched with the known characteristic gamma ray. Wavelengths from this point on are considered nonionizing radiation, having enough energy to move atoms but not remove electrons. Above 700 nm are infrared rays, which are invisible thermal radiation emitted by objects near room temperature. The remaining wavelengths above 700 nm include radar, FM, TV, shortwave, and AM, in order of increasing wavelength. Below visible light includes ionizing radiation, having enough energy to remove electrons from atoms. Ultraviolet rays fall into the range of 300 nm-400 nm. There are 9 different types, and all are typically invisible to humans as the lens blocks this range of wavelengths and the cornea blocks shorter wavelengths. X-rays are from .01 nm-10 nm. Hard x-rays have photon energies above 5-10KeV, and soft x-rays have lower energies. Gamma rays have shorter wavelengths than x-rays. They have extremely high frequency and high-energy photons. Gamma ray ionizing radiation is caused by gamma decay, the decay of atomic nuclei as they transition from a higher to a lower energy state.

Several kinds of electromagnetic phenomena exist. Reflection is a change in direction of a wave at an interface between 2 media, so that the wave returns to the medium where it originated. Refraction is the change in direction of a wave due to a change in the transmission medium. Polarization occurs when waves oscillate with more than one orientation, so that the waves travel in different directions. Diffraction occurs with all waves and describes the various occurrences that can happen when a wave encounters an obstacle. Absorption of electromagnetic radiation is when matter takes up energy, typically when the electrons of an atom take up the energy of a photon.

Types of Radiation

Nonionizing radiation has enough energy to move atoms around within a molecule, causing them to vibrate. Ionizing radiation has enough energy to remove tightly bound electrons from atoms to create ions. It has very high frequencies and very short wavelengths, resulting in extremely high energy used to break up the nucleus of atoms. Ionization results in the formation of two charges particles or ions – one molecule with a net positive charge and a negatively charged free electron. Three types of ionizing radiation are alpha, beta, and gamma. Alpha particles are relatively heavy and positively charged high-energy particles. When the ratio of neutrons against protons is too low, certain atoms restore the balance by emitting alpha particles. The loss of an alpha particle changes the atom to a different element. Although alpha particles are considered high-energy particles, they lack the energy to penetrate the outer layer of human skin. Inhalation can be hazardous. Beta particles are subatomic particles ejected from the nucleus of some radioactive atoms. They have an electrical charge of 1^-, like electrons, but originate in the nucleus when the ratio of neutrons to protons is too high, unlike electrons. When a beta particle is formed, the number of neutrons and protons each decrease by 1, so the radionucleide changes to a different element. Direct exposure to beta particles is considered a hazard and inhalation can disrupt cell functions. Gamma rays are the most energetic photons in the electromagnetic spectrum. They are emitted from the nucleus of some radioactive atoms. Gamma rays have no mass and no charge – they are pure electromagnetic energy. Due to their high energy, they travel at the speed of light and can cover thousands of meters in air. They occur when the nucleus has too much energy, often following beta emission. Since gamma rays can pass through many materials, including human tissue, dense material, such as lead, can be used as shielding. Gamma rays and X-rays pose the same kind of hazard, but differ in origin.

Reactors

Currently, nuclear power reliably and economically contributes 20% of electrical generation in the United States. It remains the single largest contributor of non-greenhouse-gas-emitting electric power in the US.

Light water reactors are a type of thermal-neutron reactor that uses normal water as a coolant and neutron moderator. The core consists of fuel and control elements enclosed by a water-filled steel pressure vessel. Heat resulting from nuclear fission evaporates water in the pressure vessel in a boiling water reactor.

In a pressurized water reactor, water evaporates in a steam generator of a secondary unit. In both models, steam energy rotates a turbine, which generates electricity. This steam then condenses back to water and recirculates through the system. Heat is often dissipated via a cooling tower and released into the atmosphere. The Light Water Reactor Sustainability Program (LWRS), operated by the DOE's Office of Nuclear Energy, works to extend existing nuclear power plant operating life. Age licenses begin with an initial 40-year period and can be issued a 20-year renewal, for a total of 60 operating years. The LWRS program aims to extend lifetimes beyond 60 years and ensure long-term sustainability and productivity of light water reactors. This program grows in increasing importance as the nation's fleet of light water reactors is nearing 60-year limits in a time when energy demands continue to grow.

Fast Reactors rely on a fission chain reaction sustained by fast neutrons. The fission chain reaction is self-sustaining and propagating. These reactors have a much higher flux of higher energy neutrons than Light Water Reactors, so more damage and displacement occurs within core materials. The core is cooled with heavy metals such as sodium or lead. Improved cladding materials lead to the enhanced performance of Fast Reactors. They can be used to transmute minor actinides in separated LWR waste, utilizing unspent Uranium content and shortening half-lives by changing long-lived minor actinide isotopes into other isotopes through fission or transmutation. The actinide group on the periodic table encompasses 15 metallic chemical elements. All are radioactive, highly electropositive, very dense, and have distinct structures. They can form numerous allotropes, which are the different structural modifications of an element. Because of their high flux of high energy neutrons, Fast Reactors are able to cause long-lived isotopes to fission reducing the burden on future nuclear waste repositories. Burn up, or fuel utilization, is a measure of how much energy is created from a primary fuel source. It is measured by the fraction of fuel atoms that underwent fission. Currently, no Fast Reactors are operating in the United States.

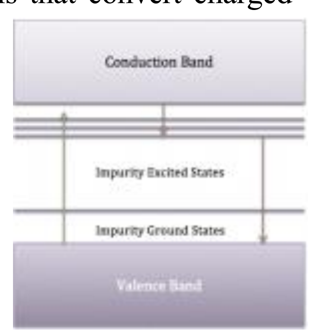
Small Modular Reactors have smaller, compact designs that can be easily transported by truck or rail to a power site. They offer low capital investment, scalability, and siting flexibility, possibly enhancing safety and security. Small Modular Reactors have the potential to be sited underground, which offers increased protection against natural disaster and attacks and also maximizes land utilization. Factory-fabricated reactors can be made available in the international marketplace.

II. Laboratory Science

Scintillators - Introduction

Single crystal scintillators are single-grain transparent crystals that convert charged particles, such as x-rays and gamma rays, into visible light.

The excitation and accompanying de-excitation of charged particles within a crystal's electronic band structure cause photon emission.

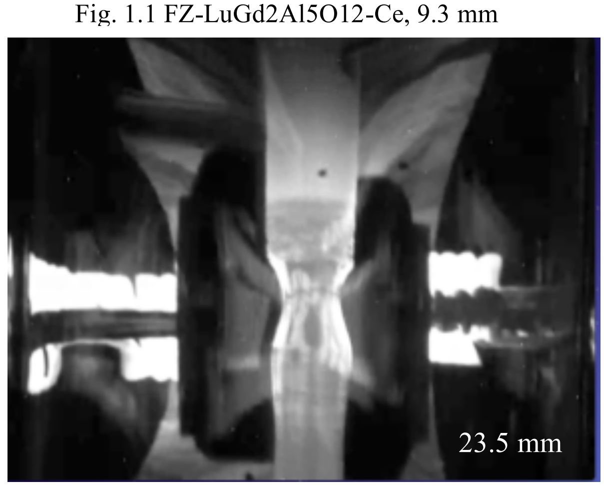


Combinations of chemical powders can be calculated, weighed out, and mixed to produce the desired crystal. High purity single crystal scintillators produced in the MSL Single Crystal Growth Laboratory contribute to the Lab's missions. DARHT, the Dual-Axis Radiographic Hydrodynamic Text facility, relies on scintillators to provide high-resolution, three-dimensional, time-sequenced images of mock-up nuclear implosions in very short amounts of time.

Growth

The growth of a new research-sized crystal begins with chemical calculations. Excel sheet calculators can be prepared and utilized to determine how much of each chemical powder is needed to produce the desired chemical formula. These calculators are useful in determining how many grams of a powder are needed when a certain percentage of elements are wanted on different sites. For example, when a garnet powder is doped with an activator, then the activator mass will "sit" on the A-site of the substance, along with the original element. An activator, a trace impurity inserted into a substance in very low concentrations to alter its properties, takes the place of elements in the crystal lattice of the base material. The calculator proves helpful for determining the ratios between the atomic percent of the activator used to the amount of the original element. Once these calculators are set, the sheet is locked and the powders are weighed out in the SCGL. The powders are combined in a single container and mixed for 15 minutes on a Spex mill. Powders are funneled and compounded into a latex bag, and the air is vacuumed out. A Cold Isostatic Press further compresses the material into feed (5-6 cm) and seed (3-4 cm) rods needed for growth methods. Two of the growth methods used in the SCGL are the Czochralski Method and the Optical Floating Zone Unit. The Czochralski Method involves pulling from the melt. A single crystal seed is place on the molten surface of powders within a rotating crucible and is gradually drawn upwards, solidifying into a continuous crystal. The Float Zone Method brings a seed rod and feed rod face to face in a vertical position. The rods are continually rotated and are eventually brought together to make contact at their melted tips. As the molten zone is moved along the rods, the molten material solidifies into a single crystal. The Float Zone growth of garnet LuGd2Al5O12:Ce can be seen in Fig. 1.1 and 1.2. The top polycrystalline rod consists of pressed powder, the middle is the molten zone, and the bottom is solidified crystal. The top and bottom rods are being rotated in opposite directions, which mixes the liquid molten zone to rid the crystal of impurities.

Fig. 1.1 FZ-LuGd2Al5O12-Ce, 9.3 mm



The diameter of the crystal when it has grown to 9.3 mm in length is slimmer than that at 23.5 mm. Manipulating rotations per minute and growth rate can control this. A garnet without Ce as an activator was also grown using the Float Zone method. Upon further analysis of the grown crystals, it is found that cerium causes the garnet to scintillate a yellow-orange color near 600 nm. The crystal without cerium did not glow under the UV light. When compared to a typical LuAG sample, the LuGd2Al5O12 crystal clearly emitts at a higher wavelength than the LuAG sample, which glows yellow-green, having a wavelength closer to 535 nm. This difference can be attributed to the presence of gadolinium in the two test samples.

Fig. 1.3 LuGd2Al5O12 with and without Ce

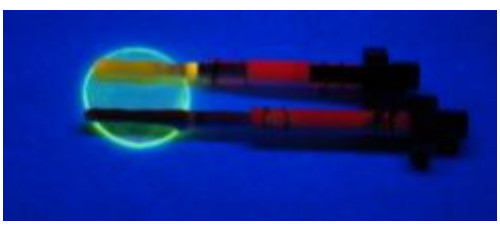


Fig. 1.4 LuGd2Al5O12 with and without Ce compared with LuAG under UV light

Applications

Imaging via scintillators provides precise three-dimensional imaging through non-destructive means, ensuring the safety and reliability of weapons. This Surveillance Diagnostic Tool evaluates the potential impact of aging on materials and provides a basis for assuring a high level of confidence in continued performance. Assessments can be used in Life Extension Programs.

Scintillators can be utilized to detect nuclear materials, delivering global security safeguards. By identifying energies of light emitted from scintillators, we can detect nuclear materials, such as Uranium and Plutonium, from a safe distance. When a material is detected, further investigative actions can be taken.

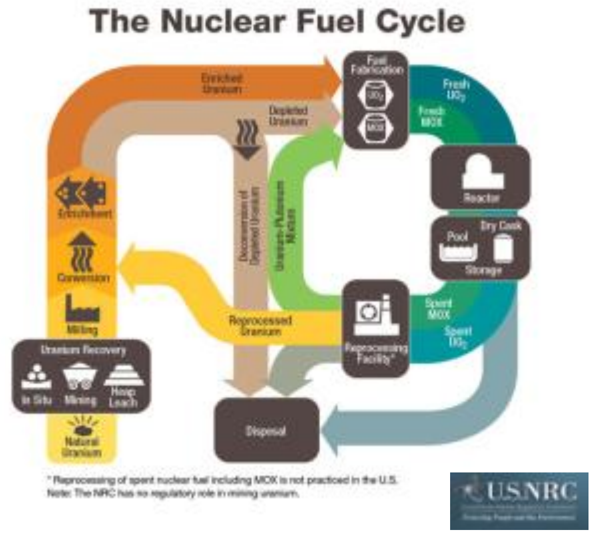
DARHT, the Dual-Axis Radiographic Hydrodynamic Test Facility, allows for the study of three-dimensional implosions of mock nuclear weapons primaries. It is the world's most powerful x-ray machine, producing freeze-frame radiographs of materials imploding at speeds greater than 10,000 miles per hour. Scintillators play an essential role within DARHT's two axis. The first axis produces high-resolution images and penetration than what is currently possible at any other facility. The second axis generates three-dimensional images and time-sequenced images, giving researchers a detailed look into implosions. The DARHT facility supports a critical component of LANL's primary mission: to ensure the safety, security, and effectiveness of nuclear weapons in our nation's stockpile. Several crystal systems found in the literature can potentially meet desired properties for further development of the DARHT facility. Two bright, dense scintillators with high emission wavelengths are being researched for the next phase of DARHT. One of these scintillators must have a fast decay time, in order to manage multiple, quick image pulses. A second scintillator is needed for a single image pulse, allowing for a slower decay time. These crystal systems are somewhat difficult to find and develop, because as light yield increases, density tends to decrease and as wavelength increases, decay time often increases as well.

The science behind scintillators used for weapons imaging and materials detection can be applied to outside research organizations for medical imaging and cancer detection, offering a broader impact. Outside organizations can utilize scintillator technology produced by LANL to research new, digital diagnostic systems with high image resolution and short generation times. X-rays, CT scans, and PET scans all rely on scintillators.

Ferritic-Martensitic Steels – Introduction

Light Water Reactors produce one-fifth of the electricity generated in the United States. While these reactors do not contribute to greenhouse gas emissions, another environmental issue lies in the disposal of nuclear materials waste. The mission of the DOE-NE's Fuel Cycle Research & Development Program is to close the nuclear fuel cycle, addressing long-term waste management challenges while enhancing performance of the nation's current and future reactors.

Technologies separate minor actinides from spent fuel to effectively perform transmutation. Transmuting long-lived isotopes from light water reactor spent fuel to different isotopes with reduced radioactive half-lives in a fast reactor inhibits long-term effects of high level nuclear waste. Reusing spent fuel produces additional energy and reduces burdens on repositories by reducing the period of actinide toxicity. Transmutation of minor actinides in a fast reactor places high demands on reactor cladding and structural materials. Cladding contains the nuclear fuel, preventing transuranic isotopes from entering the primary coolant.



Improved cladding materials made of advanced alloys can withstand higher radiation doses, increasing the lifetime of nuclear fuel and decreasing the amount of waste generated. Cladding materials must have excellent radiation tolerance (>300 dpa, 40% burn up), maintain strength and ductility to avoid dimensional changes, fracture, and deformation, and resist corrosion and liquid metal embrittlement.

Development of improved ferritic-martensitic steel alloys with higher radiation tolerance supports the mission of the FCRD program and increases the performance and safety of current and future reactors. Improved structural materials also improve the economics of fast reactors by allowing higher operating temperatures, giving higher thermal efficiency and power output, reducing replacement costs by extending lifetimes, and giving more flexibility in construction and operation.

Sample Preparation

In pursuit of cladding materials with improved radiation tolerance, ferritic-martensitic alloys with controlled levels of carbon and nitrogen are being developed. HT9 is a tempered-martensitic steel of interest for fuel cladding and duct material in fast reactors. It has high swelling resistance to doses above 200 dpa, high strength, good corrosion resistance in sodium, and has adequate thermal creep resistance at prototypic reactor temperatures. To investigate the initial microstructure, heat treated alloys are polished, etched, and imaged via an optical microscope. The newly developed alloys with controlled interstitial content are first normalized at 1040°C for 30 minutes and then tempered at 760°C for 60 minutes to achieve an initial desired microstructure. Metallurgical preparation techniques are then used to analyze the microstructure.

Several heat treatment methods exist. Annealing involves heating steel to a high temperature and then cooling it very slowly to room temperature to remove stresses, resulting in high ductility and toughness but low hardness. The normalizing process involves heating steel and keeping it at the same high temperature for a period of time before cooling it in air. The remaining sample is a mixture of martensite and ferrite, giving high strength and hardness, but lower ductility. Quenching is the rapid cooling from an elevated temperature, which prevents low temperature processes, such as phase transformations from occurring. It hardens steel by introducing martensite. Tempering is a low temperature process that provides a way to carefully decrease hardness and increase toughness and ductility.

Once heat-treated, an abrasive saw is used to section off a representative sample of the material. This step does not alter or destroy the structure, though a small amount of deformation formed on the surface is removed in the next steps. The sample is then mounted on a compatible material to facilitate handling during grinding and polishing. Grinding on abrasive silicon carbide paper achieves a flat surface with minimal damage. Progressively finer abrasive grits are used to rid the sample surface of any scratches or other abnormalities. Polishing with a chemical lubricant, such as colloidal silica, and a cloth wheel removes the last thing layer of the deformed metal, producing a smooth, reflective surface. Hardness tests measure the resistance a material has to deformation or indentation. Etching in a proper etchant reveals microstructural details, such as grain boundaries, twins, and other features otherwise not seen.

Results

Optical light microscopes use visible light and a system of lenses to magnify images. Grain boundaries are imaged on an optical light microscope, revealing variations in grain size and the martensite volume fraction compared with carbon content. Before a sample is imaged, hardness testing can predict its composition. Looking at the 6 HT9 samples, a manual indenter can be used to collect hardness data. It can be assumed that the harder a sample is, the greater its martensite content. The manual indenter utilizes optical microscopy and applied weight to create a small indent on the sample surface. This diamond shaped indent is measured by length and width, creating the hardness calculation. Five tests were performed on different areas of each sample. This data were then averaged and are presented below.

Heat Treatment	High Impurity	Low Impurity
Quenched	410.56	306.76
Tempered 760°C, 1 hr.	226.1	195.38
Tempered 760°C, 2 hrs.	231.68	205

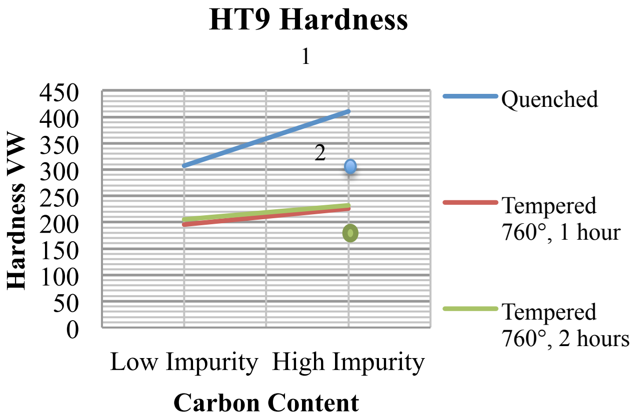


Fig. 2.1

These results reveal that quenching a high impurity sample, with greater carbon content, produces the greatest volume of martensite compared to carbon content, as it has the greatest hardness (2.1, 1). The volume of martensite produced is a function of amount of carbon in the samples. Quenching produces martensite by rapidly cooling the sample, as can be deduced from Fig 2.2. The resulting

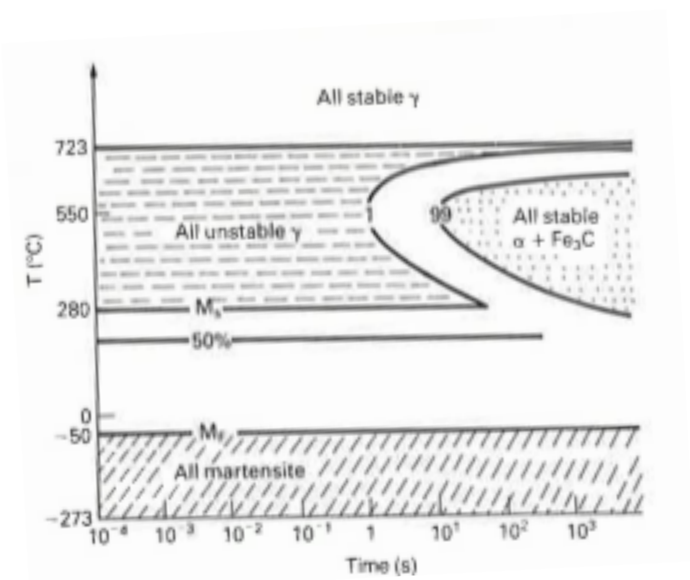


Fig. 2.2, [1]

sample is very hard and brittle. Martensite is a supersaturated solid solution of carbon in iron, having a distorted tetragonal lattice. This distortion increases linearly with the amount of dissolved carbon. As Figure 2.3 illustrates, the hardness of martensite increases with carbon content. So, the quenched sample with the

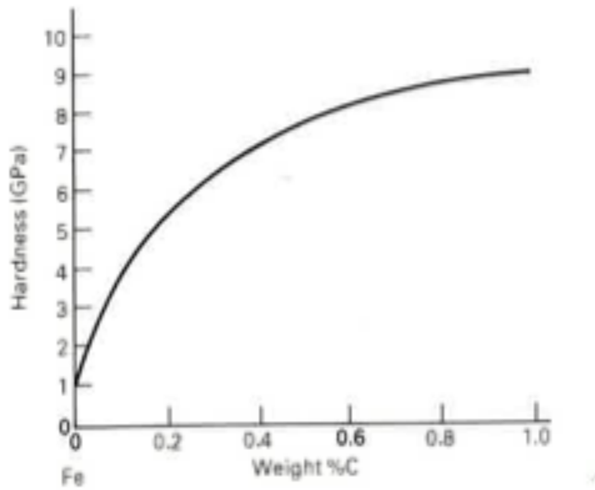


Fig. 2.3, [1]

greatest carbon content displays the greatest hardness (2.1, 1), due to increased martensite content.

Tempering the martensite, reheating it to a certain temperature, increases toughness without drastically diminishing hardness. As the sample is reheated, carbon atoms receive thermal energy to diffuse out of supersaturated solution and react with iron to form small closely spaced precipitates. The lattice relaxes back into an undistorted bcc structure and ductility increases. Since martensite volume produced is based off of temperature and not time, both high and low impurity samples tempered for 1 hour do not vary greatly in hardness from samples tempered for 2 hours (2.1, 2). Combining quenching and tempering techniques can greatly improve yield and tensile strength.

Conclusion

Summer work at Los Alamos National Laboratory gives both valuable office and experimental experience. Learning how to research topics using books, documents, and Internet database resources proves useful in work at LANL and work at school. Research such as this builds a student's work ethic and capabilities, while improving his or her foundational knowledge. Work supporting the Lab's missions, such as the growth of single crystals and the research into new cladding materials, broadens the student's worldview and aids in understanding how his or her work plays a role in accomplishing those missions. Hands-on experimental experience is a great opportunity for students to learn more about the field they are interested in and learn safety and work procedures outside of an academic setting. It allows a student's problem solving skills to improve, as when there is mechanical bumping that can ruin a crystal growth run, and it lends the opportunity to use equipment that otherwise may not be available to the student, such as a manual or automated indenter for hardness testing. Combining the two experiences creates a unique summer internship experience any student would be fortunate to have.

Reference

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