Materials Solutions for Hydrogen Delivery in Pipelines

Dr. Subodh K. Das
SECAT Inc.

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Overview

Timeline

- Project start date: 05/2005
- Project end date: 09/2008
- Percent complete: 14%

Budget

- Total project funding
  - $1650K
  - $1110K (contractor share)
- Funding received in FY04: None
- Funding for FY05:

Requested: $550K

Actual: $200K

Barriers and Targets

Barriers addressed

High capital cost and Hydrogen Embrittlement of Pipelines

Technical Targets (2015):

– Capital cost ($0.8 Million/Mile)

– Cost of delivery of hydrogen <$1.00/gge

– High Reliability of operation with metrics to be determined

Partners

SECAT CONSORTIUM

- Advanced Technology Corporation
- ASME Standards and Technologies, LLC
- Chemical Composite Coatings Intl
- Columbia Gas
- Hatch Moss MacDonald
- Oregon Steel Mills
- Schott North America
- DGS Metallurgical Solutions, Inc.

Oak Ridge National Laboratory

University of Illinois

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Objectives

- Overall goal of the project is to develop materials technologies that would enable minimizing the problem of hydrogen embrittlement associated with the high-pressure transport of hydrogen

- The overall objectives of the project are:
  - To identify steel compositions and associated welding filler wires and processes that would be suitable for construction of new pipeline infrastructure
  - To develop barrier coatings for minimizing hydrogen permeation in pipelines and to develop *in-situ* deposition processes suitable for these coatings
  - To understand the cost factors related to the construction of new pipelines and modification of existing pipelines and to identify the path to cost reduction

Key Technical Barriers

- Extent of hydrogen embrittlement of base material, and welds in pipeline steels and other common steels on exposure to high pressure H_2 is not known
- Only a limited understanding of the mechanisms of hydrogen embrittlement along with the effect of metallurgical variables such as alloying element additions, and microstructure of steels is available at the present time; hence the path to remediation and control is not well defined
- Although it is known that barrier coatings are effective in reducing hydrogen embrittlement, detailed knowledge of the effectiveness of various metallic and non-metallic coatings in minimizing the deleterious effect of H_2 under high pressures is not known
- Very little information is available on the potential avenues for reducing the cost of construction of pipelines for transport of hydrogen and the cost of technologies to remediate the effect of hydrogen embrittlement

Approach

Our approach consists of the following major tasks:

Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen

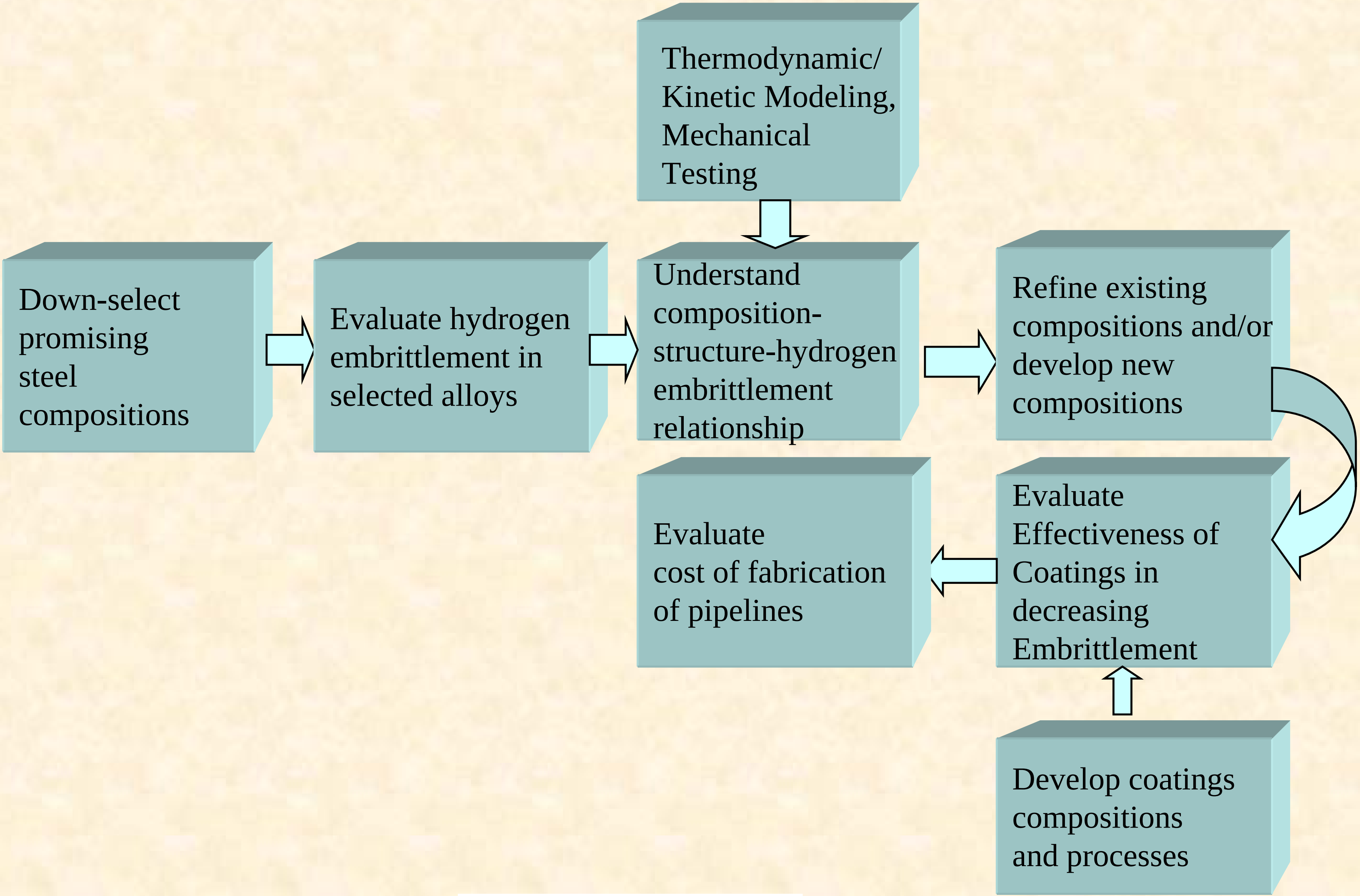
Task 2: Develop and/or identify alternate alloys and evaluate hydrogen embrittlement

Task 3: Develop coatings to minimize dissolution and penetration of hydrogen

Task 4: Evaluate the hydrogen embrittlement in alloys coated with selected coatings

Task 5: Perform financial analyses and incorporate knowledge into codes and standards

Schematic of Overall Approach



Thermodynamic/ Kinetic Modeling, Mechanical Testing

Down-select promising steel compositions

Evaluate hydrogen embrittlement in selected alloys

Understand composition-structure-hydrogen embrittlement relationship

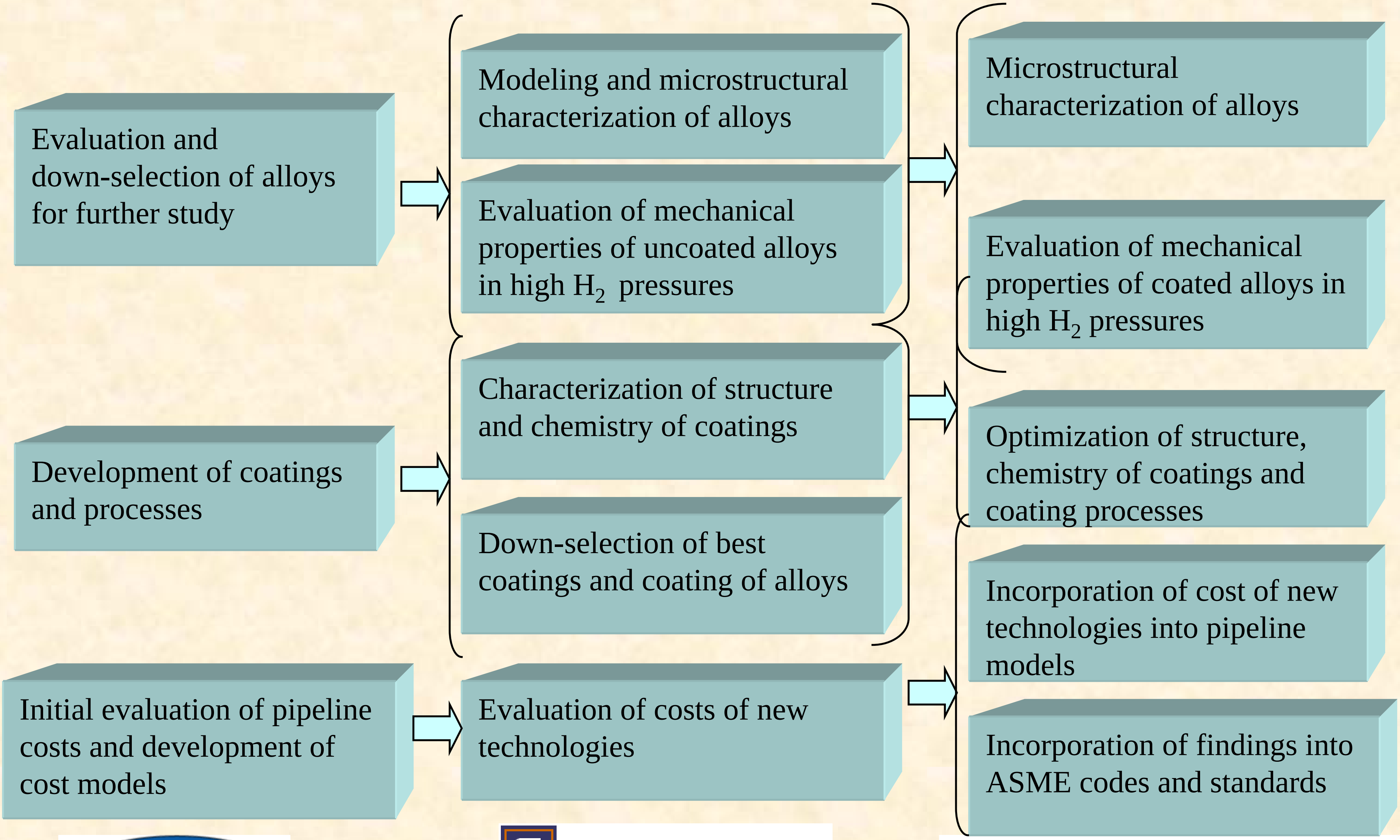
Refine existing compositions and/or develop new compositions

Evaluate Effectiveness of Coatings in decreasing Embrittlement

Evaluate cost of fabrication of pipelines

Develop coatings compositions and processes

Breakdown of Major Activities by Year



YEAR 1

Evaluation and down-selection of alloys for further study

Development of coatings and processes

Initial evaluation of pipeline costs and development of cost models

YEAR 2

Modeling and microstructural characterization of alloys

Evaluation of mechanical properties of uncoated alloys in high H_2 pressures

Characterization of structure and chemistry of coatings

Down-selection of best coatings and coating of alloys

Evaluation of costs of new technologies

YEAR 3

Microstructural characterization of alloys

Evaluation of mechanical properties of coated alloys in high H_2 pressures

Optimization of structure, chemistry of coatings and coating processes

Incorporation of cost of new technologies into pipeline models

Incorporation of findings into ASME codes and standards

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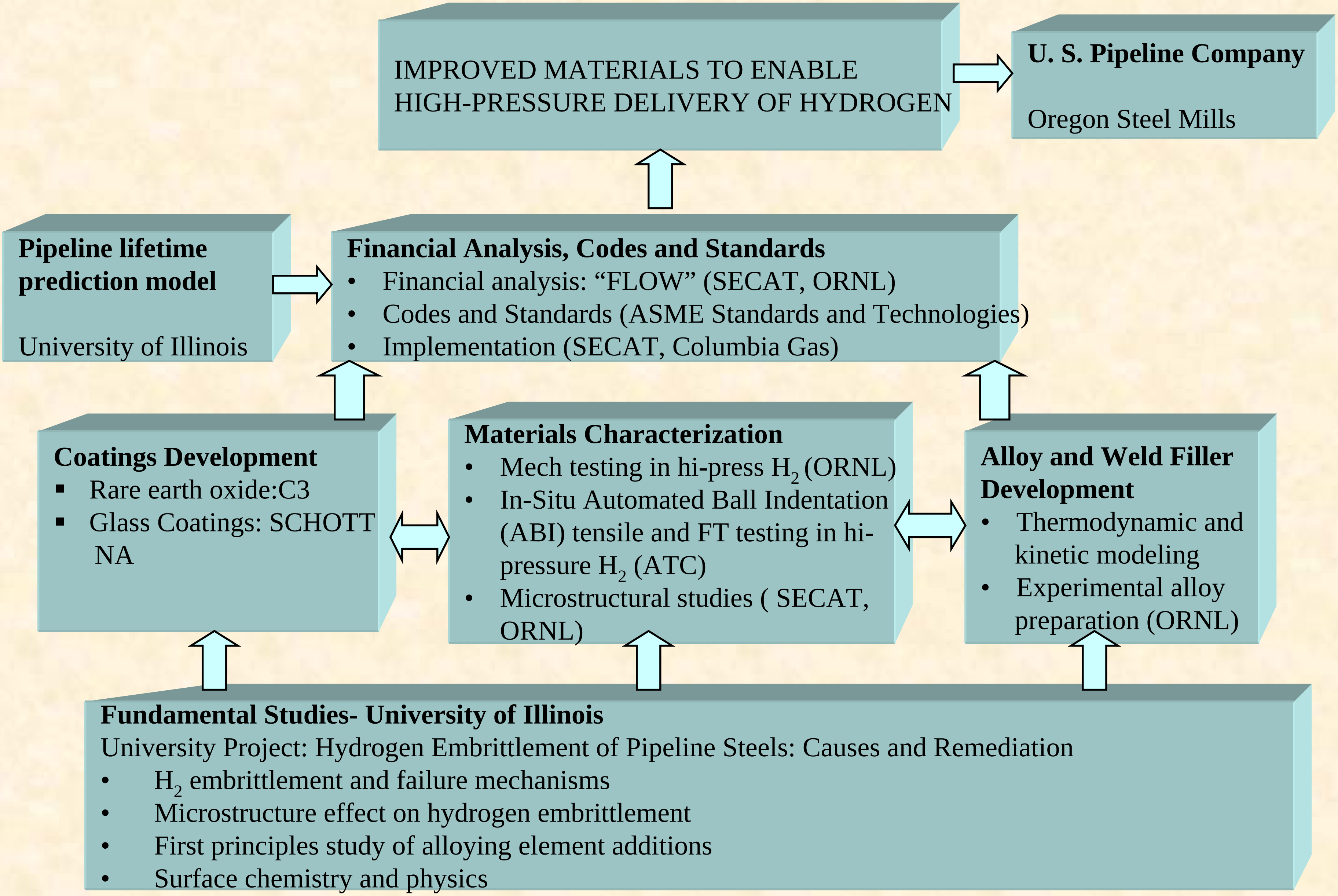
Roles of Project Partners



IMPROVED MATERIALS TO ENABLE
HIGH-PRESSURE DELIVERY OF HYDROGEN

U. S. Pipeline Company

Oregon Steel Mills

Pipeline lifetime prediction model

University of Illinois

Financial Analysis, Codes and Standards
- Financial analysis: “FLOW” (SECAT, ORNL)
- Codes and Standards (ASME Standards and Technologies)
- Implementation (SECAT, Columbia Gas)

Coatings Development
- Rare earth oxide:C3
- Glass Coatings: SCHOTT NA

Materials Characterization
- Mech testing in hi-press H_2 (ORNL)
- In-Situ Automated Ball Indentation (ABI) tensile and FT testing in hi-pressure H_2 (ATC)
- Microstructural studies (SECAT, ORNL)

Alloy and Weld Filler Development
- Thermodynamic and kinetic modeling
- Experimental alloy preparation (ORNL)

Fundamental Studies- University of Illinois
University Project: Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation
- H_2 embrittlement and failure mechanisms
- Microstructure effect on hydrogen embrittlement
- First principles study of alloying element additions
- Surface chemistry and physics

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Technical Accomplishments/ Progress/Results

- Project Kick-off meeting conducted March 15-16 at Lexington, KY
  - Near-term activities were outlined
  - Internal milestones for individual project team-members were defined
  - Contract details and agreement for intellectual properties were discussed

Details of Approach- Task 1

Task 1: Evaluate hydrogen embrittlement characteristics of existing commercial pipeline steels under high-pressure hydrogen

- Very little data is available on the effect of high pressure hydrogen on the mechanical properties and hydrogen embrittlement of pipeline steels
- Typical pipeline steel compositions will be down-selected
- Mechanical properties of these steels will be measured *in-situ* in high pressures of H_2 (up to 5000 psi) as a function of metallurgical variables such as heat treatments, grain size, and processing such as welding
- Automated Ball Indentation (ABI), a novel test method, will be used to characterize the effects of various times of exposure to high pressure hydrogen on the fracture toughness and tensile properties of base metal and welds of several pipeline steels
- Failed specimens will be characterized to understand the failure mode and compare with existing knowledge of failure modes
- Thermodynamic and kinetic modeling will be combined with microstructural characterization to understand the relationship between hydrogen embrittlement, alloy composition, and microstructure
- Best compositions will be down-selected for further work with barrier coatings

Proposed Work For FY 2005/2006

Steels

- Survey compositions of pipeline steels and other steel compositions for applicability in pipeline construction
- Identify a screening test to rapidly evaluate hydrogen embrittlement characteristics of steels of interest
- With the use of screening tests and industrial input, down-select four steel compositions for further detailed study of hydrogen embrittlement characteristics under high pressure H_2 (FY 2005 milestone)
- Initiate microstructural characterization, thermodynamic, and kinetic modeling
- Initiate permeability testing of selected steel compositions in high pressure hydrogen atmosphere
- Start assembly of equipment for *in-situ* mechanical testing of materials under high hydrogen pressures along with setting up associated safety measures and controls at ORNL
- Prepare preliminary chamber design to perform *in-situ* high pressure H_2 Automated Ball Indentation (ABI) mechanical testing (tensile/fracture toughness) at ATC

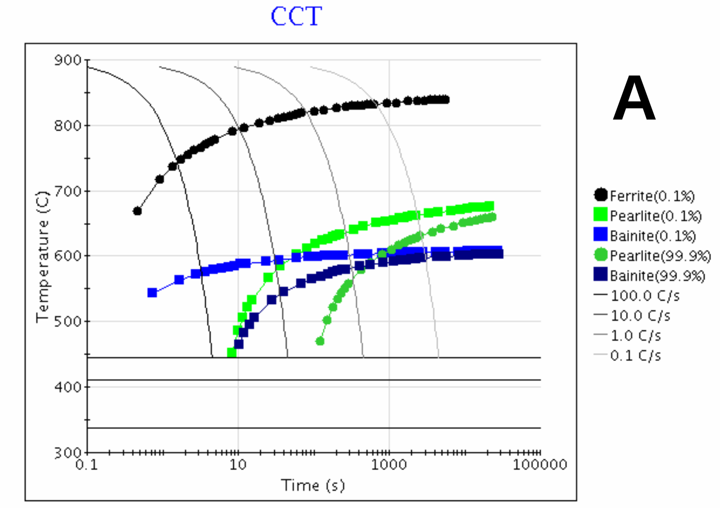
Steels and Their Compositions

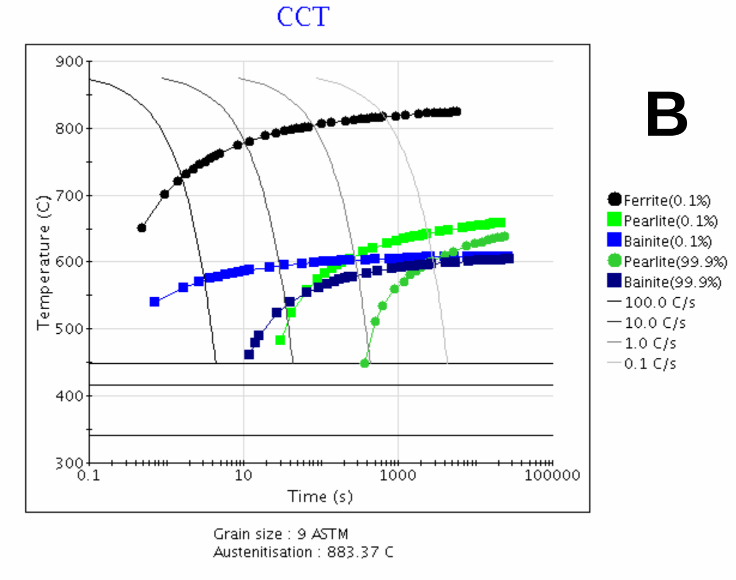
- Four steels have been down-selected for initial study

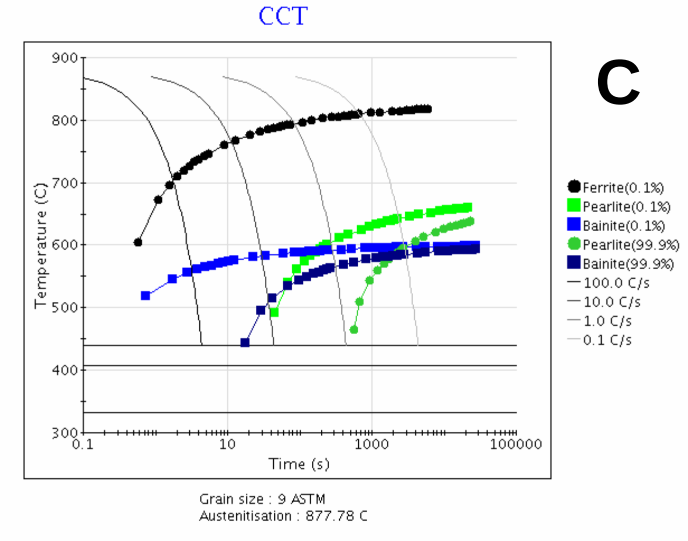
A: Represents chemistry used in pipelines in the past 10-15 years
B, C: Represents chemistry used recently in pipelines
D: Represents a sour service grade

	API Grade	**C**	**Mn**	**Si**	**Cu**	**Ni**	**V**	**Nb**	**Al**	**Cr**	**Ti**
A	X70	0.08	1.53	0.28	0.01	0.00	0.050	0.061	0.031	0.01	0.014
B	X70/ X80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.036	0.25	0.012
C	X70/ X80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.037	0.42	0.015
D	X52/ X60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.034	0.16	0.014

Continuous Cooling Transformation Diagrams Have Been Calculated for Three Alloys

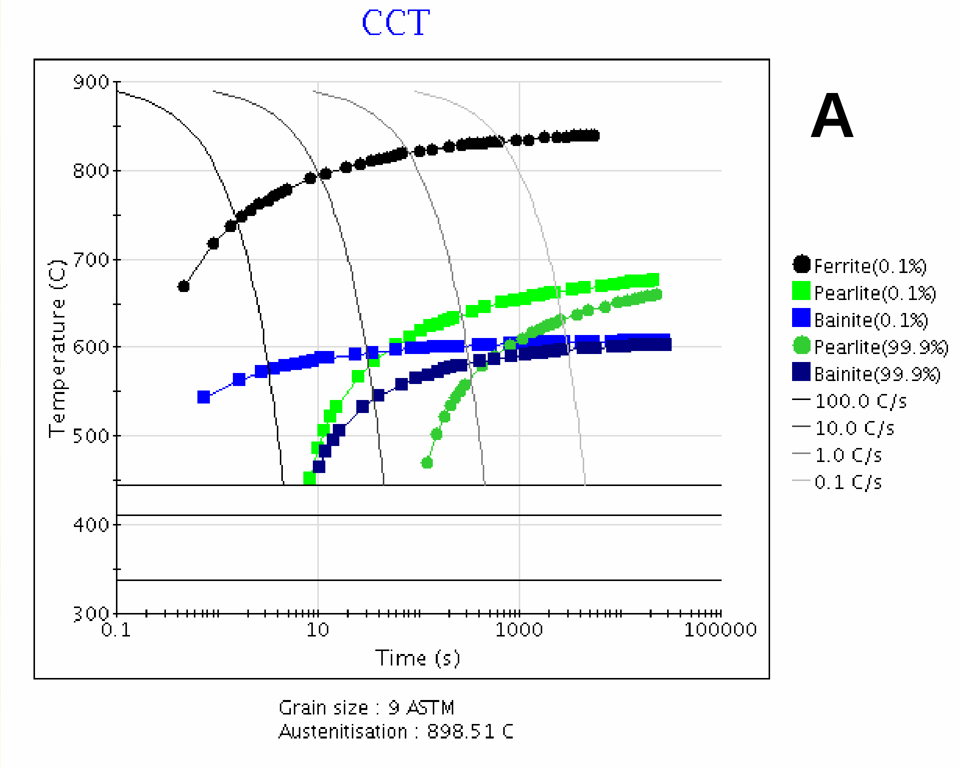




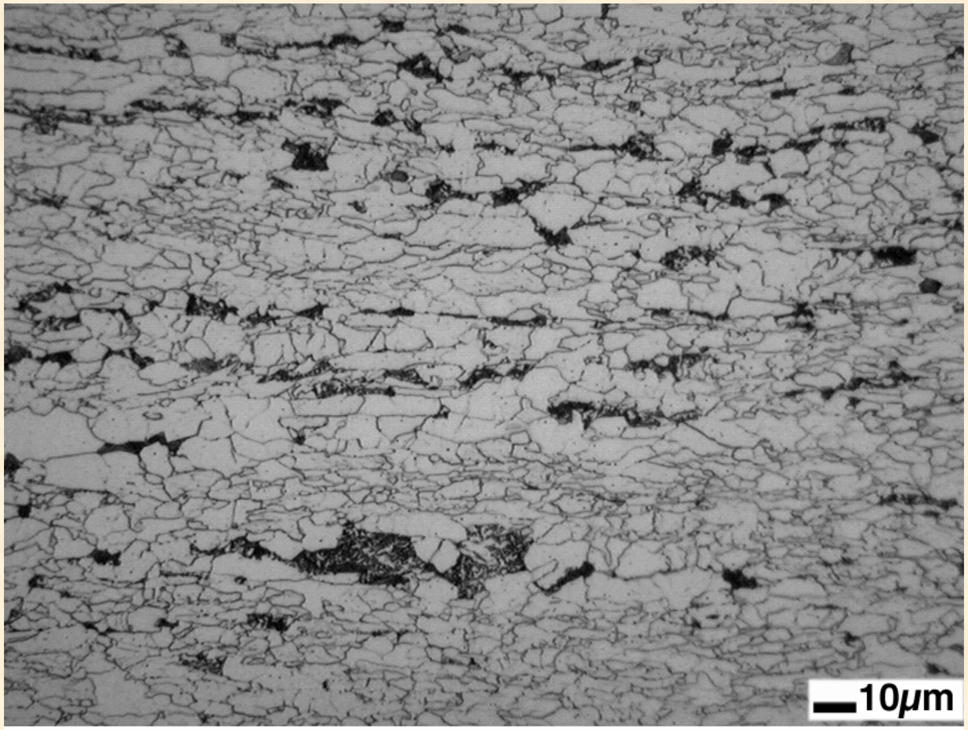


Pearlite start line shifts to the right (time increases) from A to C

Comparison Between CCT Diagram and Observed Microstructure of Alloy A



Transverse Section



Microstructure of Alloy A shows presence of both ferrite and pearlite

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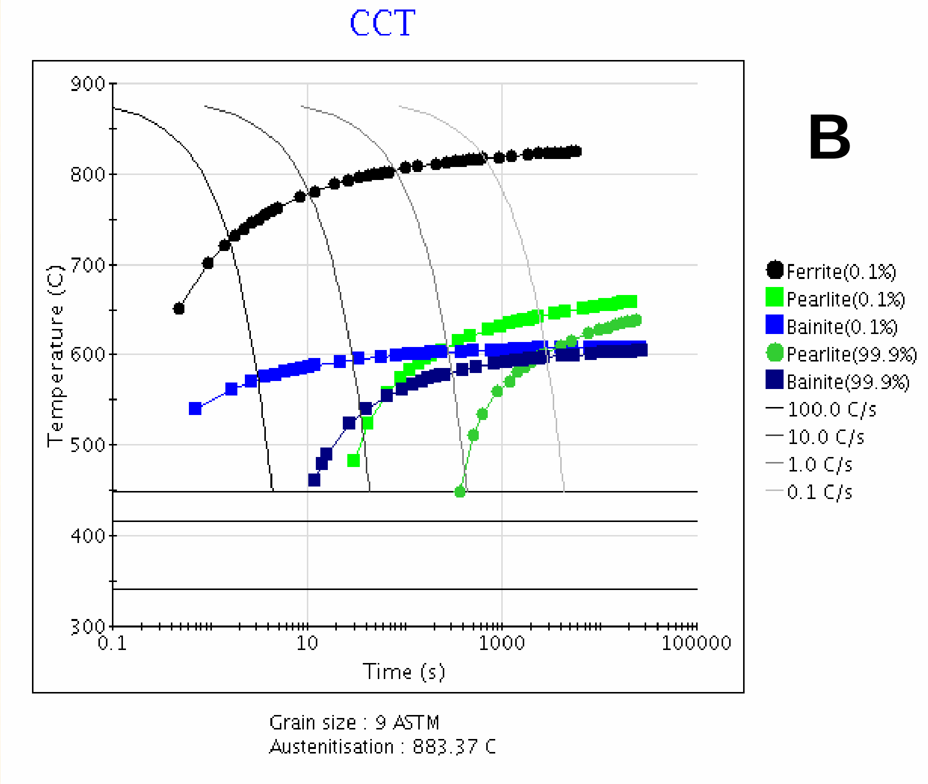
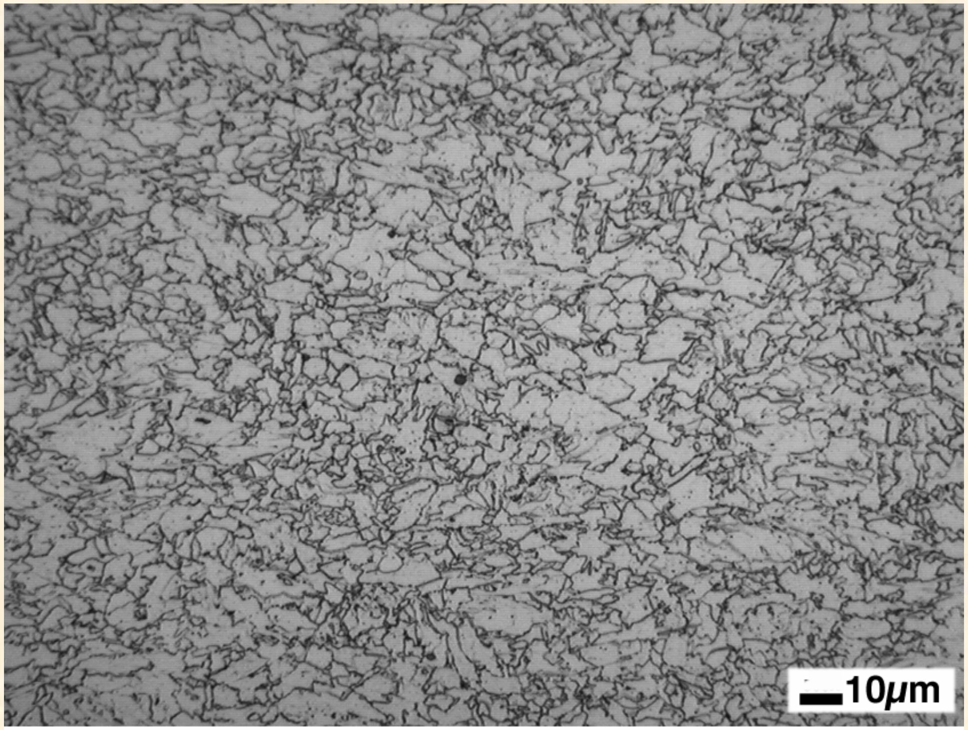
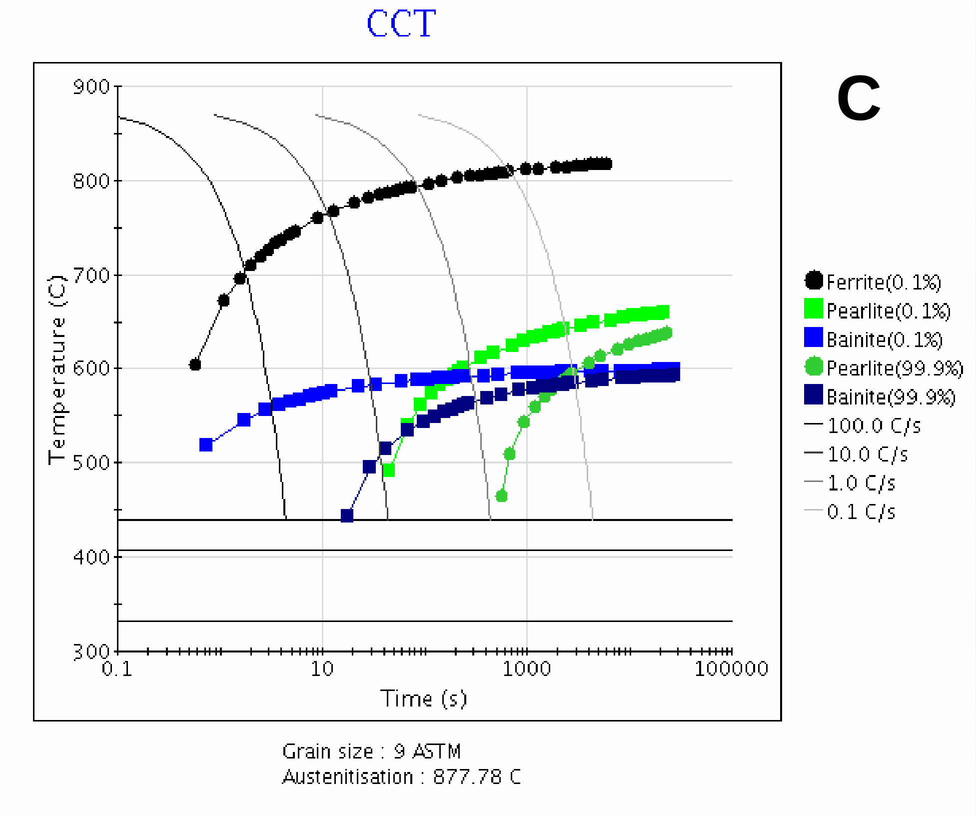
Comparison Between CCT Diagram and Observed Microstructure of Alloy B

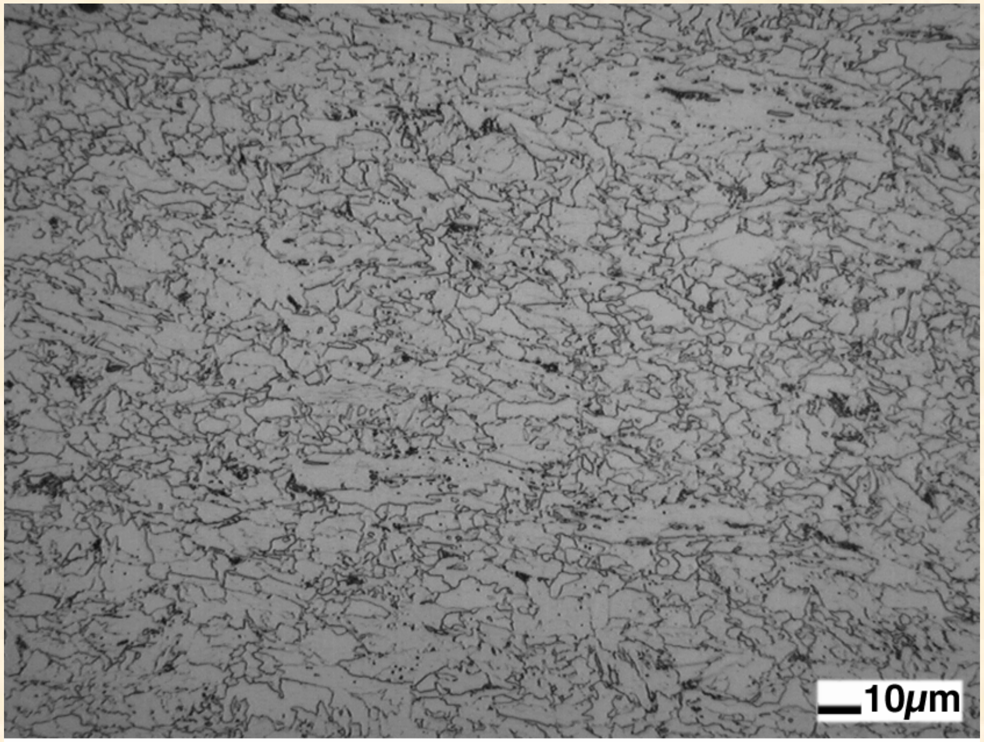




Microstructure of Alloy B shows very little pearlite mixed with ferrite and acicular ferrite

Comparison Between CCT Diagram and Observed Microstructure of Alloy C





Microstructure of Alloy B shows very little pearlite mixed with ferrite and acicular ferrite

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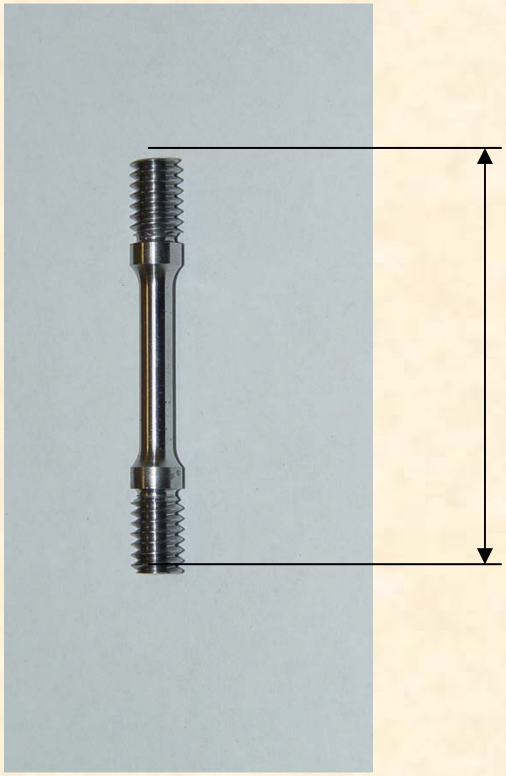
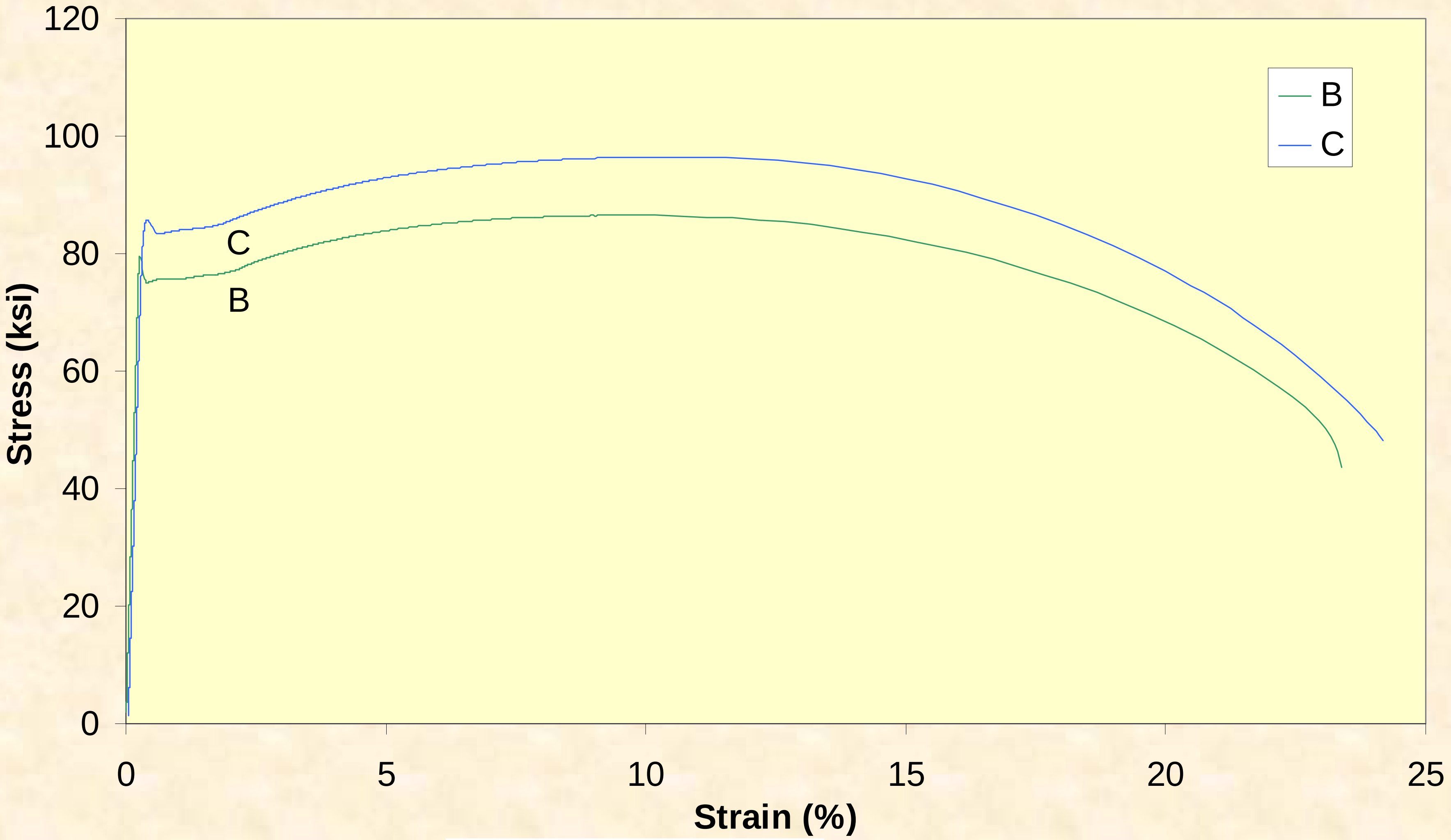
Specimens Have Been Prepared for Evaluation of Hydrogen Embrittlement with *ex-situ* Tests

- Tensile specimens conforming to ASTM-E8 have been machined from three alloys, A, B, and C
- Tensile tests have been conducted at ORNL
- Samples have been sent to Dr. Brian Somerday at Sandia National Laboratory, Livermore for study of embrittlement using
  - •Ex-situ high-pressure hydrogen charging, and
  - •Tensile testing



Tensile Tests Are Being Performed in Transverse-Oriented Samples at ORNL



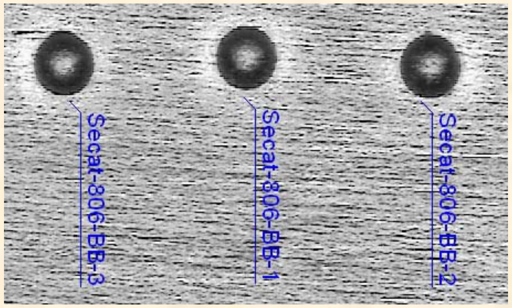
Mechanical Properties Determined at ATC using the Automated Ball Indentation (ABI) test of the SSM System

ATC’s Patented SSM system is used to determine the following key mechanical properties from each single ABI test :

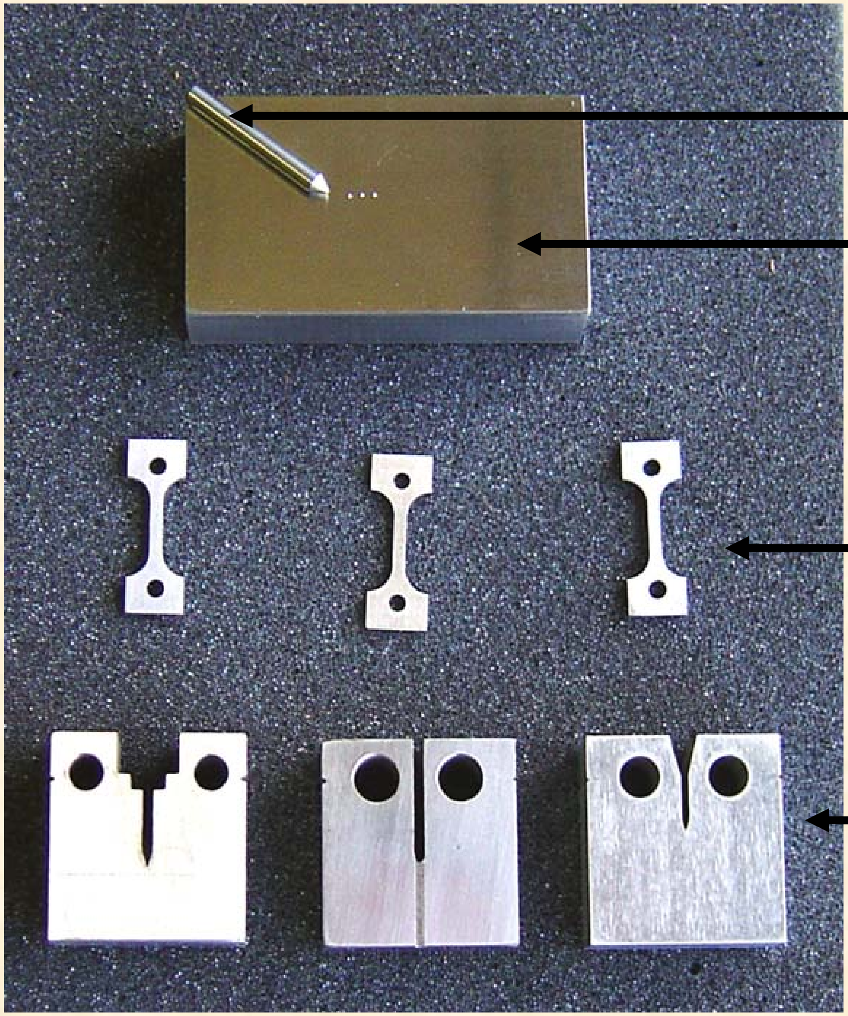
- True-Stress/True-Plastic-Strain
- Yield Strength
- Work-Hardening Exponent and Strength Coefficient
- Estimated Engineering Ultimate Tensile Strength
- Uniform Ductility
- ABI-Hardness
- Fracture Toughness and Reference Temperature

Baseline Tensile and Automated Ball Indentation (ABI) Tests Have Been Completed at ATC

Comparisons were made between the non-destructive physical testing utilizing the ABI method vs. traditional destructive physical testing.



ABI indents made using a 0.030-in (0.76-mm) Tungsten Carbide indenter



Ball Indenter

Block for ABI Tests

Miniature Tensile Specimens

Fracture Toughness Specimens

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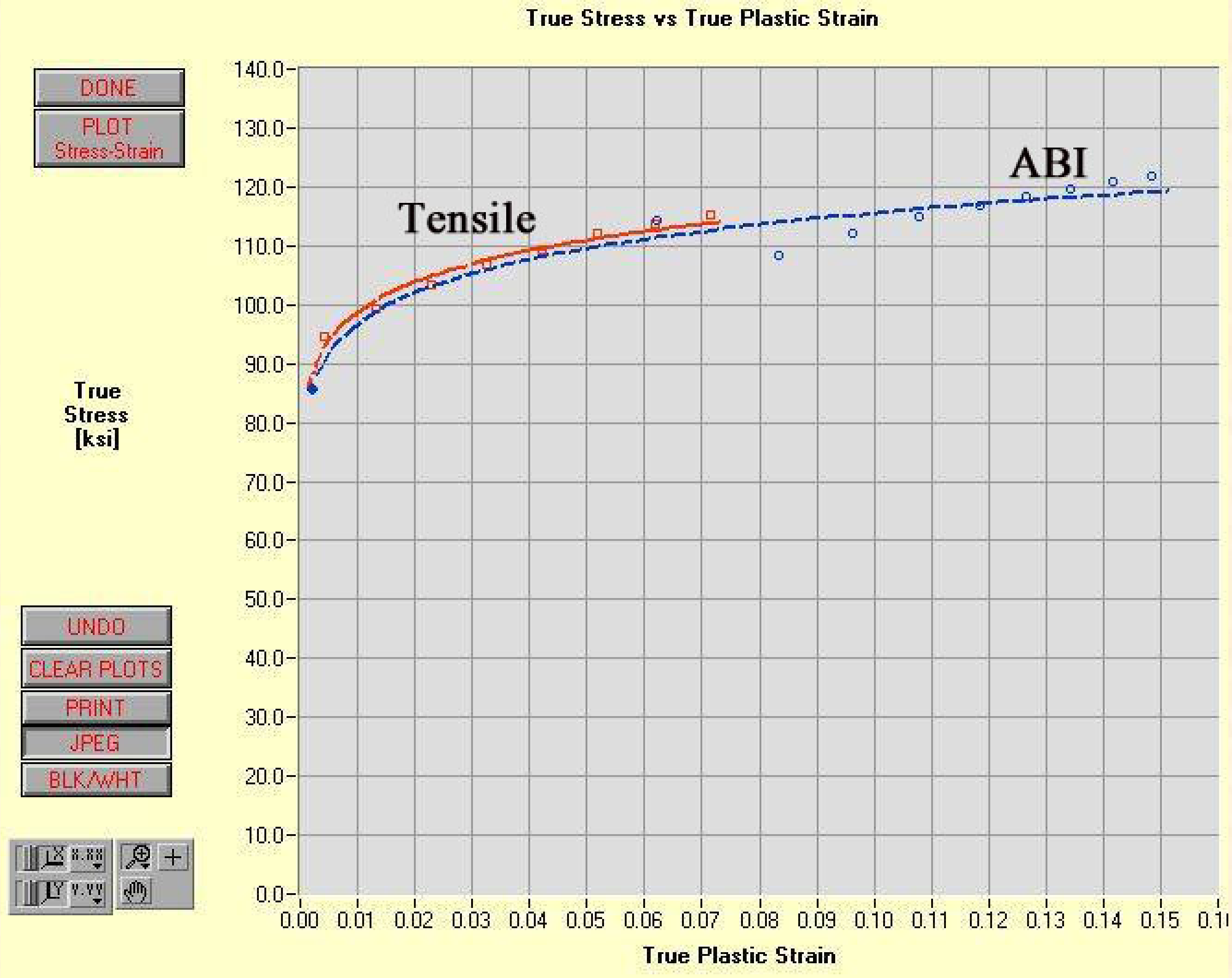
Example Comparison Between True-Stress/True-Strain Data Using Miniature Tensile Testing and ABI Testing of Steel Sample C



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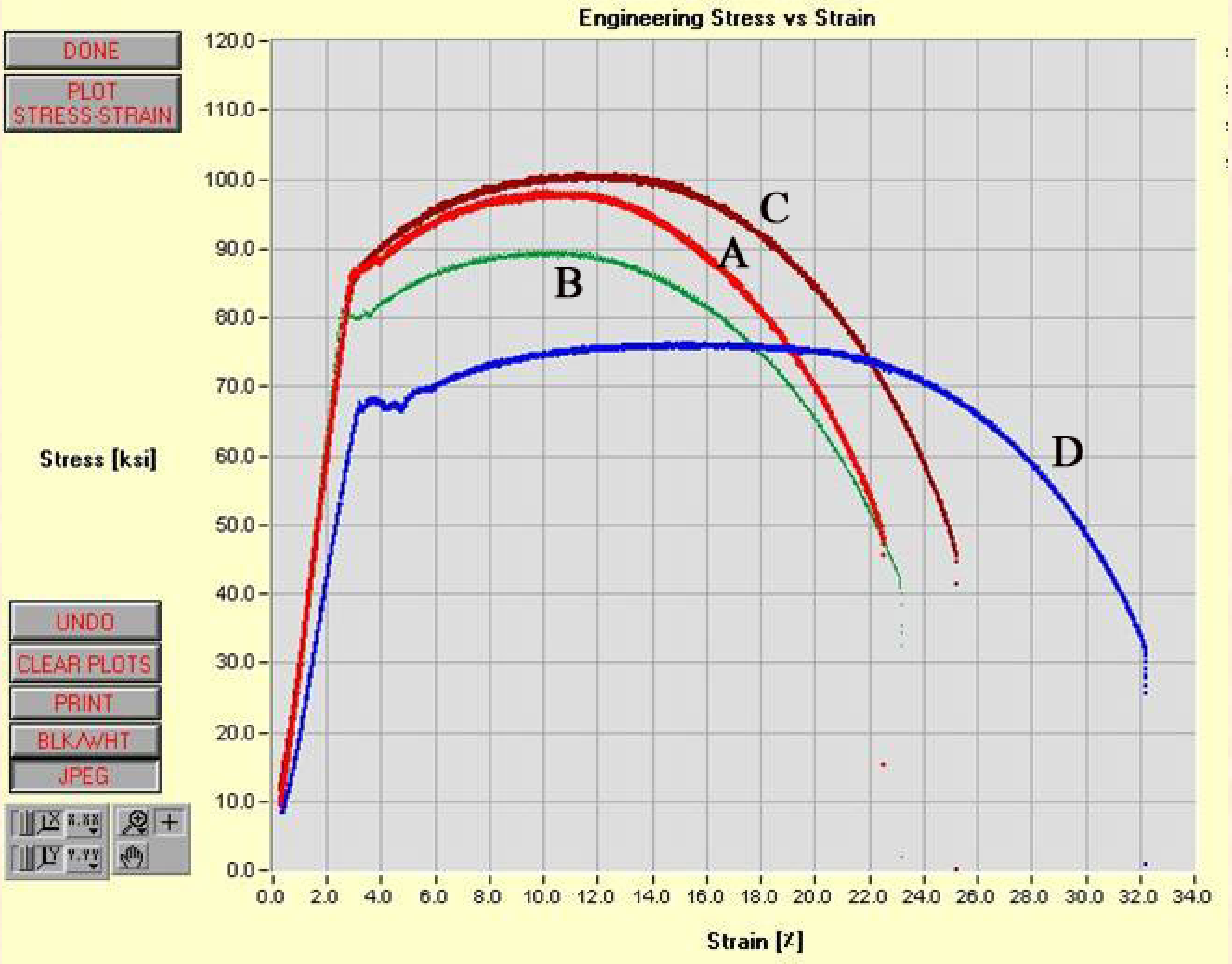
Baseline Tensile Tests of Four Selected Steels Have Been Completed by ATC



Summary of ABI Measured Mechanical Properties of Four Selected Steels

Sample ID	YS	Calc. Eng.	Calc. Unif.	YS/UTS	Hardness	Fracture
All API Plate Samples	(ksi)	UTS	Ductility	Ratio	ABI-H	Toughness
		(ksi)	(%)			(ksi*in^0.5)
API X70, A-1	82.8	102.3	7.9	0.81	242	217.8
API X70, A-2	82.3	101.3	7.8	0.81	240	216.2
API X70, A-3	81.4	100.9	8.0	0.81	239	214.4
API X80, B-1	74.9	93.4	8.1	0.80	220	207.0
API X80, B-2	75.0	94.7	8.3	0.79	221	210.4
API X80, B-3	77.4	94.3	7.6	0.82	225	208.5
API X80, C-1	86.4	104.8	7.5	0.82	252	219.4
API X80, C-2	84.8	104.5	7.9	0.81	248	216.3
API X80, C-3	86.2	105.9	7.6	0.81	252	218.9
API X60, D-1	64.6	77.6	7.3	0.83	185	191.6
API X60, D-2	63.9	77.6	7.5	0.82	185	190.7
API X60, D-3	63.8	78.4	8.1	0.81	189	194.5

Future work

- Complete assembly of equipment for *in-situ* mechanical testing of materials in high hydrogen pressures along with setting up associated safety measures and controls at ORNL
- Complete fabrication and installation of high pressure hydrogen chamber to perform *in-situ* Automated Ball Indentation (ABI) mechanical testing for various hydrogen exposure times at ATC
- Complete measurement of mechanical properties and hydrogen embrittlement characteristics of at-least two down-selected steels at ORNL and ATC
- Complete thermodynamic, and kinetic modeling of initial down-selected steel compositions
- Complete microstructural characterization of tested steels before and after exposure to hydrogen to understand the effect of microstructure on embrittlement

Details of Approach-Task 3

- **Task 3: Develop coatings to minimize dissolution and penetration of hydrogen**
  - Laboratory studies have shown that surface barrier coatings (both metallic and non-metallic) including stainless steel liner materials are effective in reducing hydrogen embrittlement due to an external source of hydrogen
  - This work will evaluate the effectiveness of coatings from two industrial partners: multi-component oxides with rare earths from C^3, and glass coatings from Schott North America
  - Coating chemistries and processes to deposit coatings on steel substrates (including techniques appropriate for *in-situ* deposition in the field) will be developed
  - Quality, integrity of coatings, adhesion to the substrate, microstructure of coatings and that of substrates, wear characteristics, and barrier properties of coatings will be characterized
  - Chemistries of coatings, and deposition processes will be modified to optimize required properties and two best coating compositions will be down-selected for Task 4

Proposed work for FY 2005

- Identify processing needs for deposition of coatings on steel substrates (thermal expansion coefficients, temperature and time of curing, wetting characteristics etc) and deposit coatings
- Characterize coatings with particular reference to their adhesion with the substrate, integrity (free from pinholes, cracks etc), and the substrate for structural changes due to the deposition process

Status of Coatings Work at Schott NA

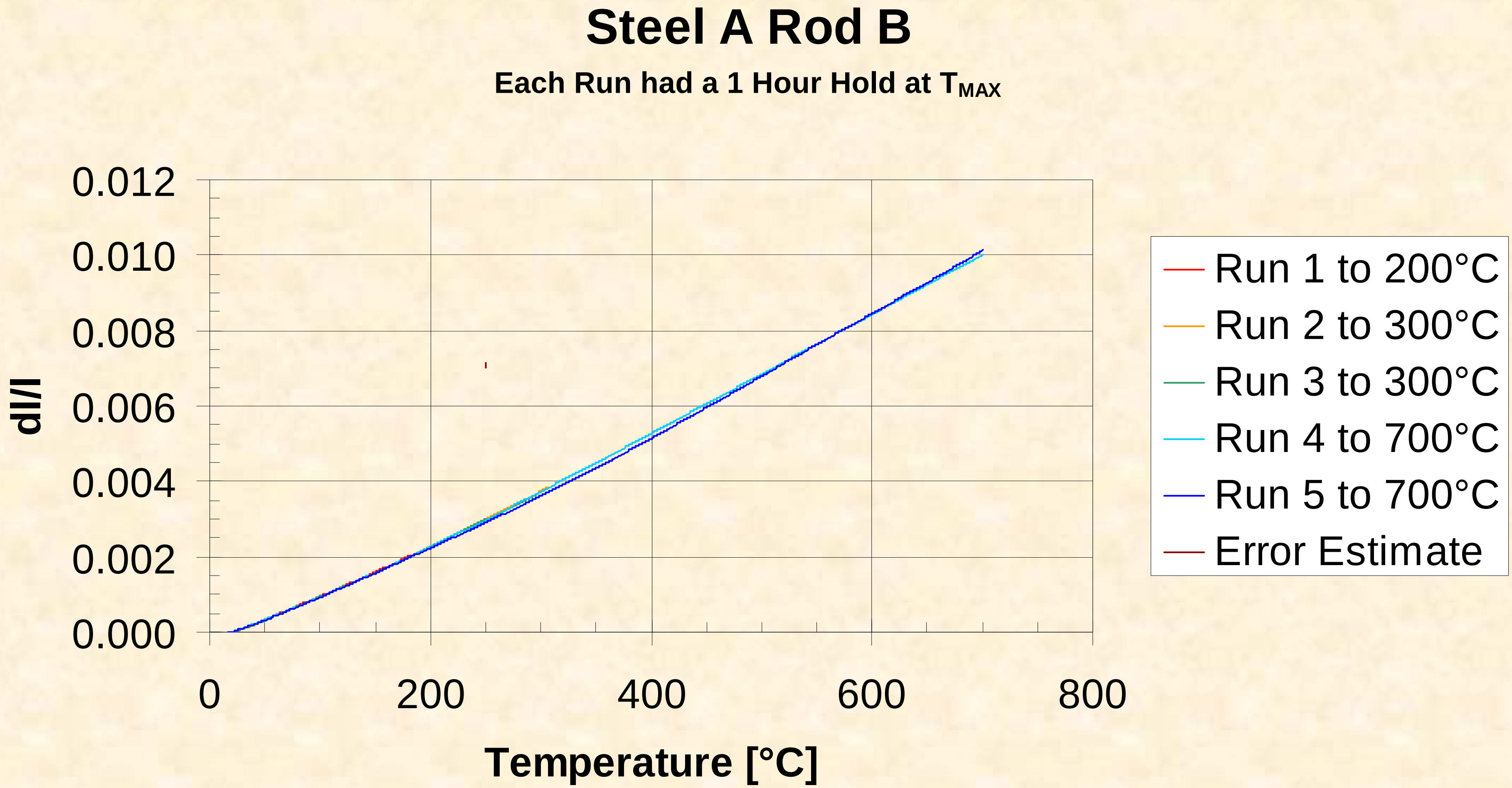
- Steel Characterization
  - Measured thermal expansion of two selected steel compositions

- Glass Development
  - Selected two glass compositions, and adjusted composition to match the thermal expansion of said steel compositions
  - Manufactured 0.5l of each glass for coating tests

- Coating
  - Based on glass properties, selected coating approach for samples and started to optimize technique

- Next Steps
  - Supply coated steel samples to ORNL to measure H_2 permeation

Thermal Expansion of Steel A



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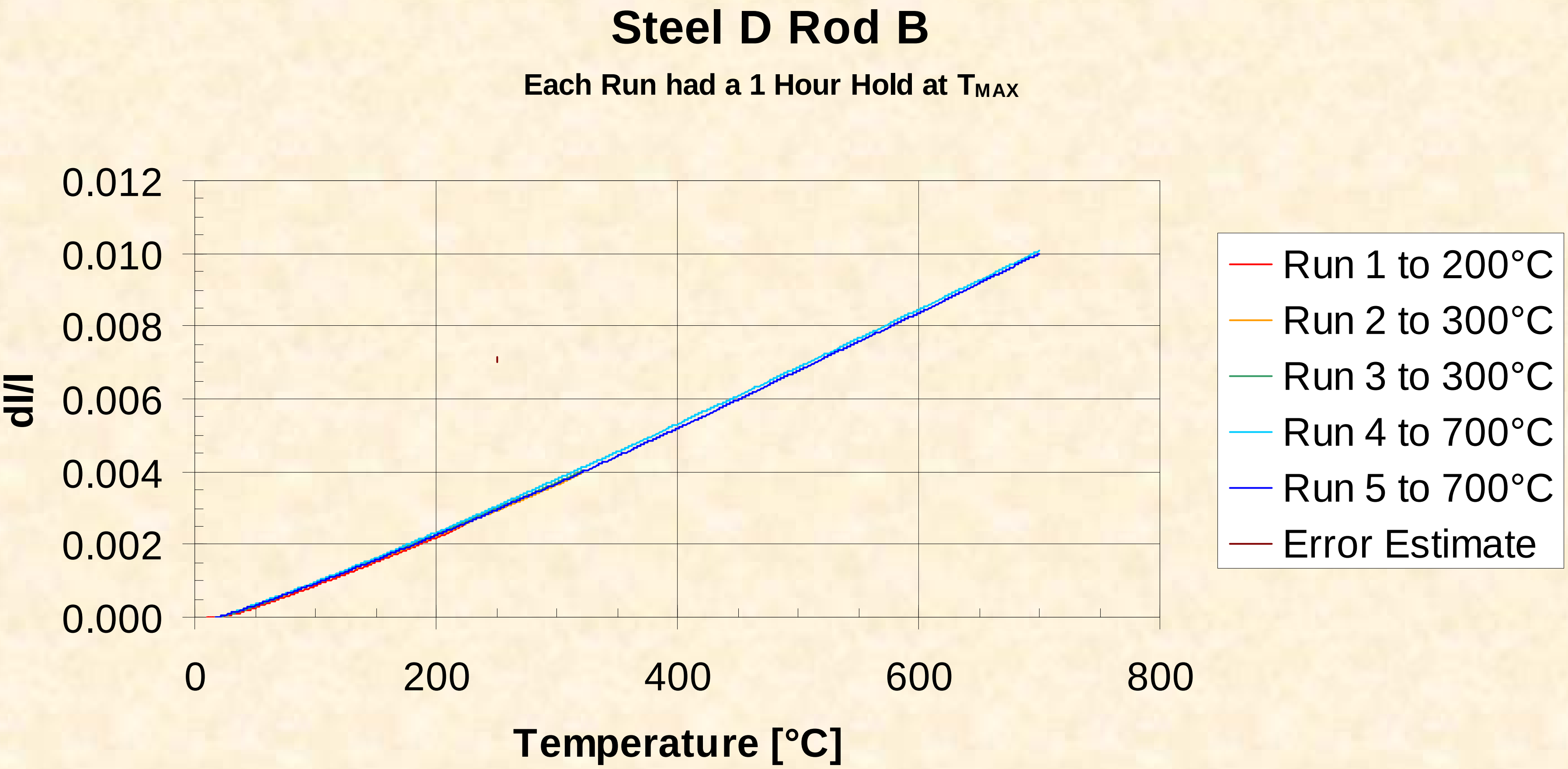
Thermal Expansion of Steel D



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Comparison of the Thermal Expansion of the Two Steels

Steel A

All CTE values below are in ppm/K

Run#	CTE20..200	CTE20..300	CTE20..416	CTE20..460	CTE20..520	CTE20..700
1	12.66	Ice pack was not used on Run#1. Result is hook at start of data and a lower CTE value then expected.				
2	12.51	13.33				
3	12.54	13.28				
4	12.54	13.29	13.93	14.11	14.32	14.71
5	12.37	12.88	13.62	13.90	14.24	14.89

Steel D

All CTE values below are in ppm/K

Run#	CTE20..200	CTE20..300	CTE20..416	CTE20..460	CTE20..520	CTE20..700
1	12.11	Ice pack was not used on Run#1. Result is hook at start of data and a lower CTE value then expected.				
2	12.37	12.95				
3	12.62	13.20				
4	12.91	13.51	14.01	14.17	14.35	14.80
5	12.46	13.10	13.72	13.92	14.16	14.70

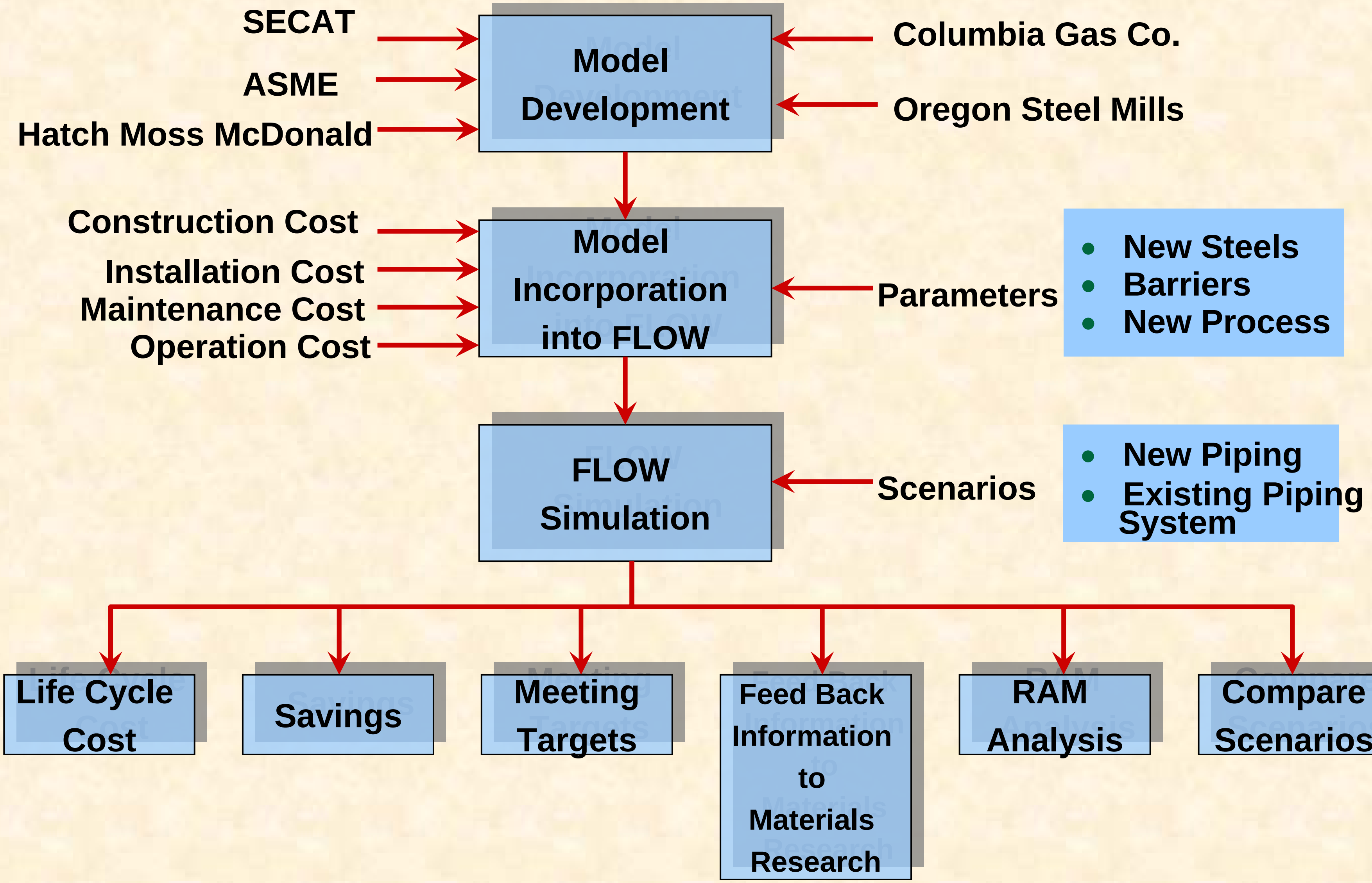
Future work on Coatings

- **Coatings:**
  - Barrier properties of the coatings will be characterized using permeability testing
  - Coating compositions and/or depositions processes will be modified based on the results of physical, mechanical, and barrier property testing
  - Coatings with new compositions will be deposited and tested

Details of Approach-Task 5

- **Task 5: Perform financial analyses and assist in the incorporation of knowledge into codes and standards**:
  - The cost of a typical pipeline installation includes many components such as that of materials, construction, inspection, engineering survey, right of way permits, and overhead costs; cost of ownership also includes the cost of maintenance over the lifetime of the pipeline
  - As part of this project, with the help of industrial partners and an ORNL developed financial analysis model-FLOW, we will analyze the current cost components of pipeline construction and maintenance, analyze potential savings that could be feasible, and methods to achieve cost reductions
  - Cost analysis will be updated as the additional cost of newly developed technologies become available and the different possible scenarios for reduction in costs of construction and maintenance will be reevaluated
  - Work will be coordinated with the H2A analysis being carried out as part of the DOE hydrogen program
  - The results of this analysis will be used to re-focus the project if and as appropriate vs. the goal, objectives, and targets for the DOE hydrogen Delivery Multi-Year R&D Plan

Steps in Financial Analysis



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ASME

Hatch Moss McDonald

Model Development

Columbia Gas Co.

Oregon Steel Mills

Construction Cost

Installation Cost

Maintenance Cost

Operation Cost

Model Incorporation into FLOW

Parameters

- New Steels
- Barriers
- New Process

FLOW Simulation

Scenarios

- New Piping
- Existing Piping System

Life Cycle Cost

Savings

Meeting Targets

Feed Back Information to Materials Research

RAM Analysis

Compare Scenarios

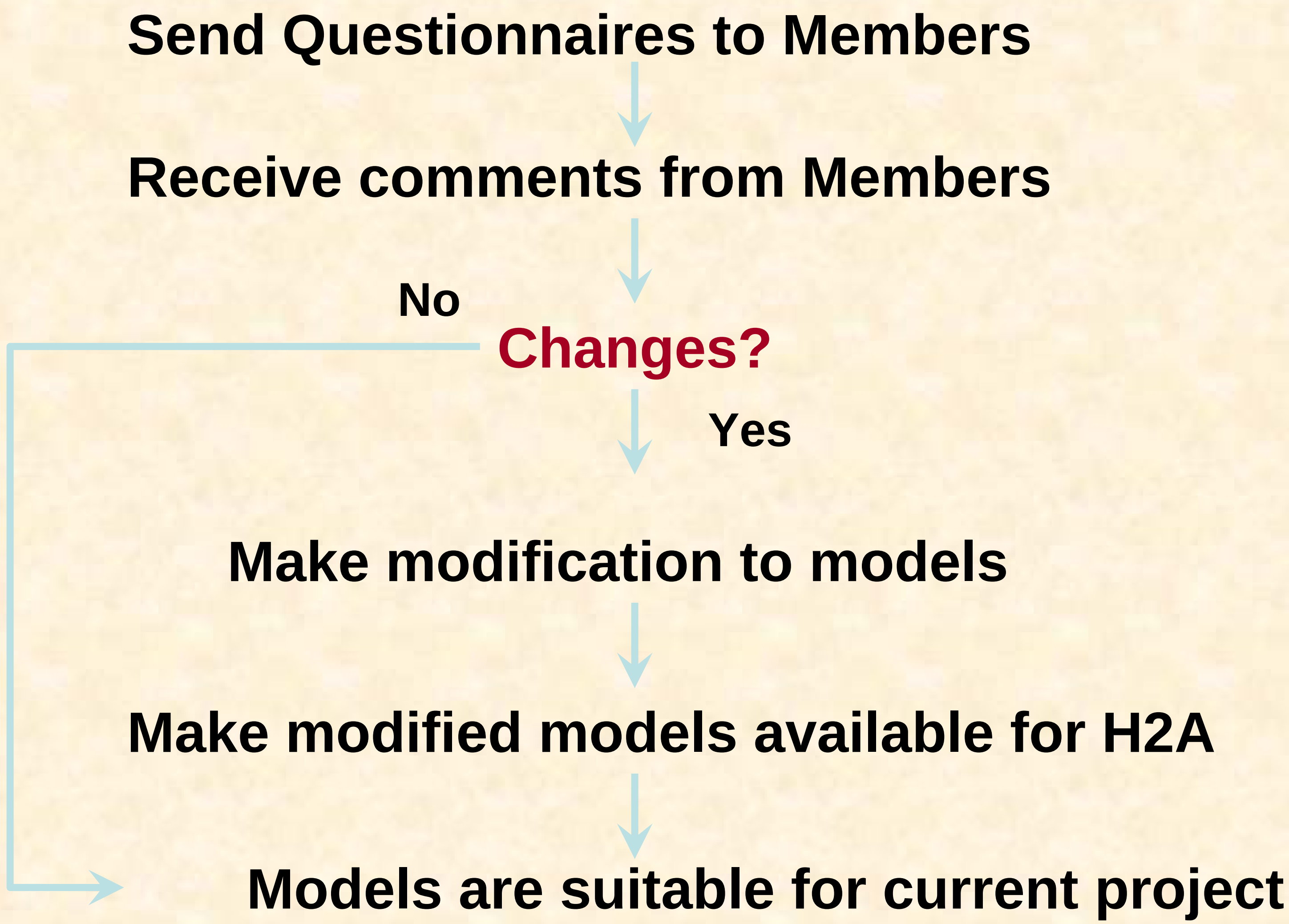
Proposed Work for FY 2005

- Obtain from industrial partners, data on the magnitude of the individual components of costs related to pipeline construction and maintenance
- Develop a preliminary model for the pipeline cost function using FLOW for evaluating sensitivity, and uncertainty
- Coordinate information collection and model development with the H2A effort

Progress on Task 5

- H2A model has been analyzed and extracted equations required for cost analyses
- Model will tailored for the current project
- Questionnaire has been prepared to collect information from the industry on various relevant cost factors specific to the on-going work

Next Steps



Send Questionnaires to Members

Receive comments from Members

No

Changes?

Yes

Make modification to models

Make modified models available for H2A

Models are suitable for current project

Future Work on Financial Analyses

- Finalize cost model for steel pipelines
- Analyze various scenarios using FLOW software and evaluate sensitivities to various parameters in the cost function
- Derive potential avenues for achieving cost savings from the analyses of various scenarios
- Identify research priorities based on analyses of potential cost savings
- Update cost functions as new information on developed technologies become available and reevaluate scenarios