Fusion Materials Science Compatibility and Welding program

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Fusion Materials Compatibility Research

- Why recent focus on V alloy oxidation kinetics:
  - Chemical compatibility of vanadium with Li, Pb-Li is already sufficiently understood (capsule tests and limited loop tests; additional loop testing would be required before proceeding to detailed reactor design)
  - Can V alloys be used with non-Li reactor coolants (Pb-Li, Sn-Li, He, etc.), where pickup of entrained oxygen is an issue
  - Since V has a large affinity for oxygen, pickup is controlled by kinetic factors rather than thermodynamics

- Capsule compatibility tests for SiC/Pb-Li at 800-1000˚C are scheduled to begin in early FY02 (feasibility issue for alternative blanket system identified in fusion design concept program)

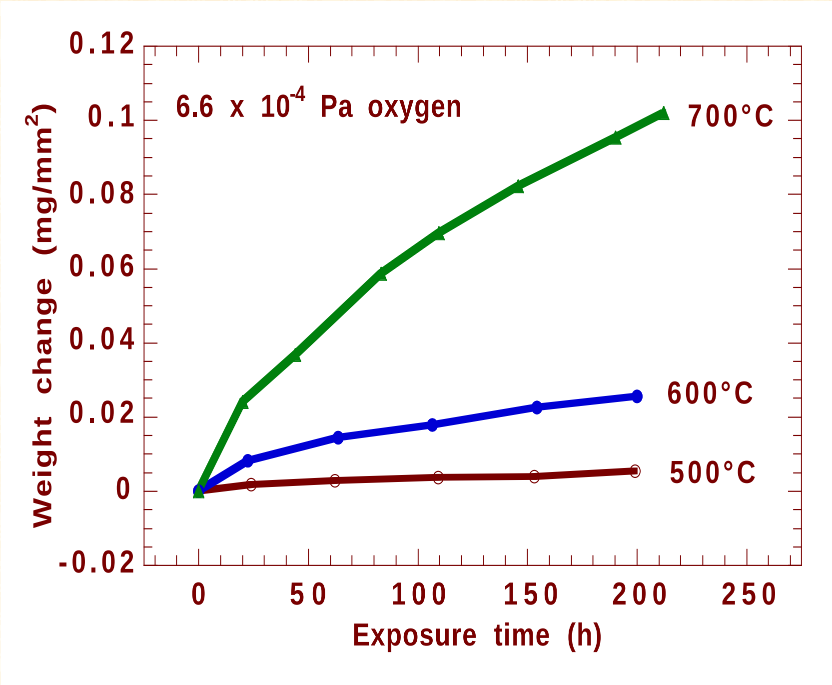
- Mo/W oxidation analysis (funded by APEX)

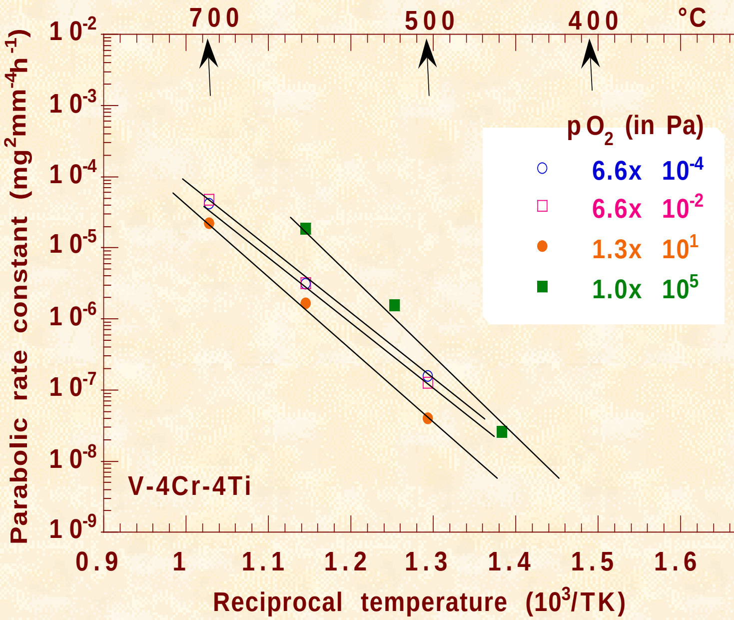
Oxygen and Hydrogen Interactions with V-Base Alloys

Objectives

- Evaluate the mechanisms for oxidation of V-(4-5)Cr-(4-5)Ti alloys in oxygen pressures in the range of 10^{-6} to 10^{5} Pa at temperatures in the range 350-700°C
- Establish the microstructural characteristics of the materials after oxidation
- Develop oxidation models to describe the role of oxygen partial pressure in the environment, oxygen concentration in the alloy and oxidation rate on the tensile properties of the alloys
- Determine the threshold oxygen pressure for crack initiation and establish the cracking propensity for the alloys in oxygenated environments
- Determine the solubility of hydrogen in V-Cr-Ti alloys and evaluate the effects of hydrogen on their mechanical properties

Oxidation of V-Alloys at intermediate P_{O_2} exhibits parabolic kinetics



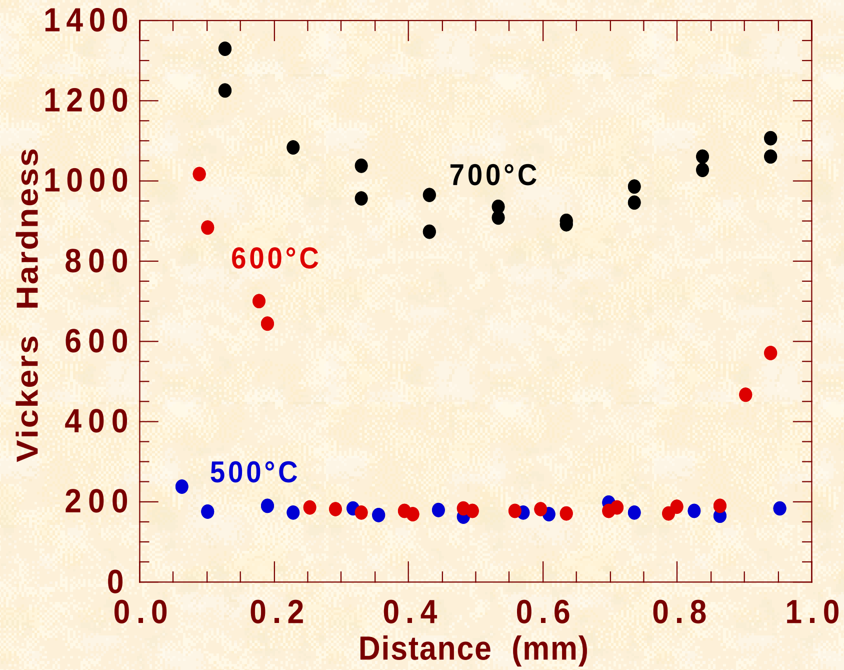


Time-dependent weight gain of V-4Cr-4Ti in intermediate pressure oxygen at 500-700°C

Parabolic oxidation rate constant for V-4Cr-4Ti in intermediate pressure oxygen at 450-700°C; Arrhenius activation energy is Q~180 kJ/mol

Oxidation of V-Alloys at Intermediate P_{O_2}

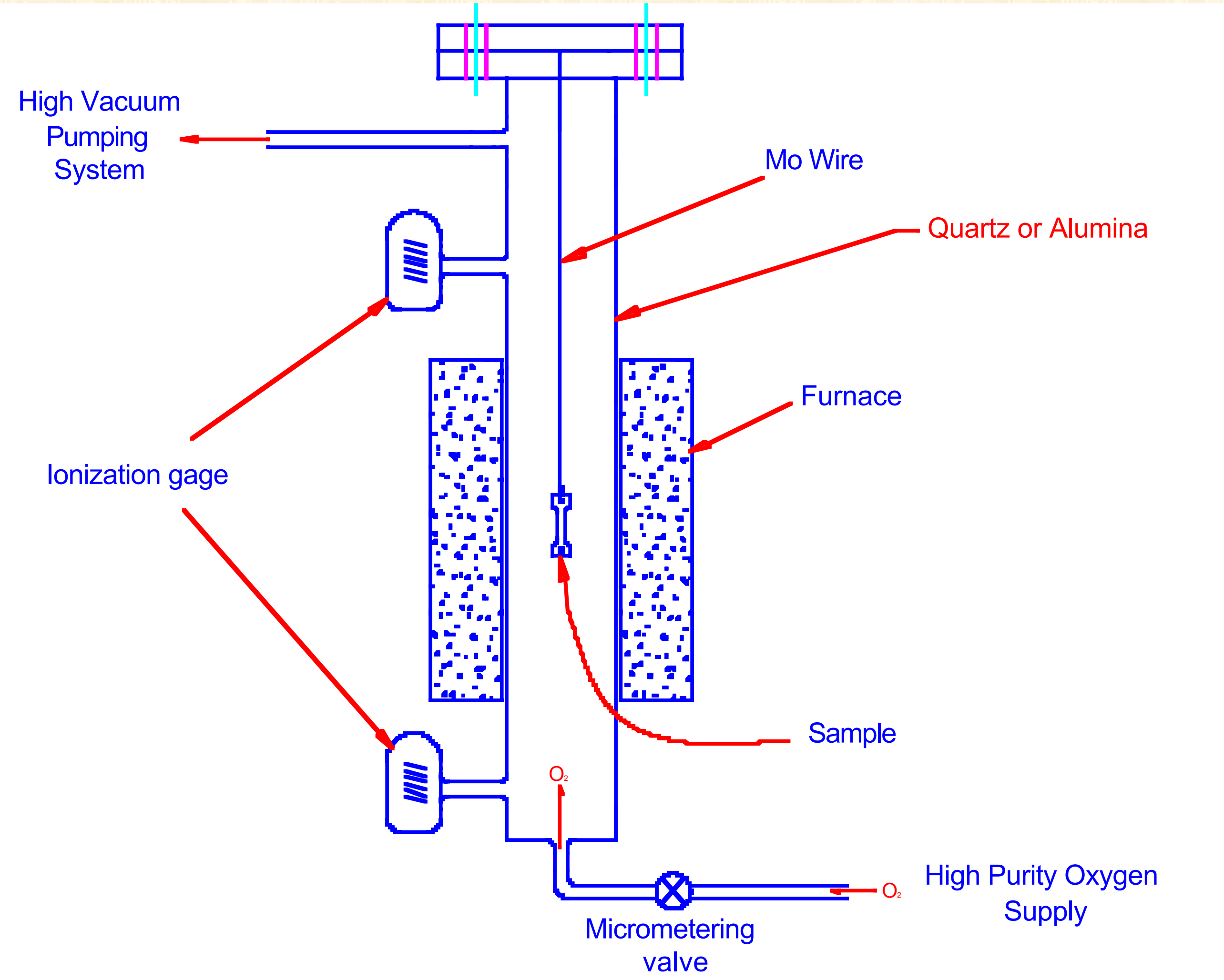
Oxygen pressure (Pa)	Temperature (°C)	Oxides identified by XRD
6.6×10^{-4}	500	VO_2, TiV_4O_{10}
	700	VO_2, $V_{16}O_3$, CrV_2O_6
6.6×10^{-2}	600	VO_2, V_2O_4, $CrVO_4$
	700	VO_2, V_2O_4, $CrVO_4$
13.3	600	VO_2, V_2O_4
	700	VO_2, V_2O_4, $CrVO_4$
1×10^{5}	375	V_2O_5, V_2O_3, V_3O_7
	600	V_2O_5, $V_2Ti_3O_9$, VO_2



Surface oxides identified on V44 Alloy after exposure to low-P oxygen at various test temperatures

Hardness profile in V44 alloy after exposure to low-P oxygen at 500, 600 and 700°C

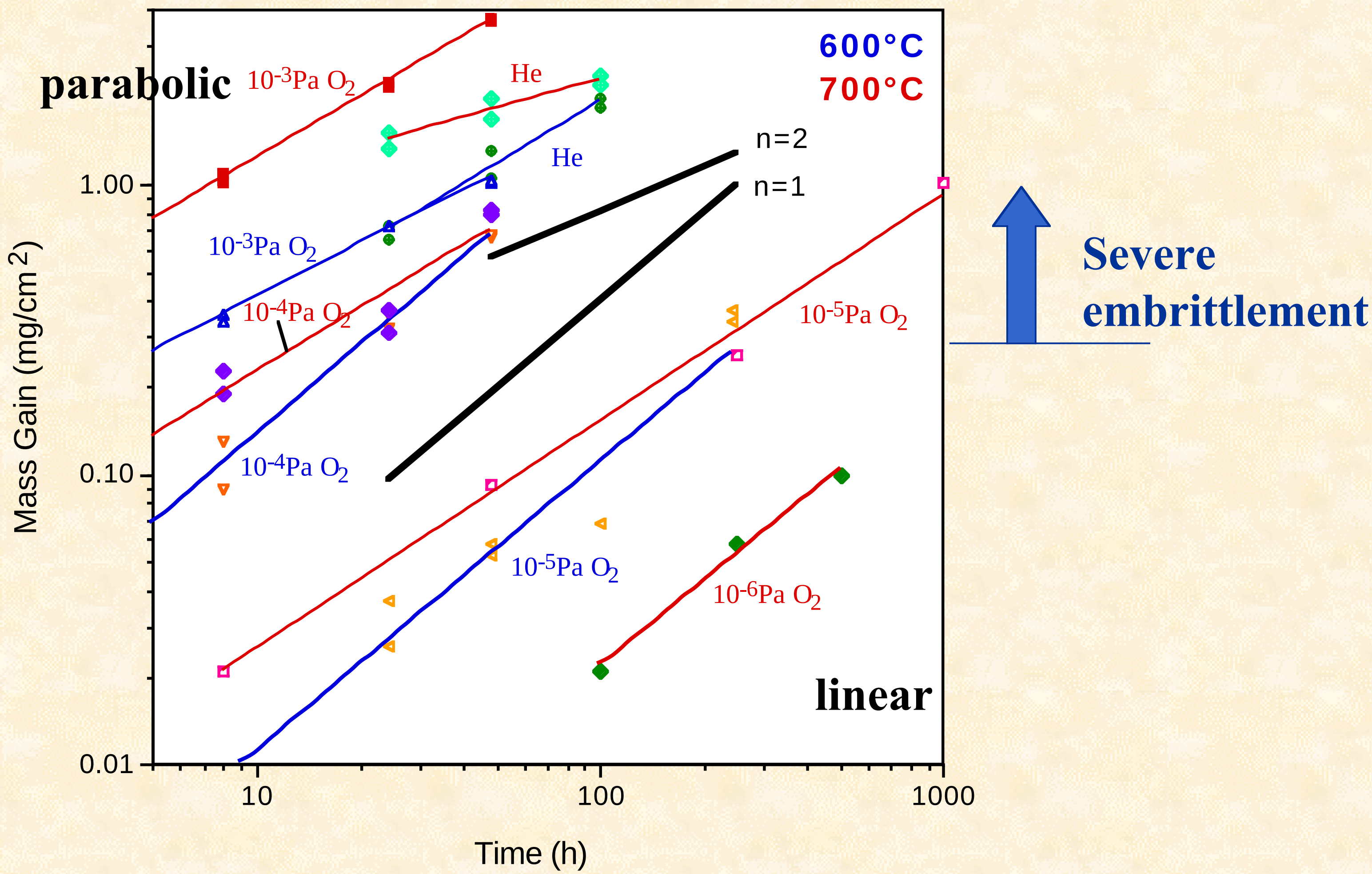
Reaction Chamber used for low pressure oxidation studies (Al_2O_3 tube, base pressure 10^{-7} Pa)



Specimen pressure:
Input from two gauges
+ pump speed
& conductance

Gas uptake measured by specimen mass gain
(O content confirmed by combustion analysis)

At low oxygen pressure, refractory metals do not form a protective external oxide; oxygen is absorbed internally

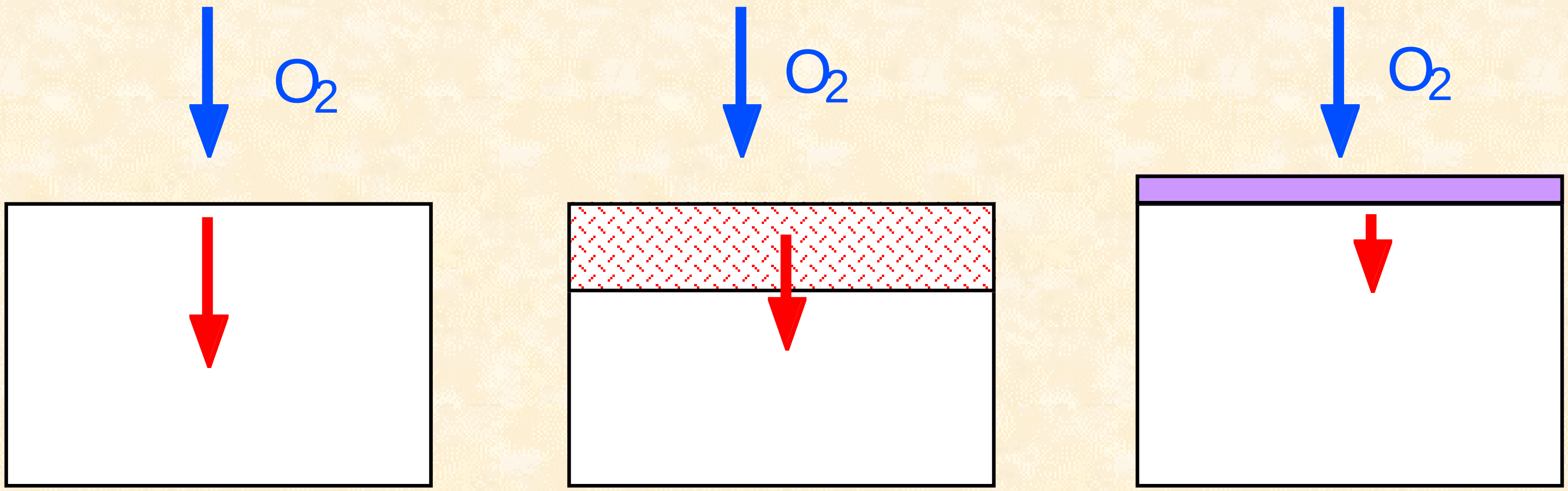


Most values are between linear (n=1) and parabolic (n=2)

Linear kinetics observed for lowest pressures at 600° and 700°C

Oxidation studies in medium-pressure helium (to simulate UHP-He) confirm kinetics

Mechanistic Explanation



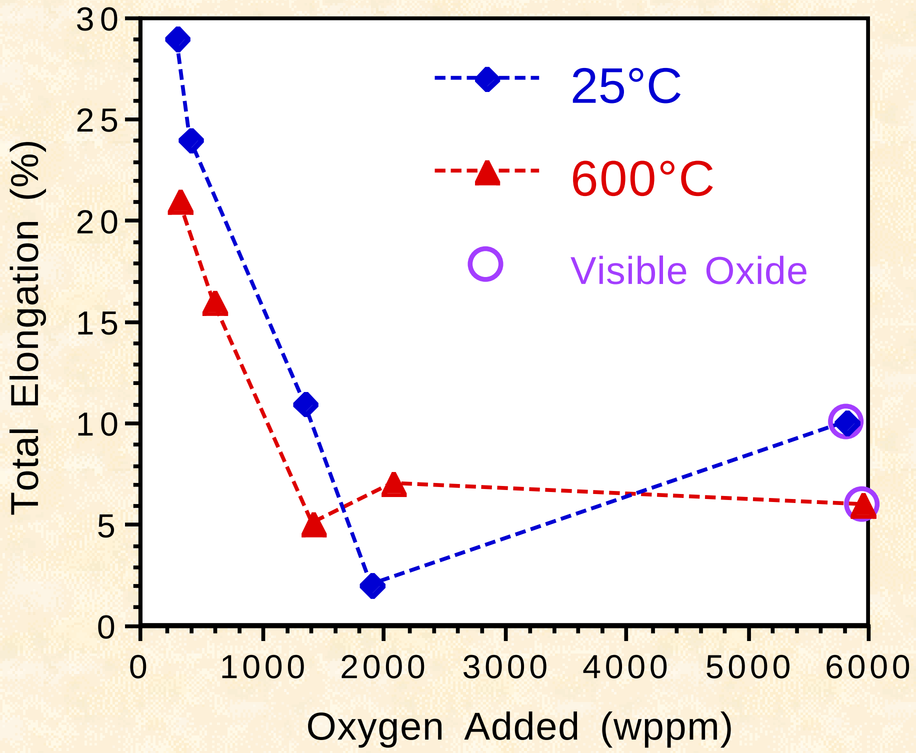
low O levels
gas phase limited
(linear)

near surface saturated
diffusion limited
(parabolic)

surface oxide layer
diffusion limited
(parabolic)

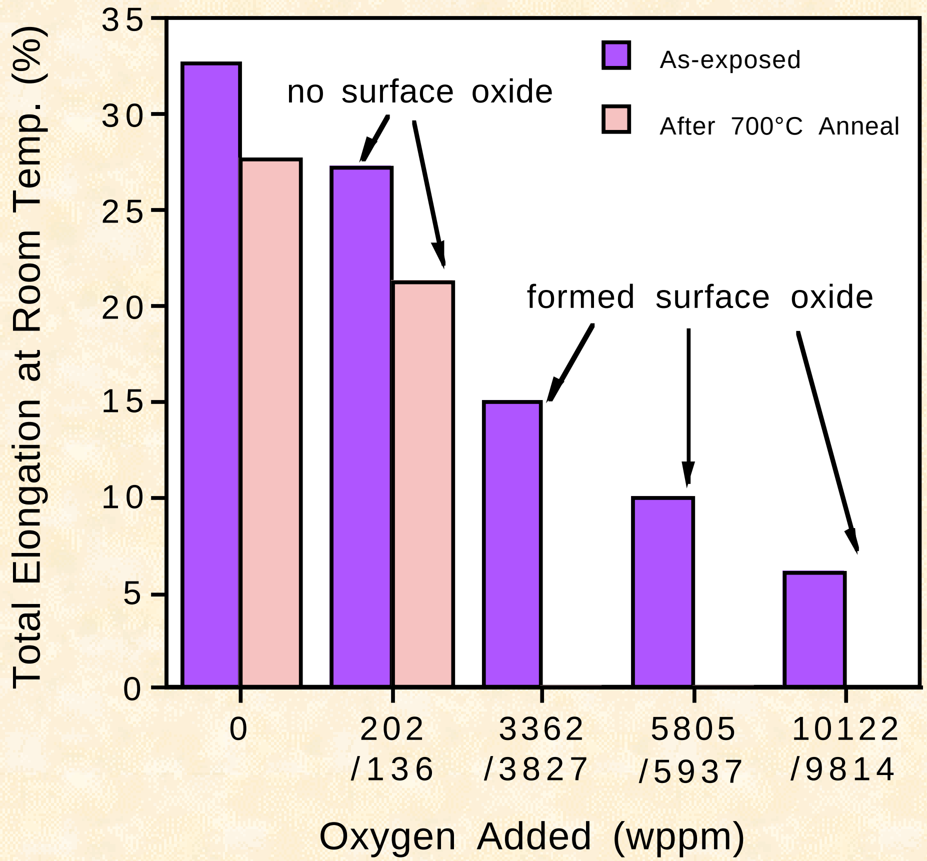
It is likely that all 3 mechanisms are occurring with V-4Cr-4Ti at 600°-700°C
Linear kinetics change to parabolic kinetics as O level in alloy increases
Linear regime is most relevant for design, otherwise V-4Cr-4Ti is embrittled!

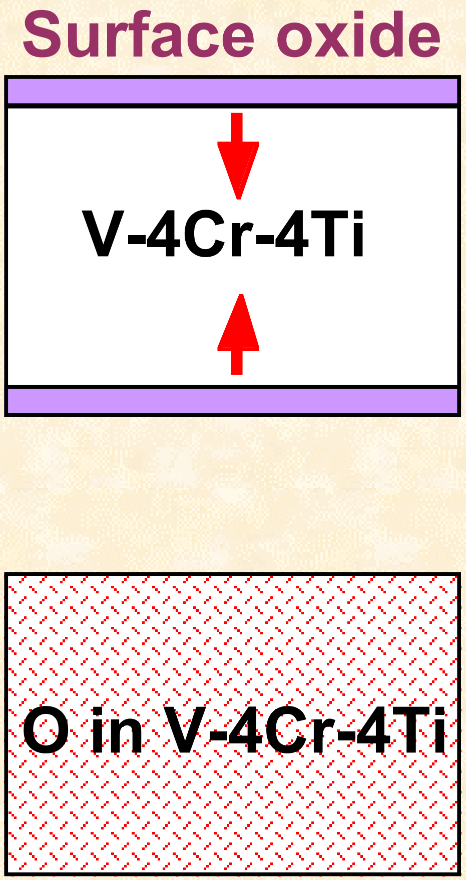
Tensile Elongation Decreases Rapidly with Oxygen Uptake



Measured oxygen levels include surface oxide and oxygen in solution
Decreasing ductility to approximately 2000wppm (all O in solution)
Very high O levels (in He or Ar) - no further drop in ductility
=> additional oxygen as surface oxide

Surface oxide in V Alloys is not Protective (2000h, 700˚C)

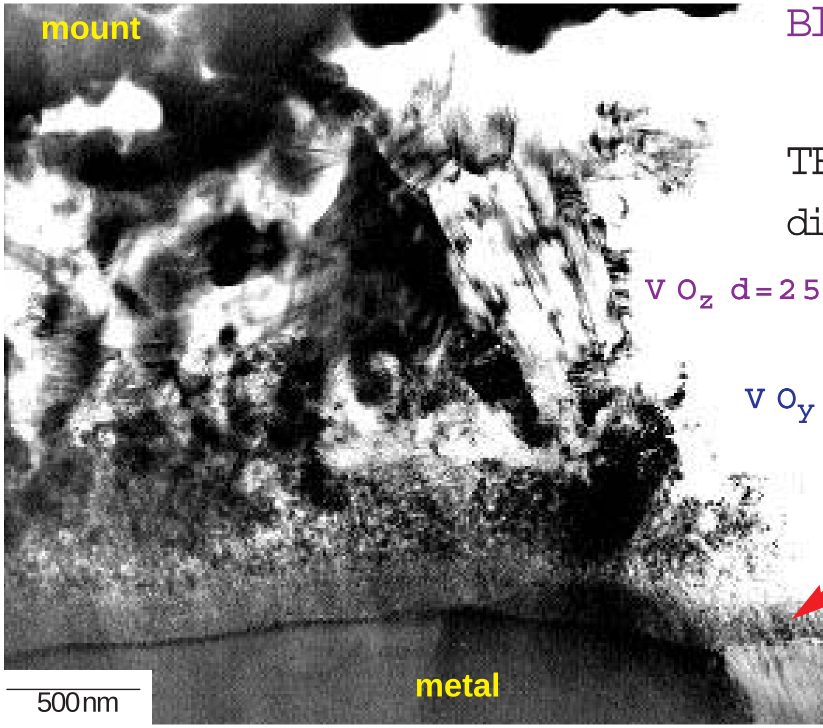




Oxide on surface dissolves into substrate causing embrittlement

Surface oxide microstructure on V-4Cr-4Ti

after 200h at 500℃ in air



Blade-like grains observed on surface by SEM

TEM/EDX - changing V/O ratio

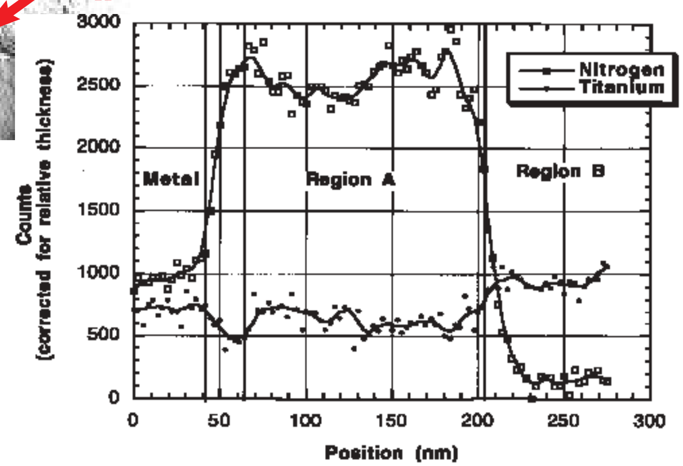
difficult to quantify due to overlap

VO_z d=250-1000nm

VO_y d=≈50nm

VO_n d=10-15nm

VN_x d<5nm



Inner oxide - decreasing grain size (d)

Nitride inner layer detected:

(but not rich in Ti!)

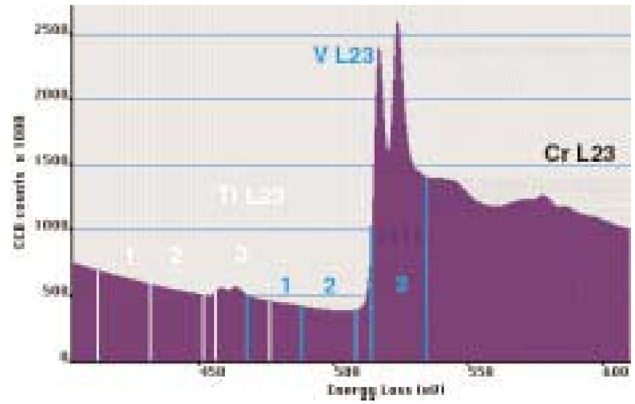
Analytical Microscopy of Denuded Zone

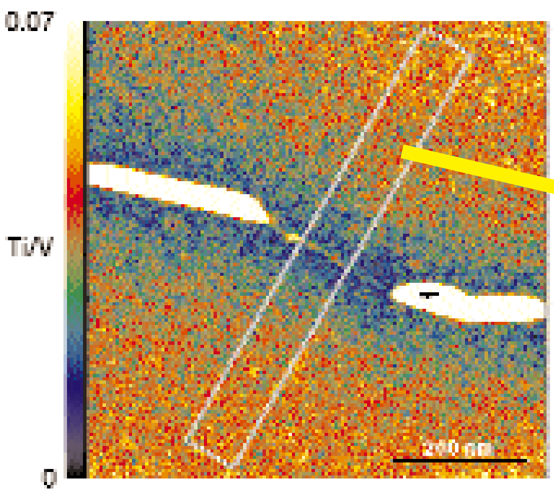
Parallel electron energy loss spectroscopy (PEELS)

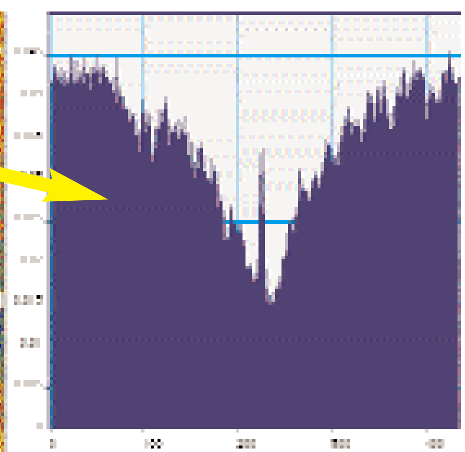
1434ppmw O added at 500℃, no 950℃ anneal

Ti-rich oxide particles
at grain boundaries

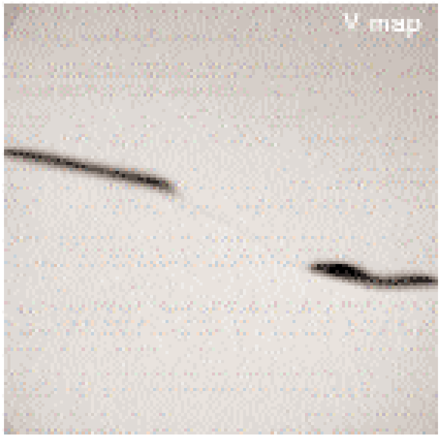
Grain boundary region
otherwise depleted in Ti





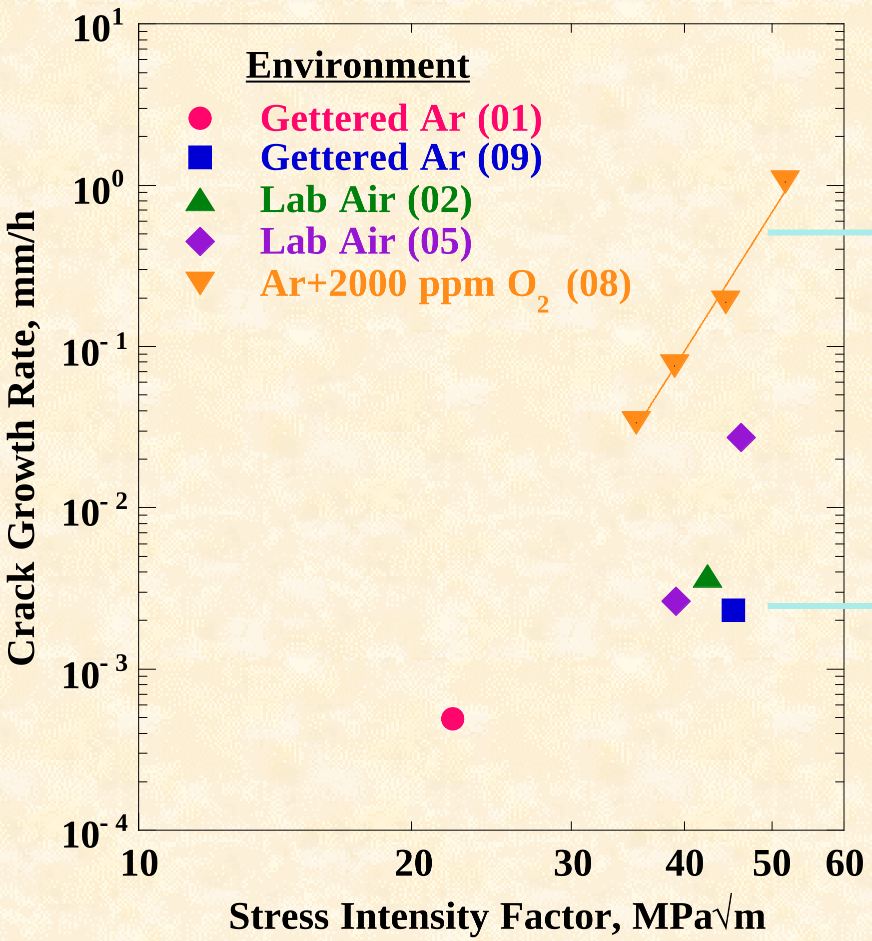


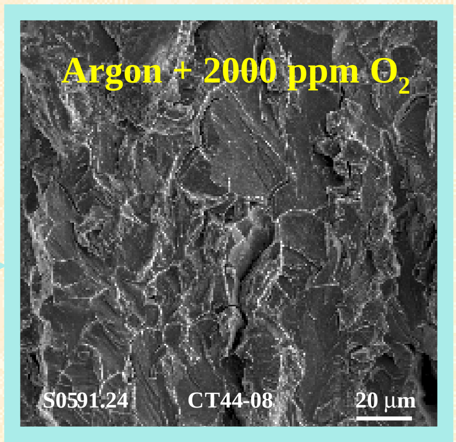
Ti profile across boundary

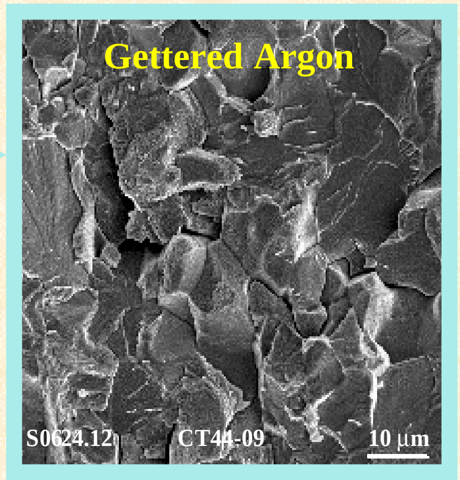


V map

Dependence of the V Alloy Crack Growth Rate on Stress Intensity Factor





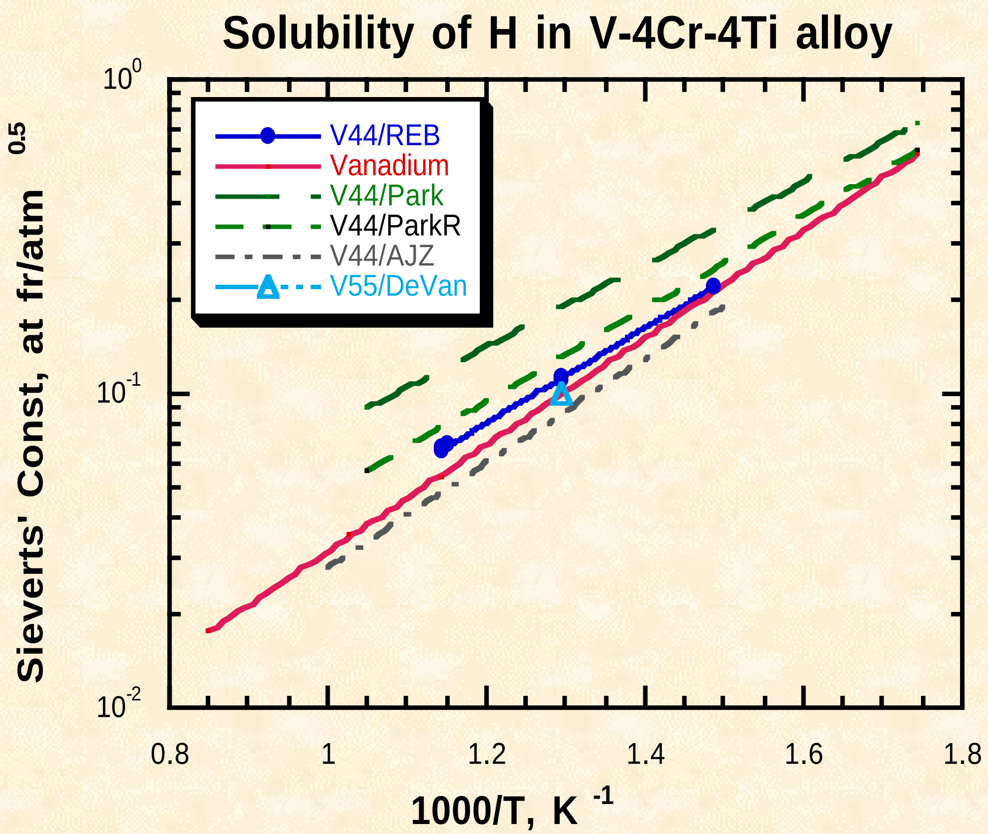


Hydrogen Solubility in V-4Cr-4Ti Alloy

Solubility data for H in V-Cr-Ti alloys provides basis for evaluation of H and T distribution in candidate first-wall/blanket systems

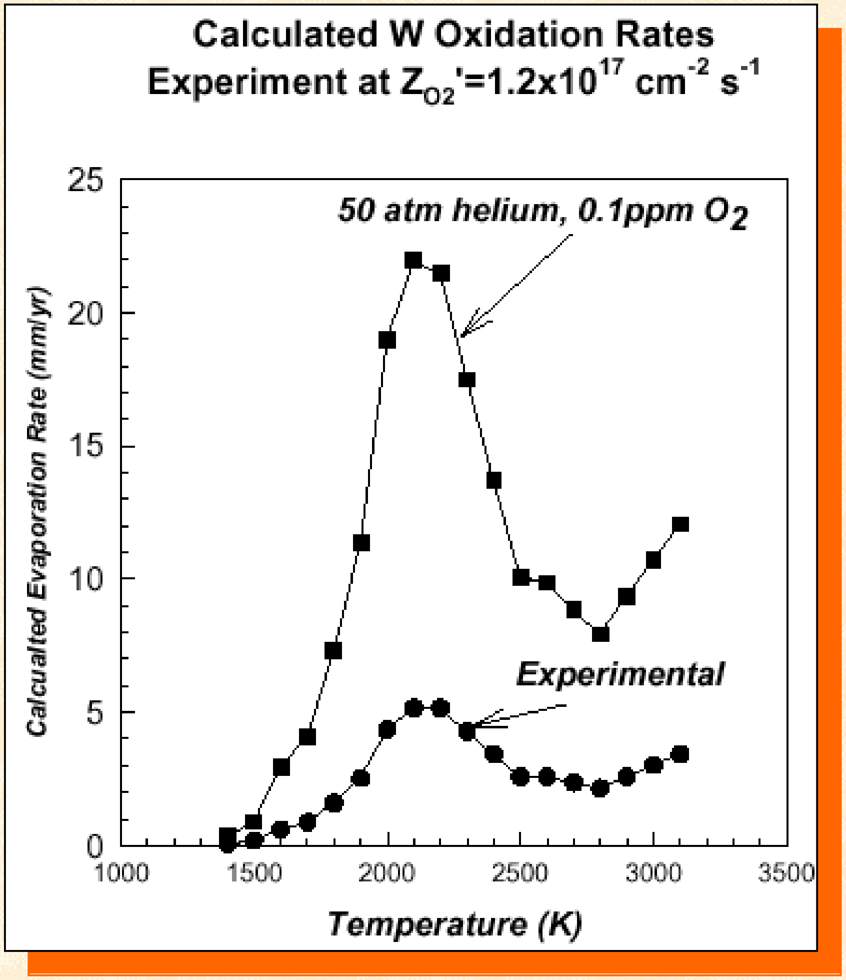
- D & T in plasma
- T generation in blanket
- H transmutation

- Quantitative adsorption/ desorption of H into flowing He with controlled H content at constant temperature
  - Avoids problems of H redistribution during cooling
  - Optimized parameters for V-H system



High-Temperature Oxidation of Refractory Alloys

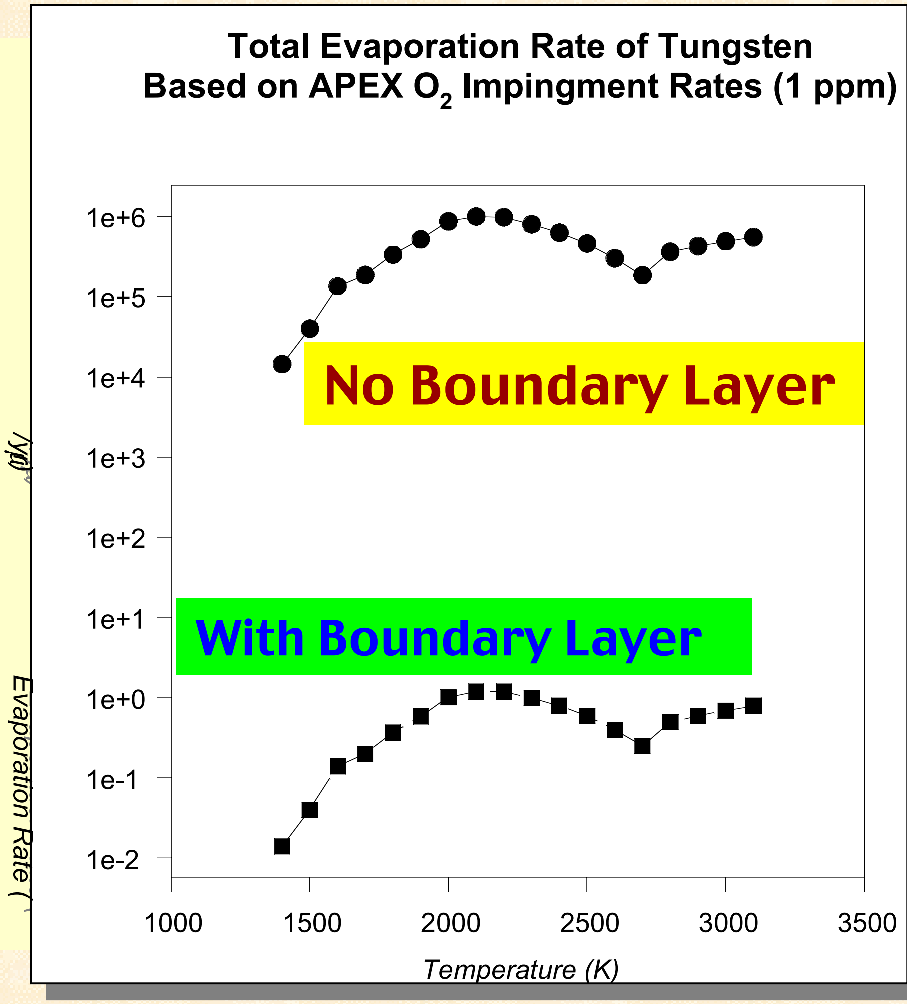
- At Normal temperatures and pressures, the chemical reaction of a gas with the solid generally results in condensed products.
- **At high temperatures and low pressures, the formation of volatile products is thermodynamically favored over the growth of the condensed phase.**
- The upper temperature limit for design with refractory metals with a helium coolant will be influenced by the formation of volatile oxides.
  - **Determine the upper limit of Oxygen impurity levels for W/He designs using Thermodynamics of Chemical Reactions**.



Funded by APEX program, OFES

Effects of Boundary Layers on Evaporation Rate of Refractory Oxides

- **Use of quasi-equilibrium treatment of heterogeneous reactions, plus boundary layer effects to determine the actual evaporation rates.**
- Based on experimental data, the impingement rate of O_2 was used to determine:
  - Static Evaporation Rates.
  - Effects of the Boundary Layer Resistance To Oxide Product
- Evaporation Rates Could Be As Low As 0.1 µm/yr for W at 1 ppm O_2 @ 1500°C.
- **For an oxidation rate limit of 0.1 µm/yr the operating temperature for W is 1600°C.**



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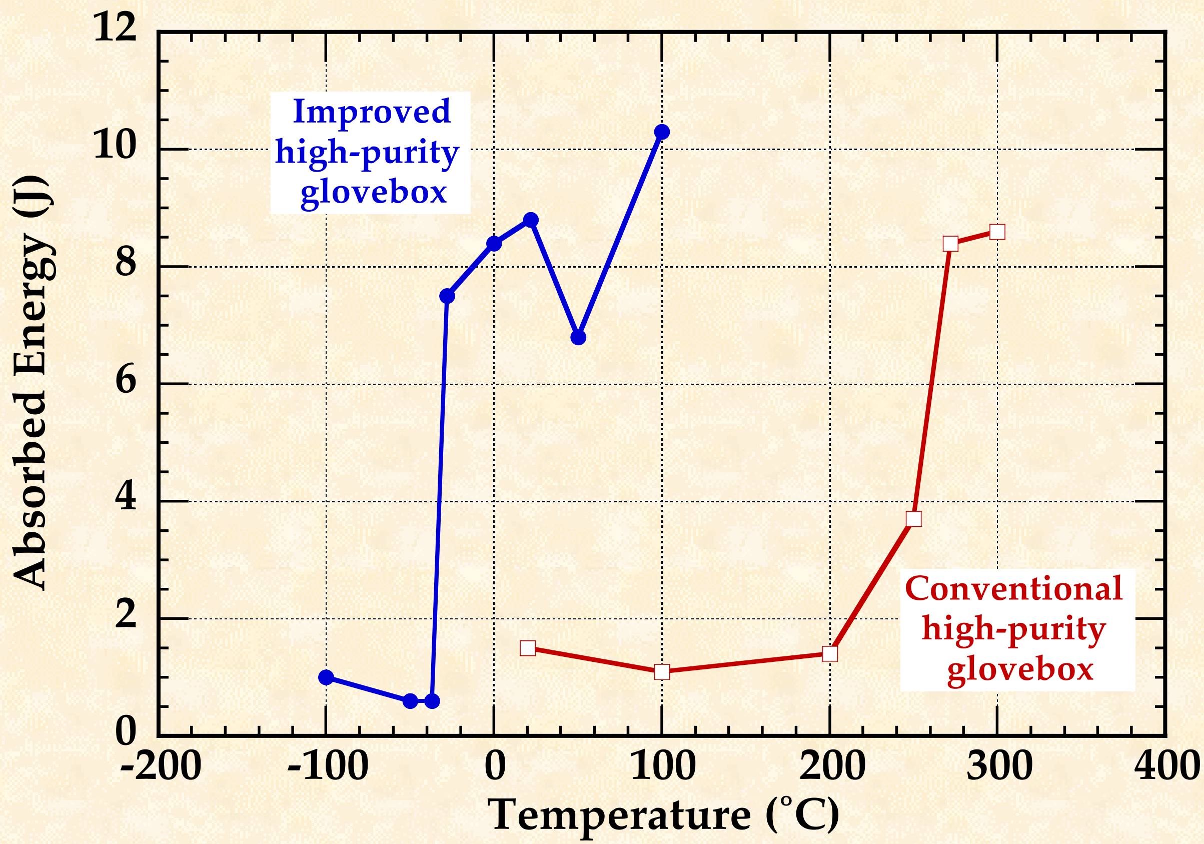
Overview of Fusion Materials Joining Research

- **Recent focus has been on V alloy joining (GTA, ebeam, laser)**
  - **Critical issue for viability of V alloys in fusion reactors**
  - **Need to understand environmental (atmosphere) requirements for successful welds; eventually progressing to field welds**

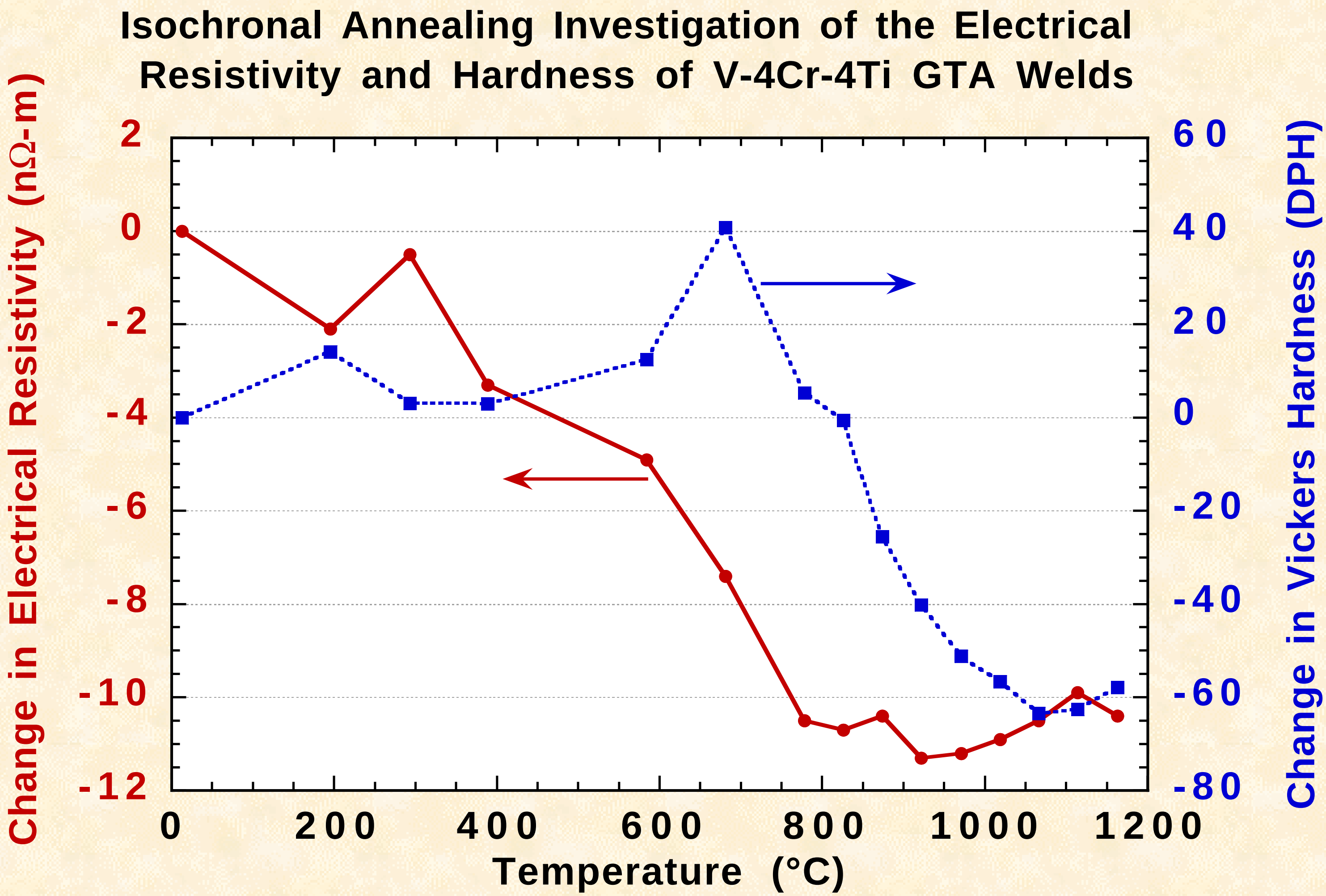
- **Analysis of potential for welding Group VI refractory alloys (Mo)--what are the microstructural factors leading to weld embrittlement**

- **Friction Stir Welding offers potential for significantly enhancing the weldability of refractory and irradiated (He-containing) materials**

GTA Welding produces an increase in the DBTT due to introduction of interstitial impurities from the atmosphere and re-solution of existing Ti(O,C,N) precipitates



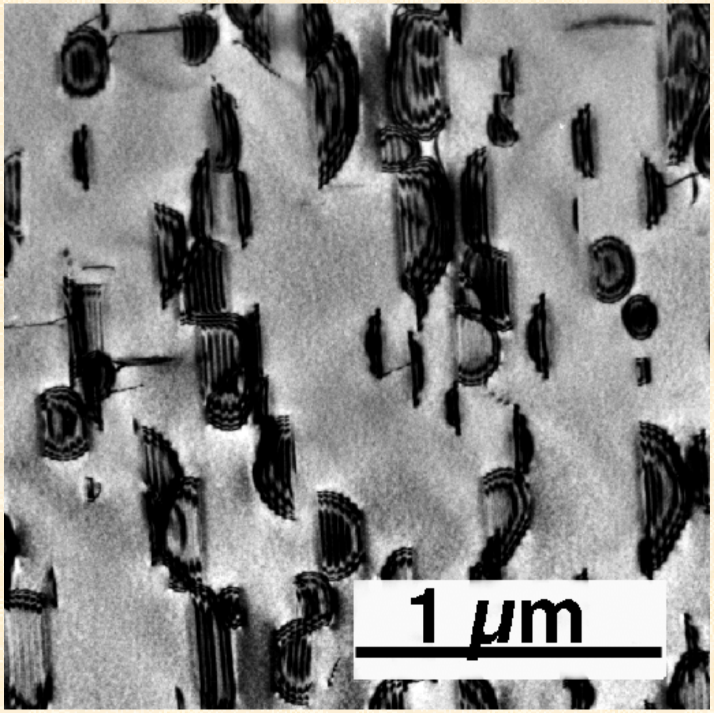
Physical Metallurgy of Welded V-4Cr-4Ti



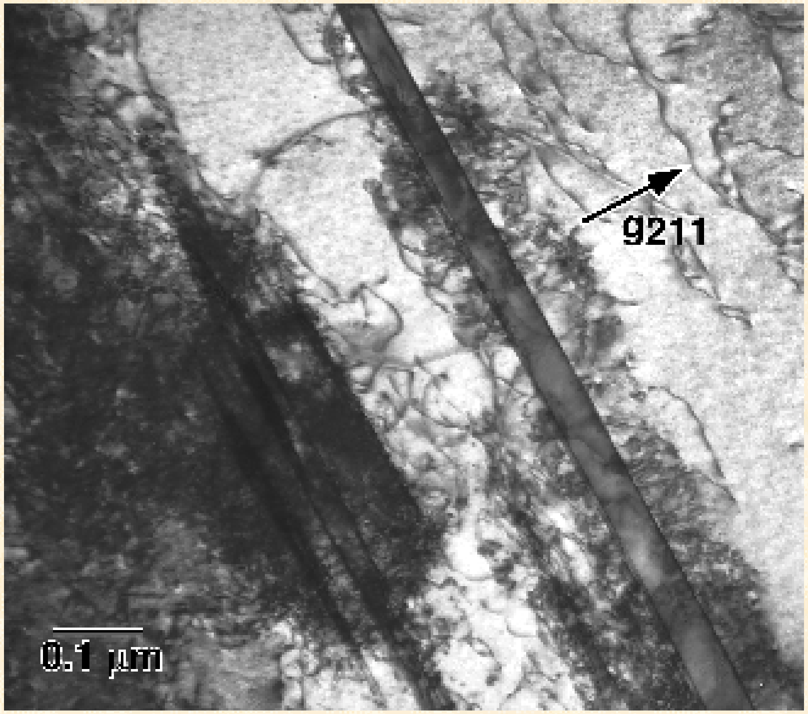
- **Precipitation of Ti(O,C,N) by post-weld heat treatment (T_{ann}~900˚C) can restore weld ductility and reduce DBTT**

Physical Metallurgy of Welded V-4Cr-4Ti

- **Microstructure of welded V alloys**
  - Twinning, precipitates (structure and composition)

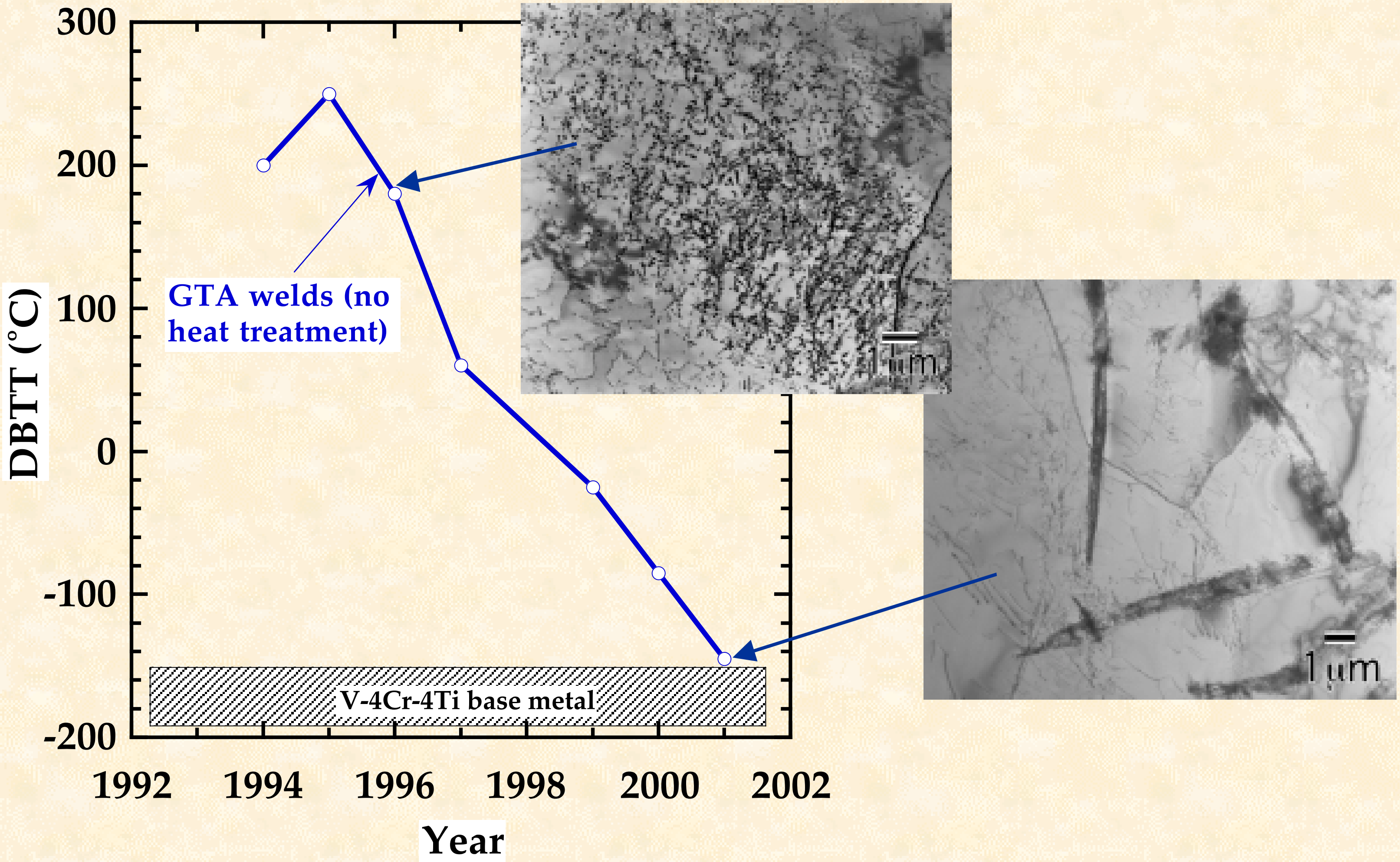


Precipitates in the fusion zones following 950˚C, 2h heat treatment were identified as $Ti_{16}O_3N_3C_2$



Twins were observed in V-4Cr-4Ti weld metal, particularly in outgassed samples (no PWHT)

The fusion materials welding program has successfully resolved one of the key feasibility issues for V alloys



Success is due to simultaneous control of impurity pickup, grain size

- **Results are applicable to other Group V refractory alloys (Nb, Ta)**
- **Use of ultra-high purity weld wire may reduce atmospheric purity requirements**

Laser Welding and Heat Treatment of Vanadium Alloys

Objective:

- Evaluate potential of laser welding for joining V-base alloys.
- Determine effects of weld parameters on properties of weldments.
- Evaluate microstructural modification and fundamental characteristics of V-alloys by heat treatments with laser (small specimen technology).

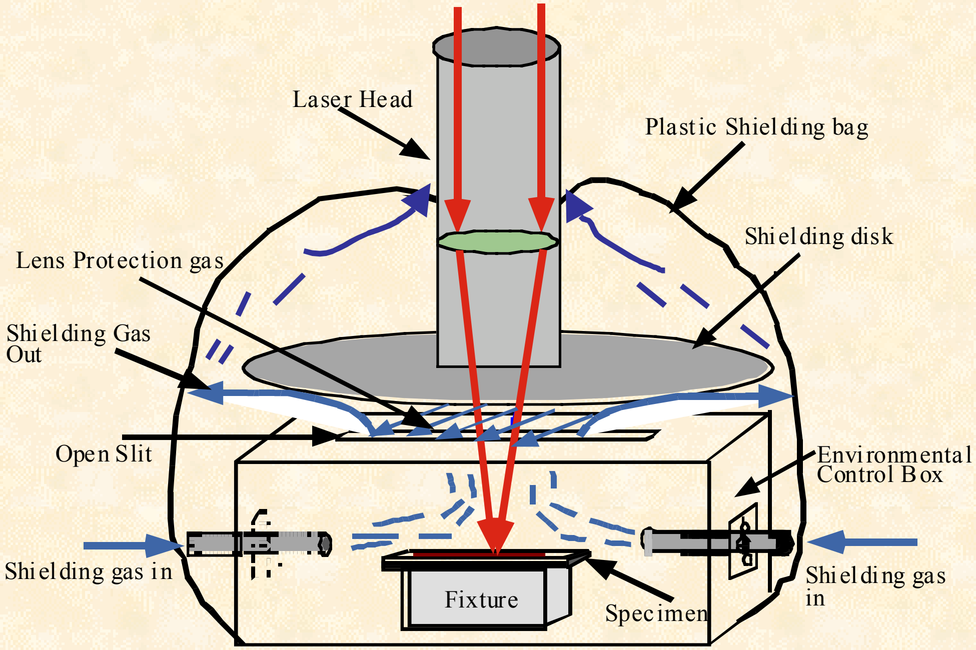
Features of Laser-Welding

- Flexibility for in-field and large-component welding.
- Automatic remote welding.
- Simplicity for atmospheric control.
- Small weld/heat affected zone.
- Simple preparation of weld joint.

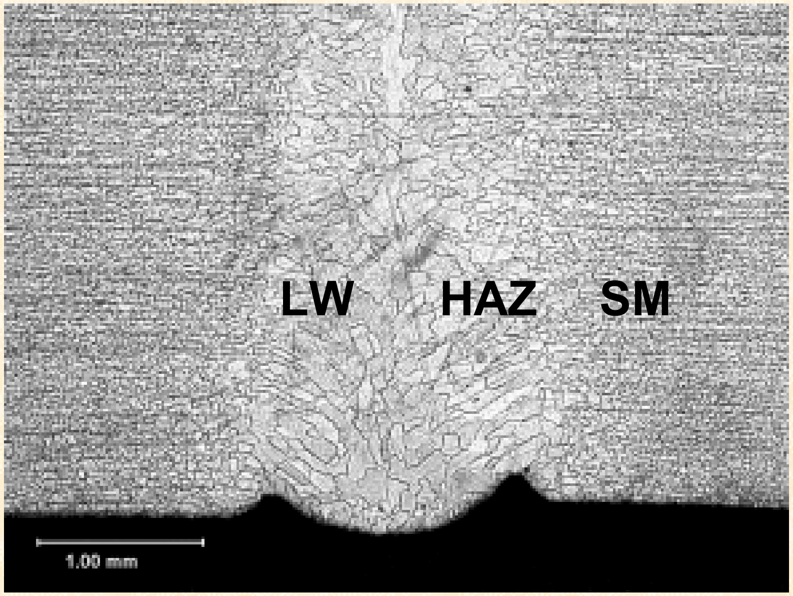
Laser Heat Treatment

- Use of laser beam for fundamental investigations of thermal treatments on microstructure and properties.
- Use of defocused beam for heat treatment.
- Variation of heat treatment with same composition.

Overview of Laser Welding

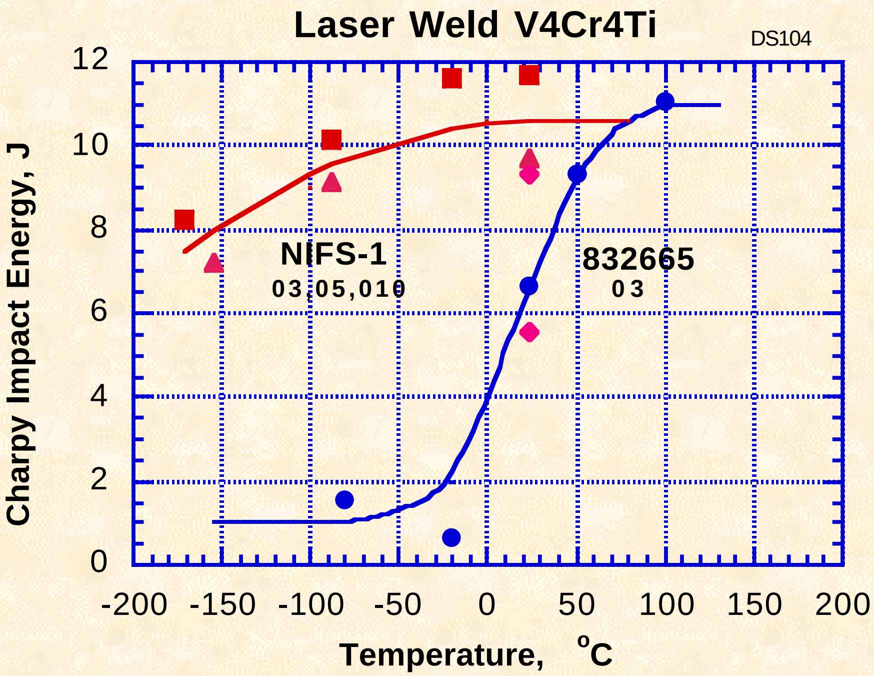


Schematic showing the set-up of the laser and welding environmental control system

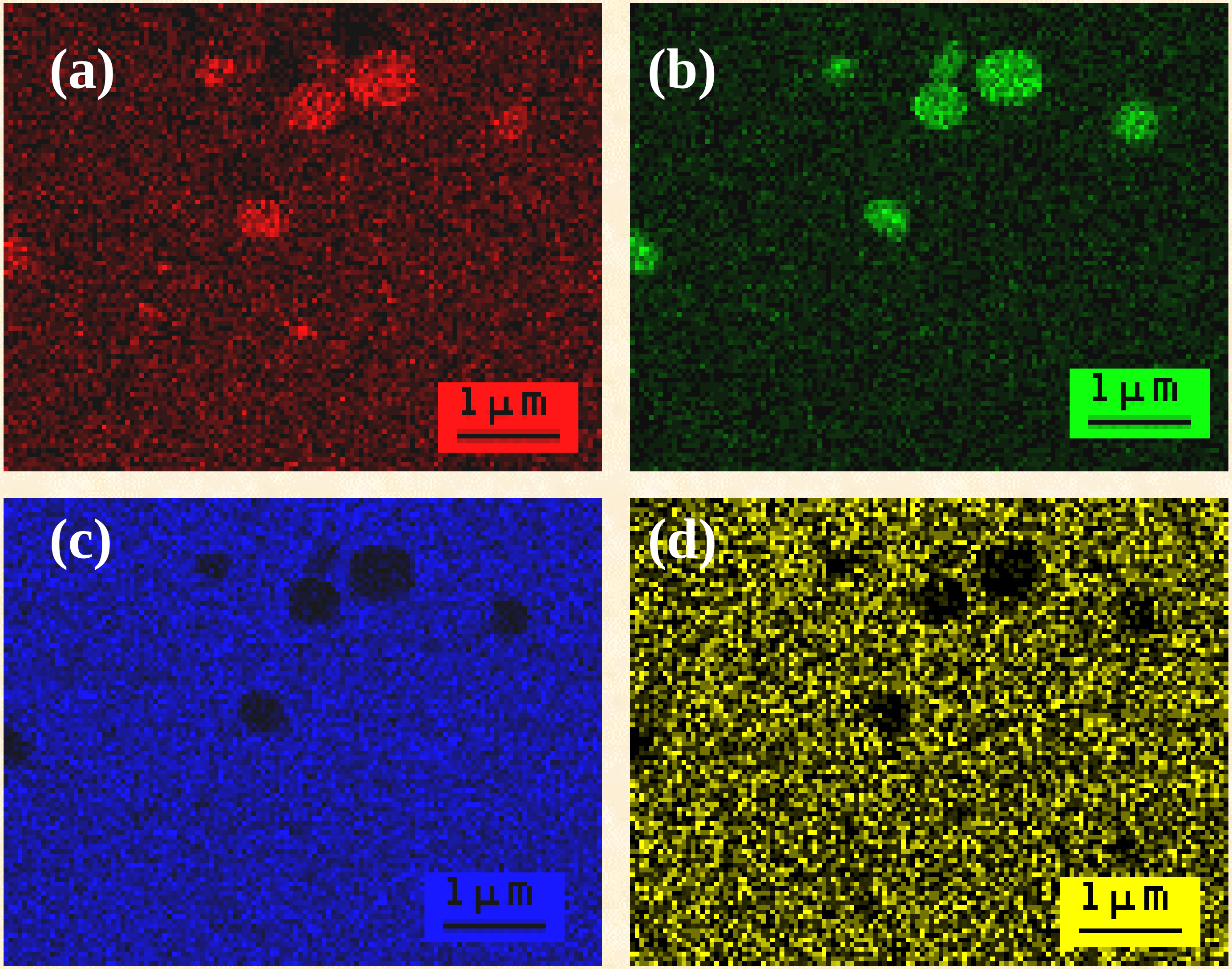


- **Simple air purge in flexible atmospheric containment adequate to avoid contamination.**
- **Applicable to field work.**

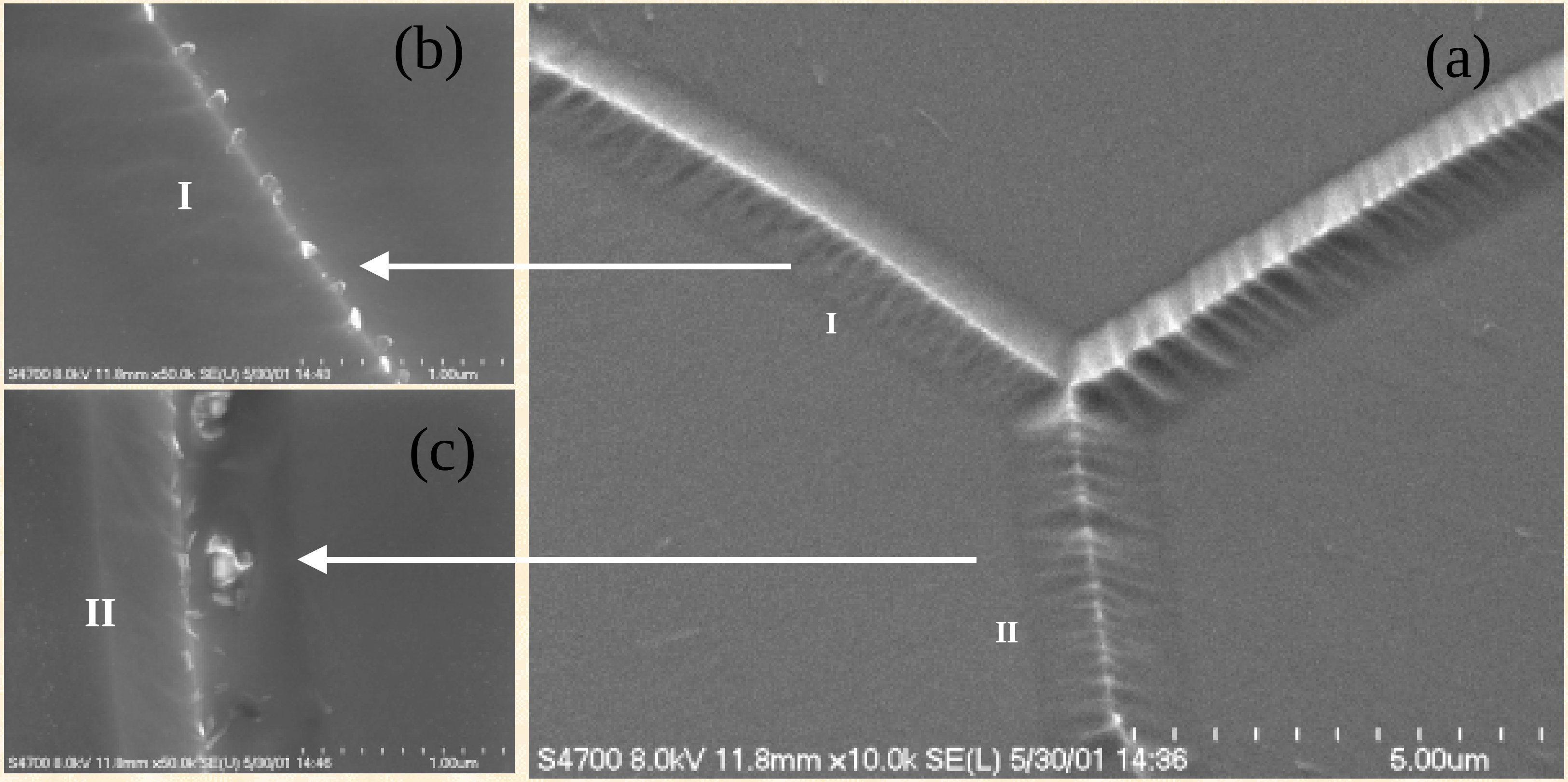
- **Simple butt weld with full penetration (4 mm).**
- **Chemical analysis of weld zone indicates no oxygen contamination.**
- **No banding structure in weld region.**



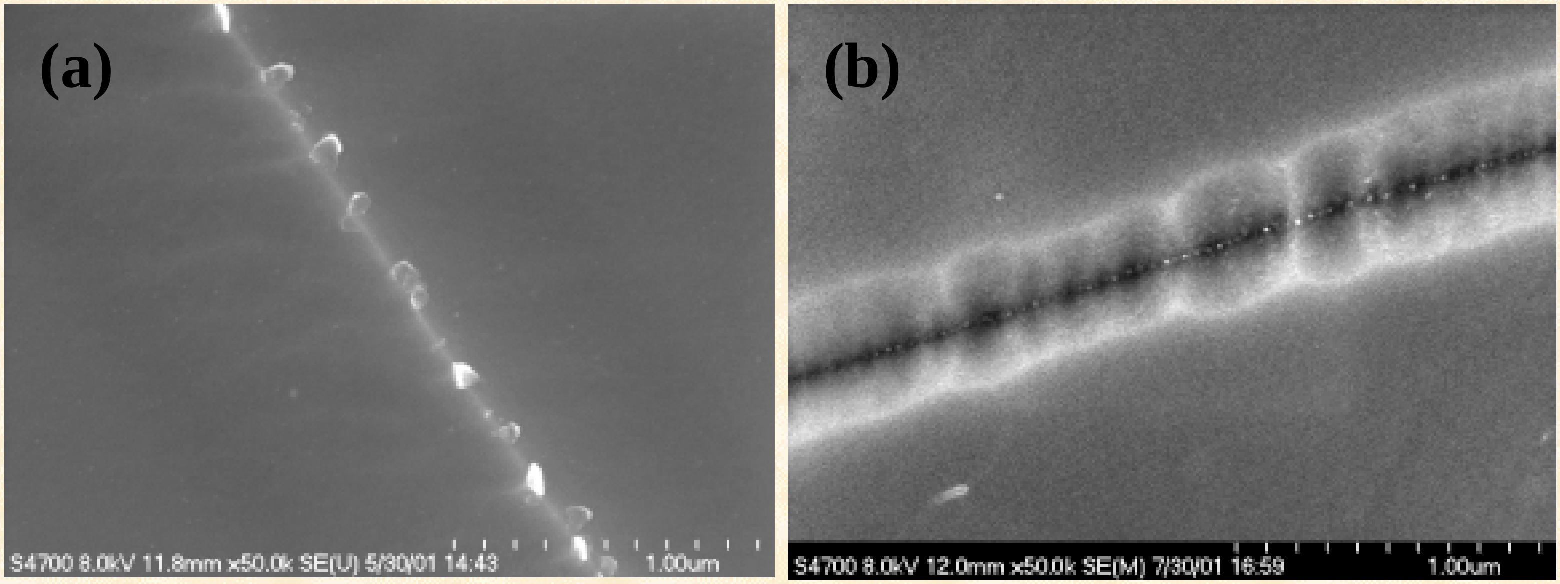
- Charpy Impact Energy for laser welds from two heats of V-4Cr-4Ti.
- Charpy Impact properties of base metal from both heats show same DBTT < -200°C (similar to NIFS-1 weldment).
- Major alloying composition of two heats and heat treatment similar.
- Significant difference in trace element composition Si, Al, O, Mo, Fe.
- These results along with microstructural examination provide insight into V-alloy performance.
- Current effort is focused on identification of trace elements contributing to large property difference.



Net-intensity X-ray maps of second-phase particles in base metal of Heat NIFS-1: (a) C-Kα map, (b) Ti-Kα map, (c) V-Kα map, (d) Cr-Kα map.



(a) SEM image of Heat NIFS-1 showing (a) etched grain boundary morphology. High-resolution SEM images showing small particles (50-100 nm) at (b) grain boundary I and (c) grain boundary II in Fig. (a).



NIFS-1: particle size -> 50-100 nm **832665: particle size -> 10-20 nm**

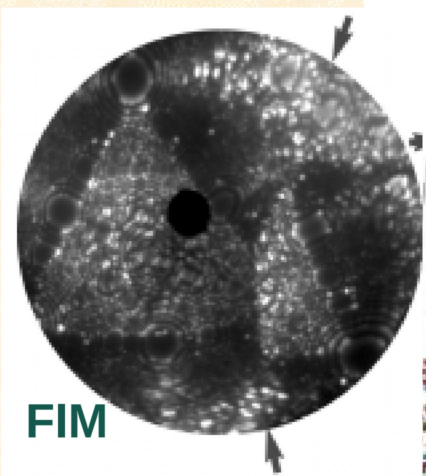
High-resolution SEM images showing a significant difference between (a) heats NIFS-1 and (b) 832665 on particle sizes at grain boundary.

Atom Probe Tomography Reveals Zr, B and C Segregation to Grain Boundaries Produces Improved Mo Weldments

- B, Zr (and C) segregation inhibits O embrittlement of grain boundaries
  - E_{tot}~20%, transgranular fracture mode instead of typical e_{tot}~3%, intergranular fracture for Mo welds
- Bulk alloy composition: 1600 appm Zr, 96 appm C, 53 appm B, 250 appm O

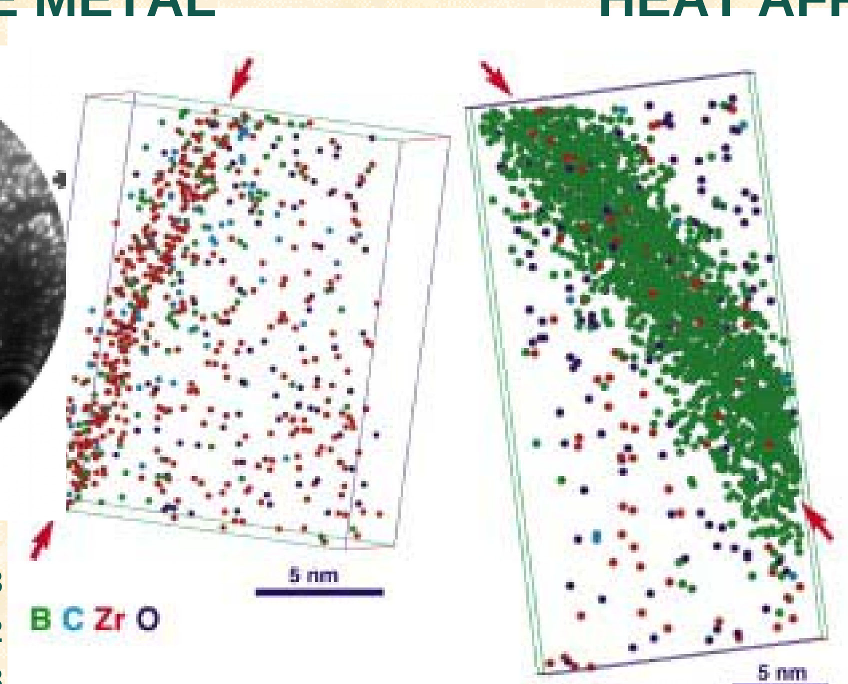
BASE METAL

HEAT AFFECTED ZONE

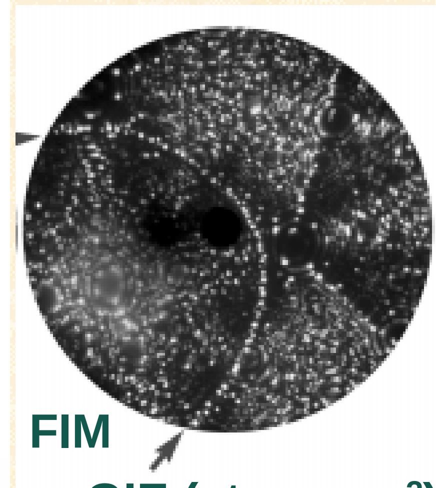


GIE (atoms m^{-2})

Zr	7.6×10^{13}
B	7.3×10^{12}
C	1.1×10^{13}
O	-3.9×10^{12}



APT atom maps



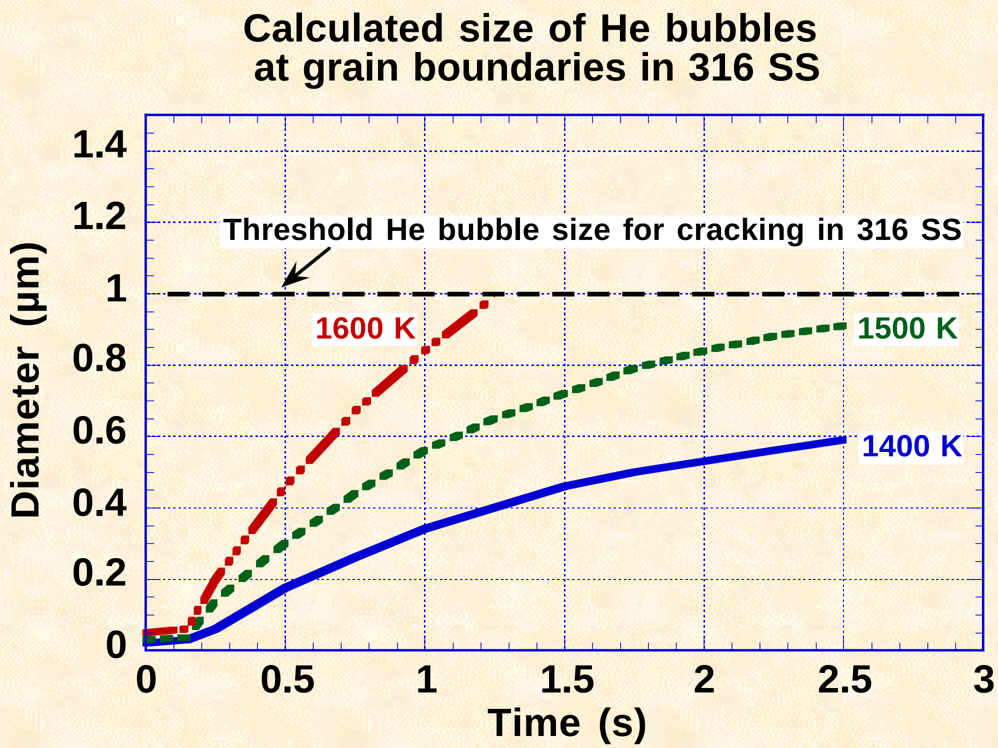
GIE (atoms m^{-2})

Zr	1.3×10^{13}
B	9.9×10^{14}
C	9.9×10^{11}
O	1.1×10^{13}

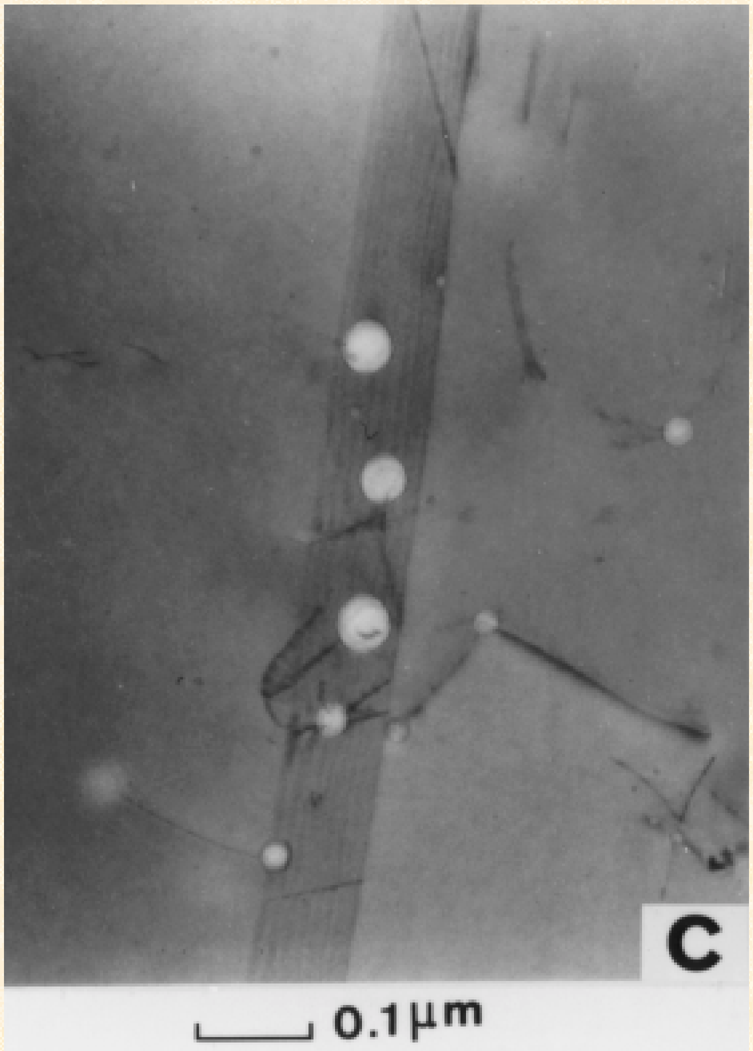
Research performed by
M. K. Miller, Oak Ridge National Laboratory
and A. J. Bryhan, Applied Materials

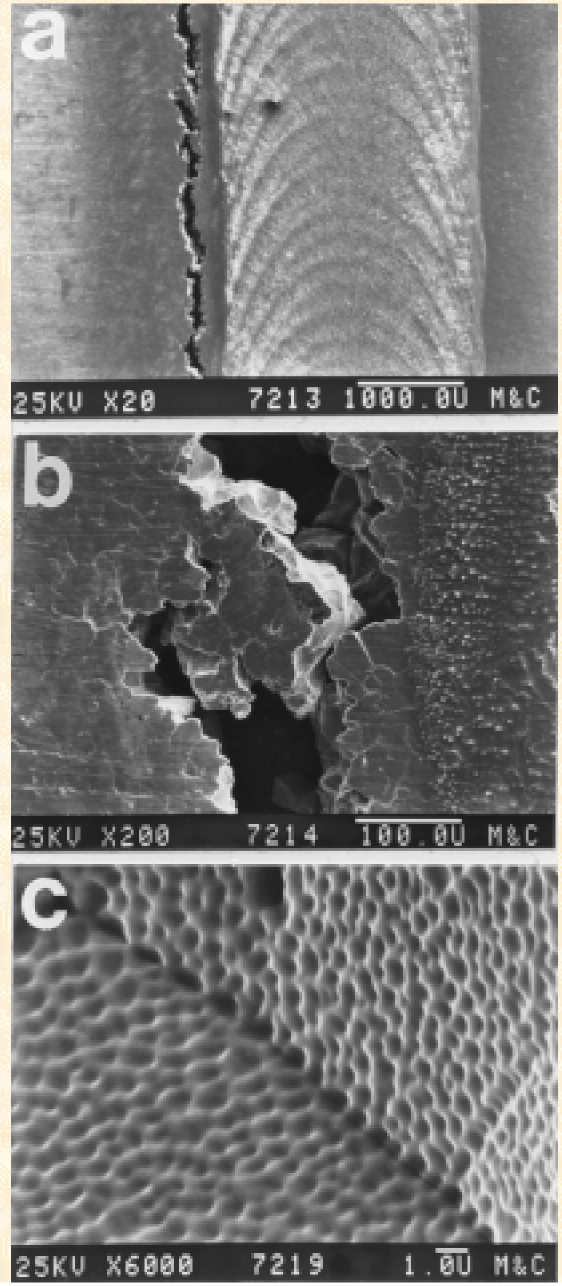
Motivation for pursuing Friction Stir Welding (FSW)

- A solid-state joining process such as FSW may enable field welding of refractory alloys (V, Mo, W), due to reduced pickup of atmospheric contaminants
- Irradiated materials with He contents above ~1 appm cannot be fusion-welded due to cracking associated with He bubble growth; the lower temperatures associated with FSW may allow repair joining of irradiated materials



Cracking in the heat-affected zone of GTA welds in He-containing SS is associated with He bubble formation on grain boundaries

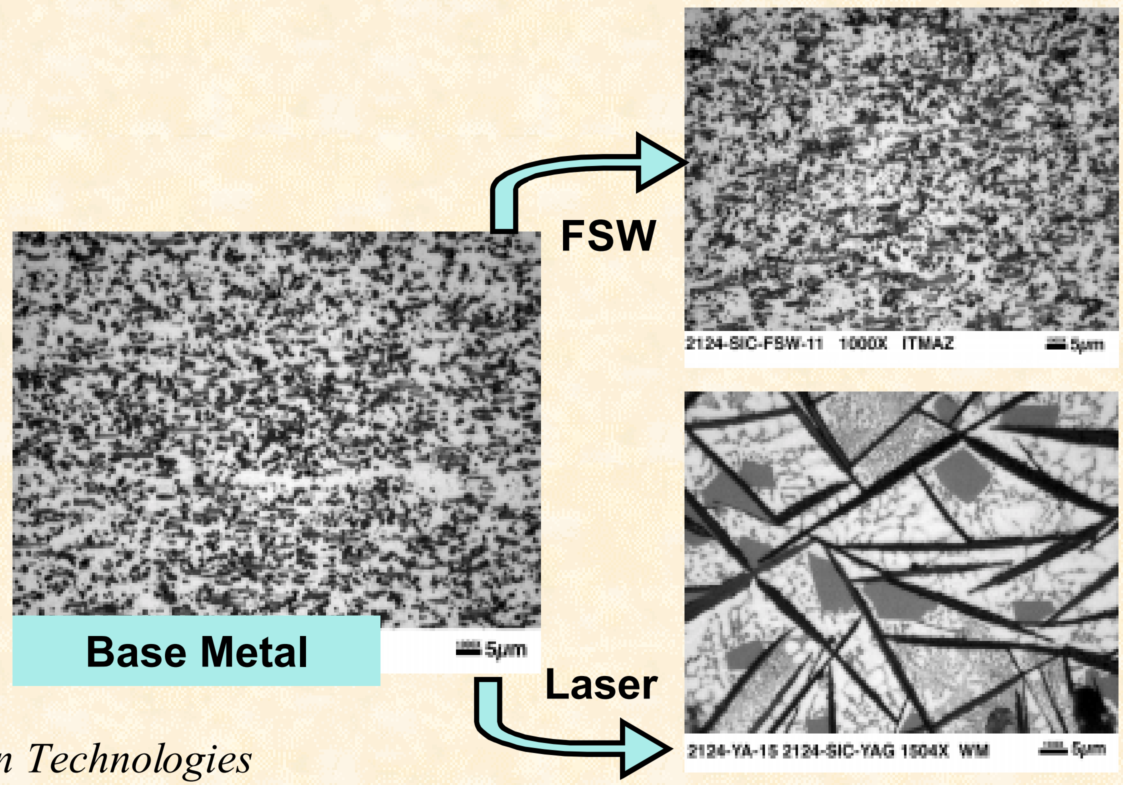




Aluminum metal matrix composites can be successfully joined with friction stir welding (FSW) process

- **Metal matrix composites (MMC) are difficult to join using conventional fusion welding processes.**
  - **Particle / fiber reinforcement deteriorate due to melting.**
  - **In Al-SiC MMC laser welds, SiC decomposes and forms Al_4C_3 carbides.**

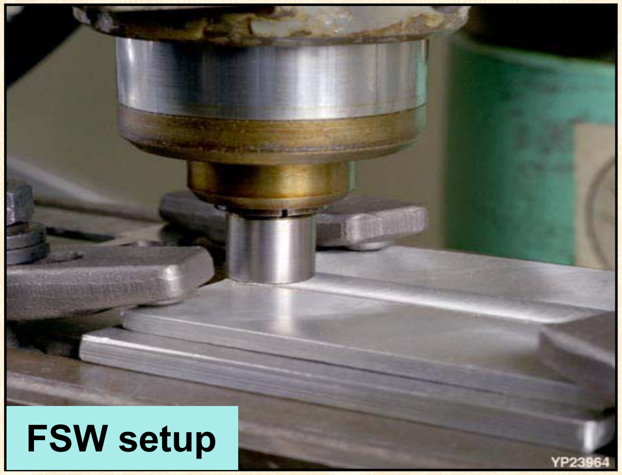
- **Friction stir welding (FSW) uses plastic deformation to join materials.**
  - **Homogeneous microstructure and properties are achieved.**
  - **SiC fibers were uniformly distributed.**



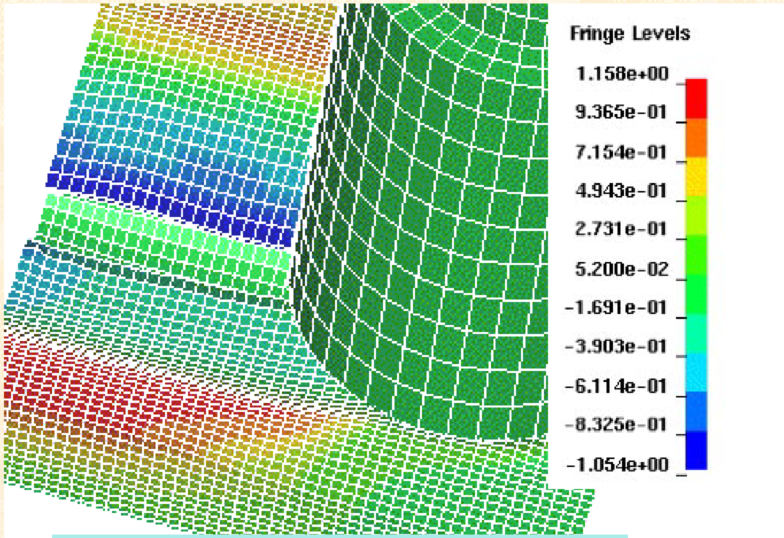
- *Sponsor: DOE Office of Transportation Technologies Office of Heavy Vehicle Technologies*

Modeling of friction stir welding (FSW) process for fusion energy applications

- Background
  - FSW is a newly developed solid-state joining process for potential application to materials that are considered difficult to join by conventional fusion welding processes
- Goal
  - To develop process model for FSW for predicting the temperature and flow fields
  - To apply the process for joining vanadium alloys and dispersion strengthened steels
- Progress
  - FSW has been made on a model alloy and temperatures were measured in different locations for computational model development and validation
  - Efforts are underway to model the kinematics of the process using the finite element code LS DYNA - 3D



FSW setup



Predicted displacements along the tool axis

Conclusions

- **Extremely low oxygen partial pressures ($<10^{-10}$ Pa) are required for non-lithium coolant blanket systems involving V alloys (in order to avoid embrittlement)**
- **High-quality welds with DBTT values approaching that of the base metal can be obtained in V alloys without any requirements for post-weld heat treatment**
  - **GTA, laser, electron beam techniques**
- **Friction stir welding offers potential for further improvements in field-welding capability of refractory alloys (and other alloys), and may improve the ability to perform repair welds on neutron irradiated (He-containing) alloys**