Indirect Paths to Final Equilibrium: Kinetics in Multi-Component Systems

J. M. Vitek

Oak Ridge National Laboratory

Oak Ridge, Tennessee, U.S.A.

Presented at

Multicomponent Multiphase Diffusion Symposium in Honor of John E. Morral

TMS Annual Meeting

San Francisco, February 16, 2005

Outline

- **Phase growth/dissolution in Fe-Cr-Ni**
- **Transformation behavior under para- and ortho-equilibrium interface conditions**
- **Ferrite growth/dissolution during weld thermal cycling**

Acknowledgement

This research was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC

Phase Growth/Dissolution in Fe-Cr-Ni

- **The austenite-ferrite transformation was simulated in the Fe-Cr-Ni (model austenitic stainless steel) system**
- **The transformation was driven by multicomponent diffusion based on an interface equilibrium condition**

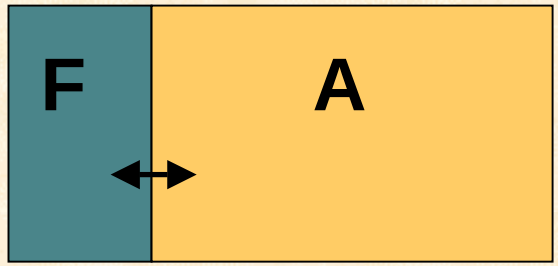
References:

Vitek, Vitek and David, Metall Mater Trans A, 26A, 1995, 2007

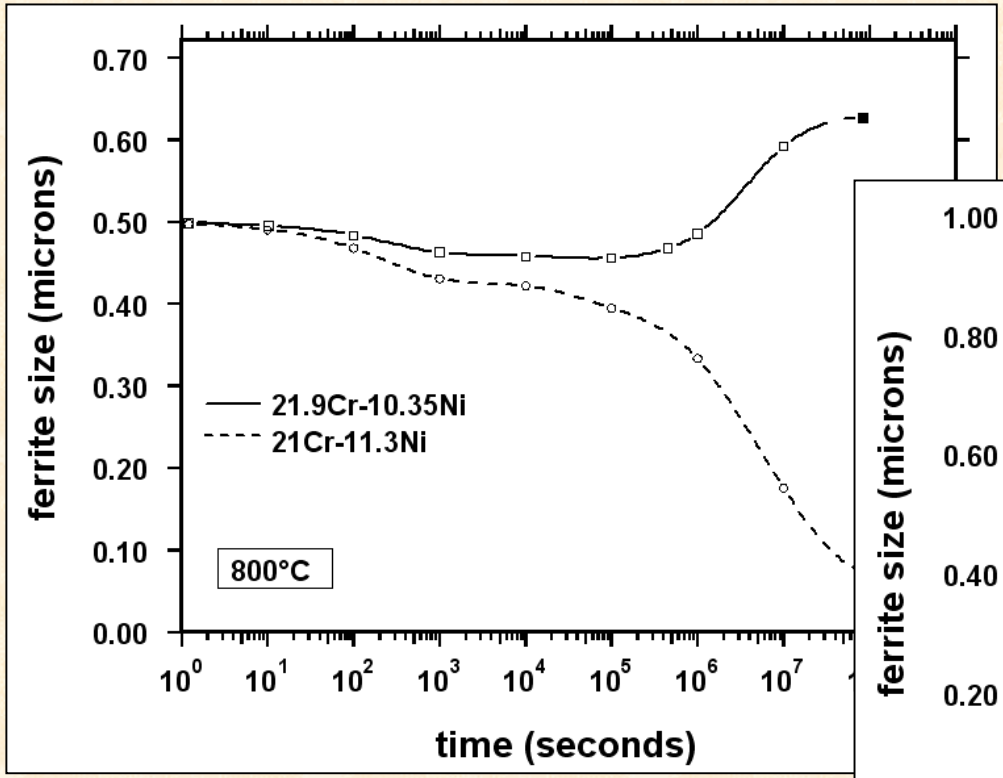
Kajihara and Kikuchi, Acta Metall Mater, 41, 1993, 2045

Behavior Varied Dramatically, Depending on the Conditions

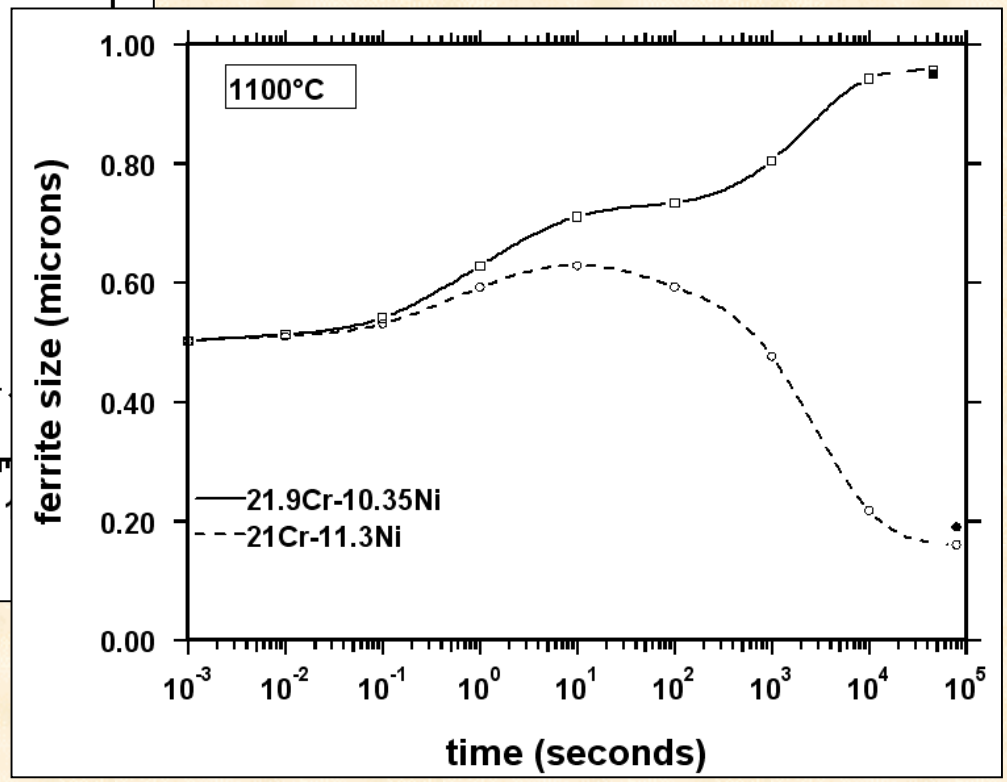
- **Initial state was two-phase austenite plus 10% ferrite, each of uniform composition**
- **At lower temperatures, ferrite is less stable; at higher temperatures it is more stable**
- **The path to final equilibrium proceeded in stages; sometimes ferrite grew and then dissolved, or grew continuously, or ….**
- **Experiments confirmed simulation results**



Different Paths to Equilibrium Were Found



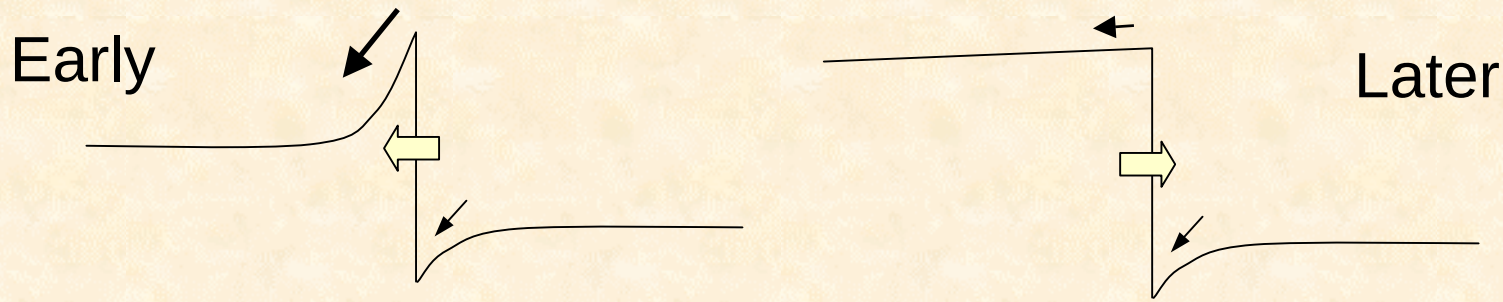
Initial Fe-21.9Cr-10.35Ni in approx. equilibrium at 1000C



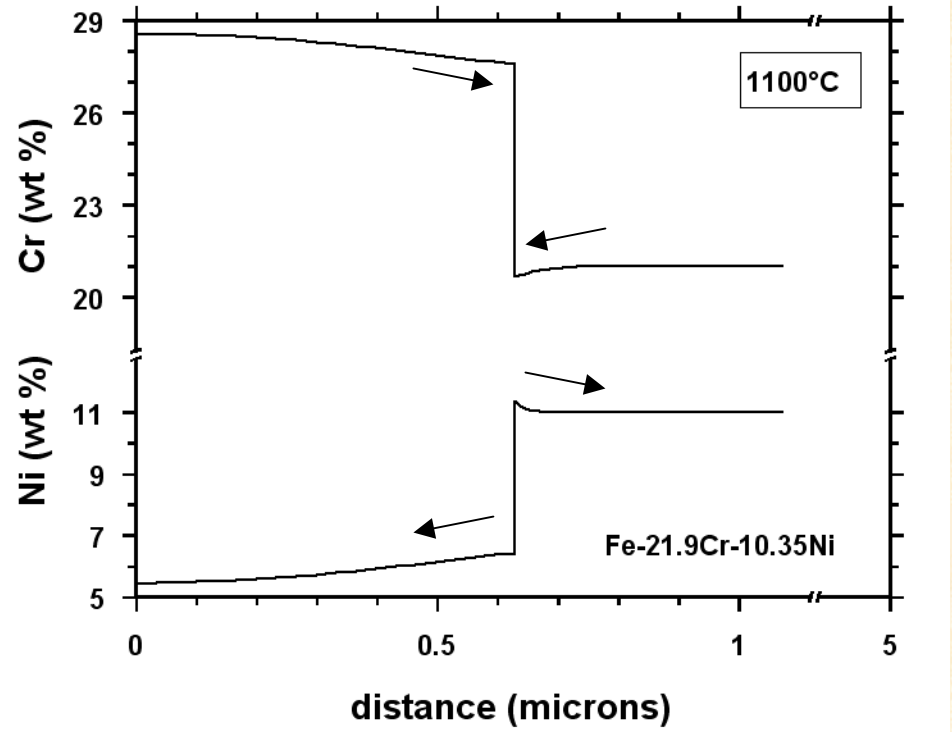
Initial Fe-21Cr-11.3Ni in approx. equilibrium at 1200C

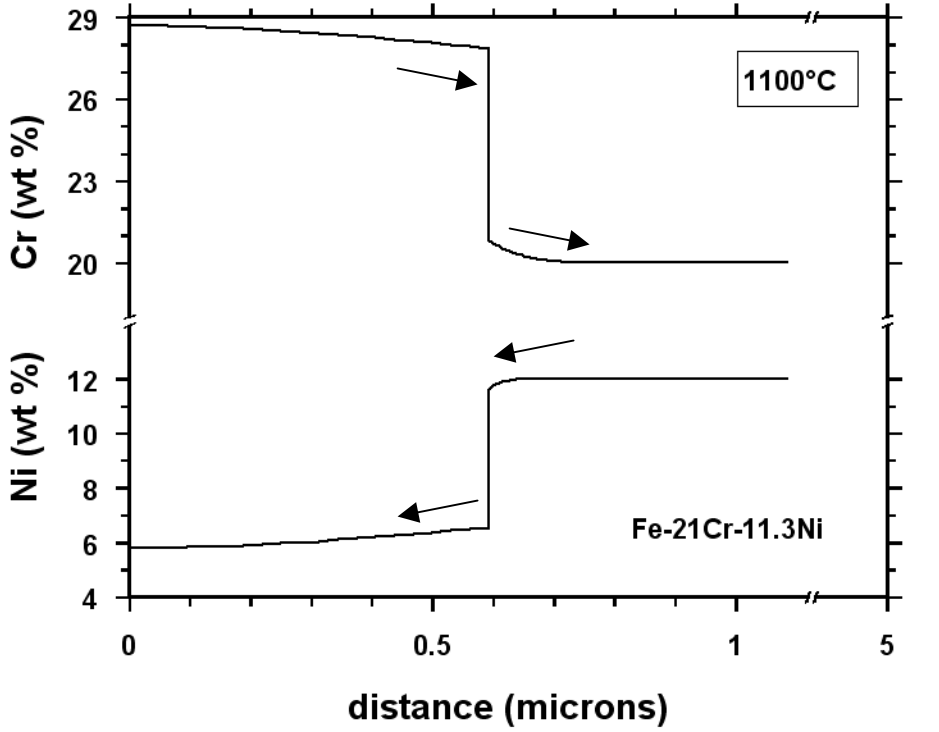
The Results Are Readily Explained by Examining the Fluxes at the Interface

- **Diffusion in ferrite is ~ 100x that of diffusion in austenite**
- **Flux is product of gradient and diffusion coeff.**
- **Flux on ferrite side of interface dominates in the early stages; once ferrite composition is nearly uniform, austenite flux controls behavior**



Different Combinations of Fluxes Were Found in Simulations





Both fluxes lead to ferrite growth

Fluxes oppose each other; larger ferrite flux controls, leading to ferrite growth

Transformation Behavior Under Para- and Ortho-Equilibrium at the Interface

- **The same ferrite-austenite problem was examined with different interface conditions**
- **Para-equilibrium was imposed at the interface at the onset**
- **Once (para) equilibrium was achieved, the simulation was continued with ortho-equilibrium constraints at the interface**

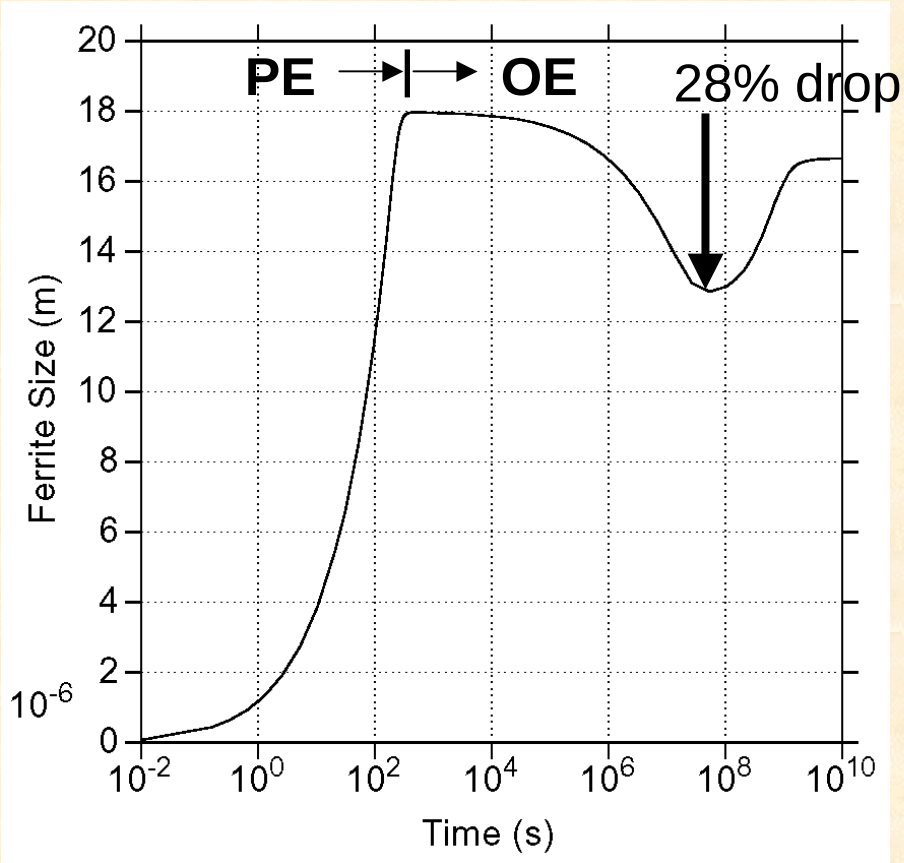
Reference:

Vitek, Babu and Kozeschnik, Austenite Formation and Decomposition, eds Damm and Merwin, TMS, 2003, p 139

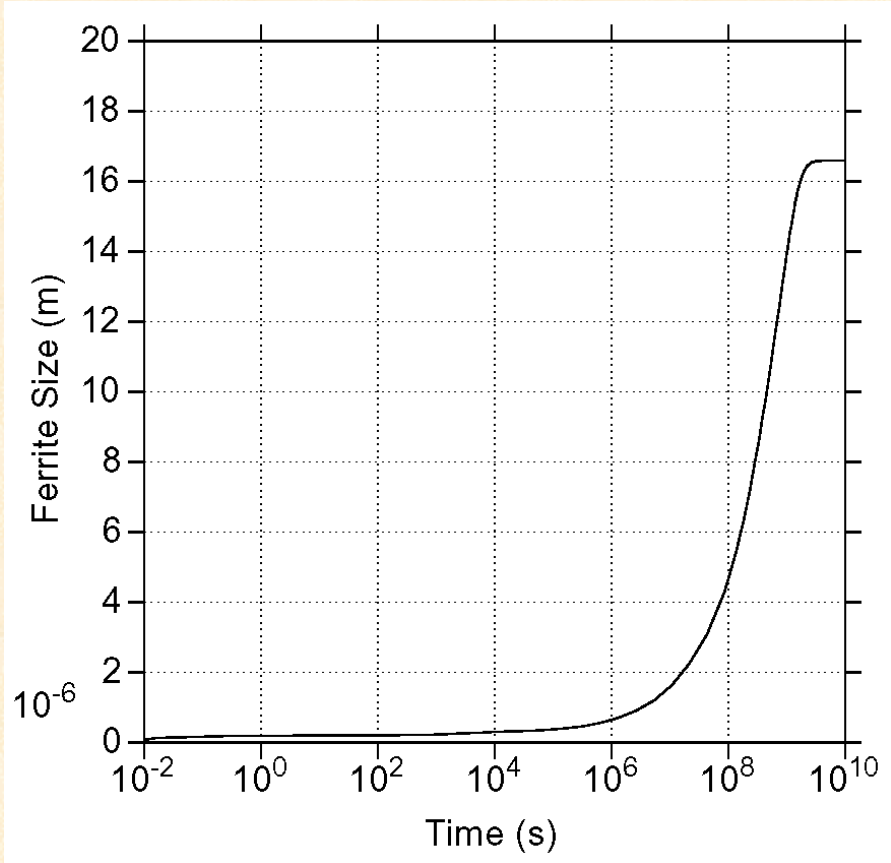
The Same Types of Behavior Were Found

- **In the transition from para- to ortho-equilibrium, ferrite dissolution followed by ferrite growth was found**
- **The change in ferrite fraction could be substantial, depending upon the conditions**
- **The same explanation applies; the behavior is determined by the relative fluxes and is dominated by the ferrite flux initially and the austenite flux later**

Simulation Results for Fe-3Mn-0.1C at 700C (initially all austenite)



Para + Ortho Equilibrium



Only Ortho Equilibrium

Ferrite Growth/Dissolution during Weld Thermal Cycling

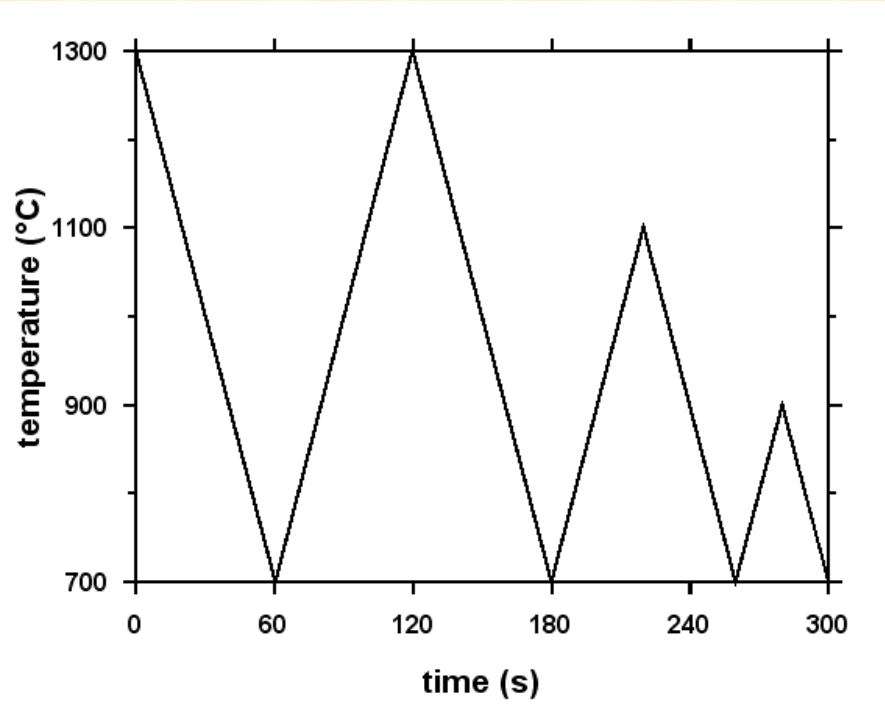
- **The same general problem of following the ferrite-austenite transformation was studied**
- **Thermal cycling was superimposed (to simulate welding conditions)**

Reference:

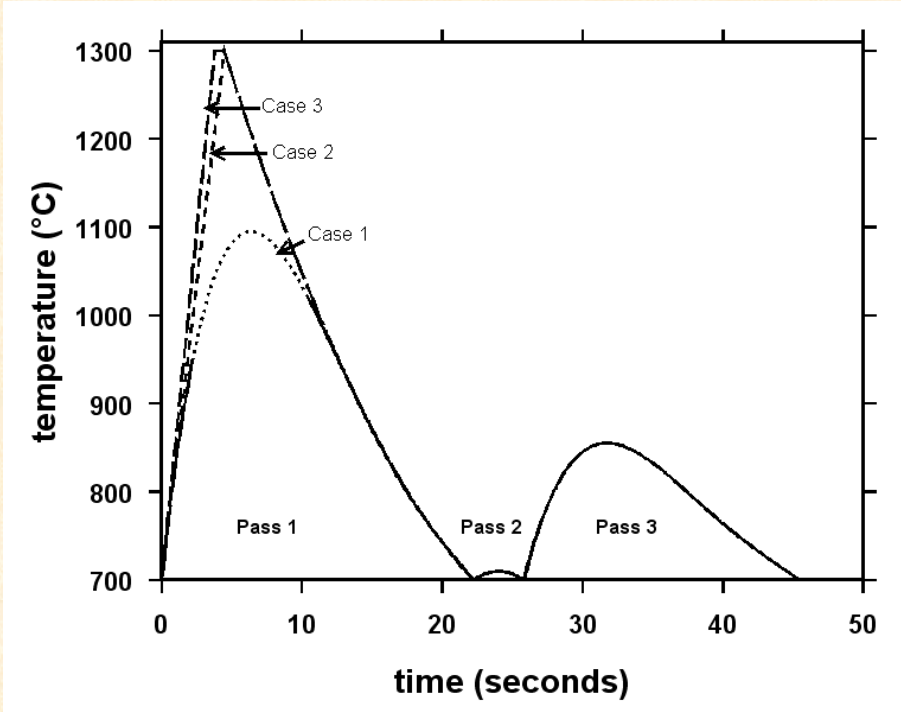
Vitek, Iskander and David, Mathematical Modelling of Weld Phenomena 3, Ed. Cerjak, Inst. of Materials, 1997, p 199

Vitek and David, Mathematical Modelling of Weld Phenomena 4, Ed. Cerjak, Inst. of Materials, 1998, p 321

Multiple Thermal Cycles Were Considered

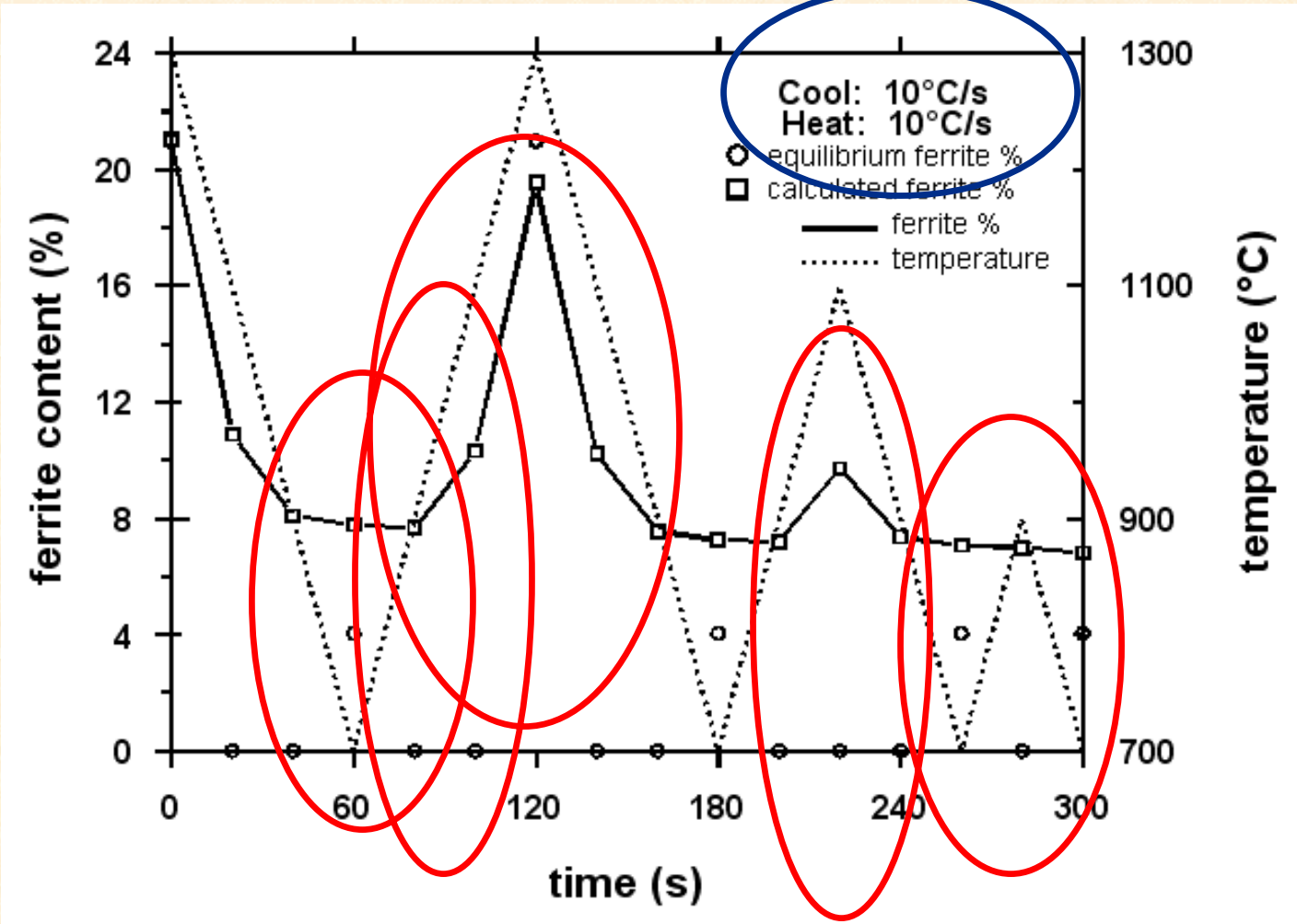


Model multi-cycle weld

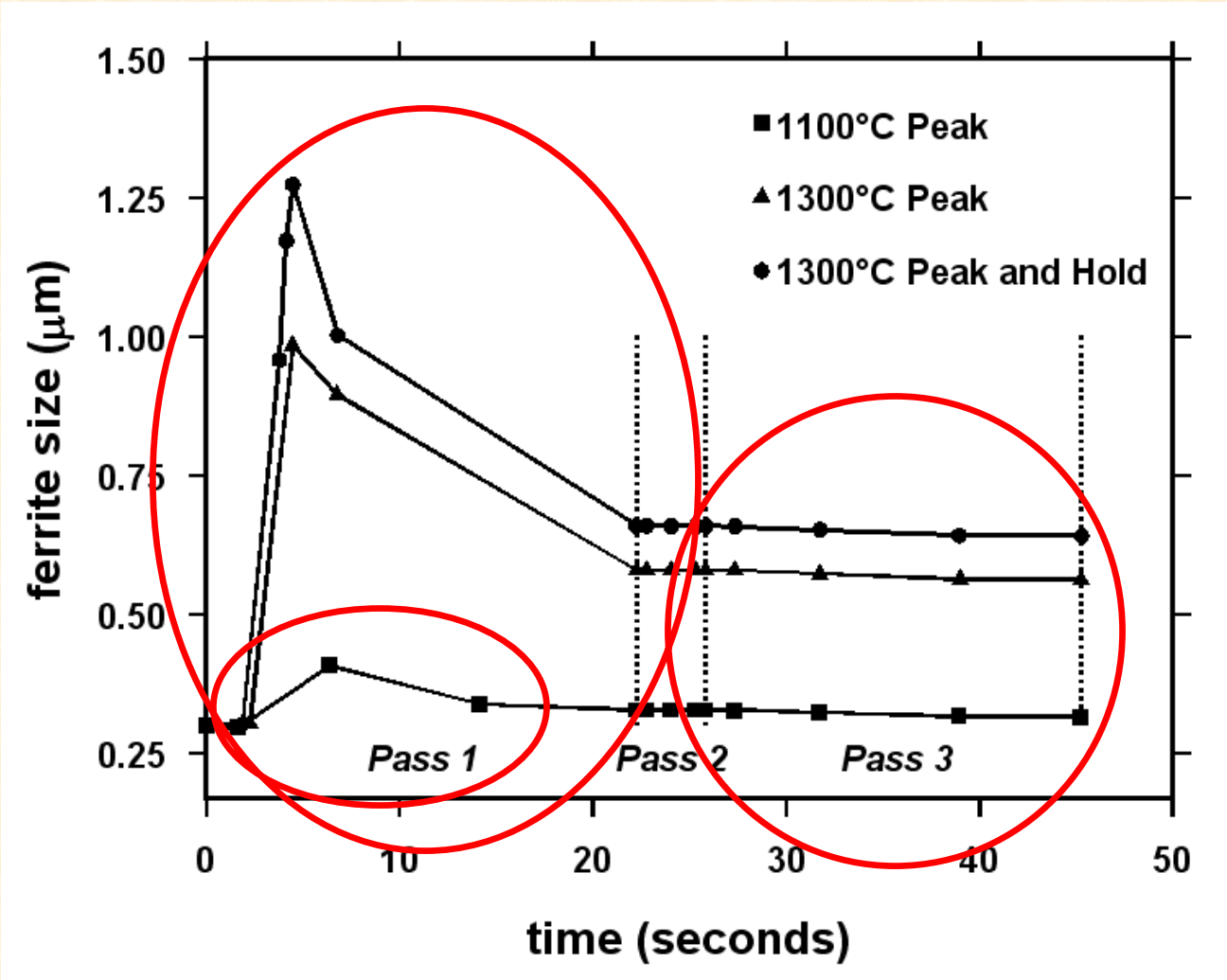


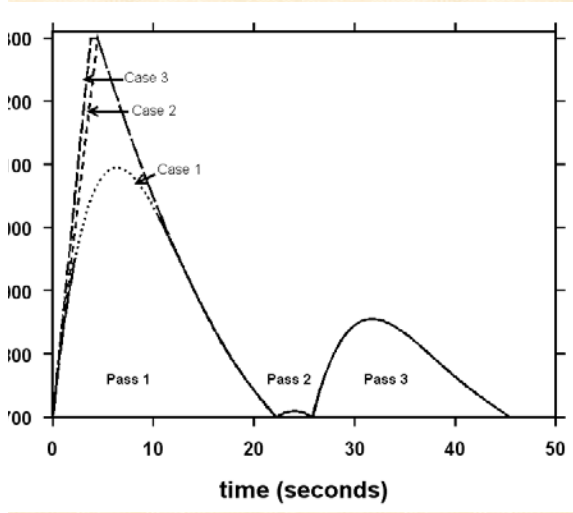
Measured multi-cycle weld

Results for Multi-cycle Welds (I)



Results for Multi-cycle Welds (II)



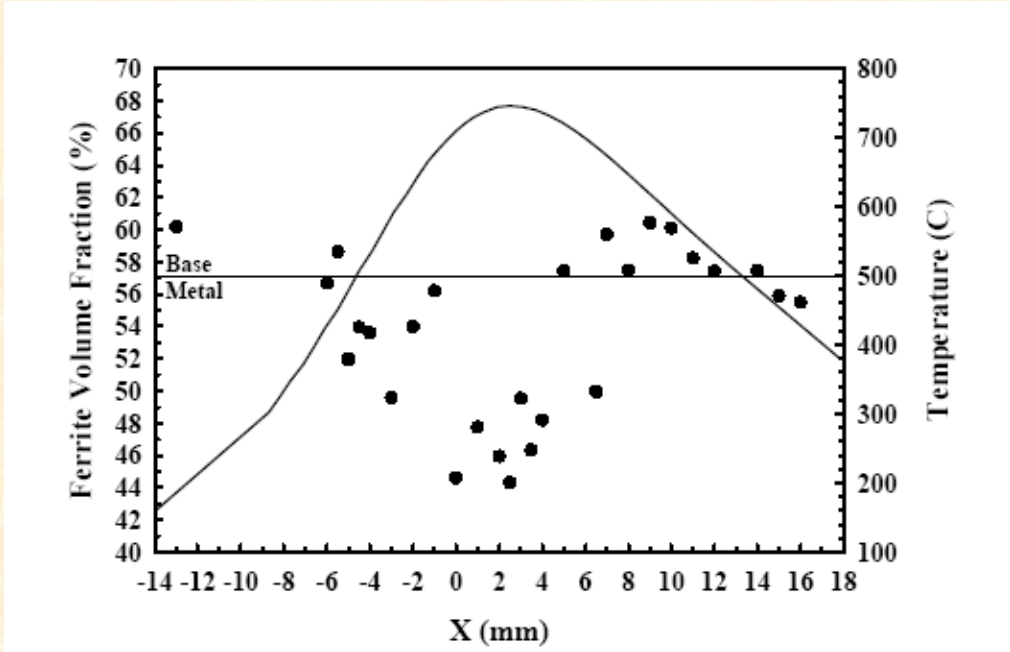


A Wide Range of Behaviors Were Found during Thermal Cycling

- **Ferrite growth or dissolution did not always proceed toward equilibrium**
- **Behavior was due to gradients that were established during thermal cycling and resultant net fluxes**
- **Thermal cycling did not produce reversible behavior**
- **Gradients that are established at onset of simulation have important consequences**

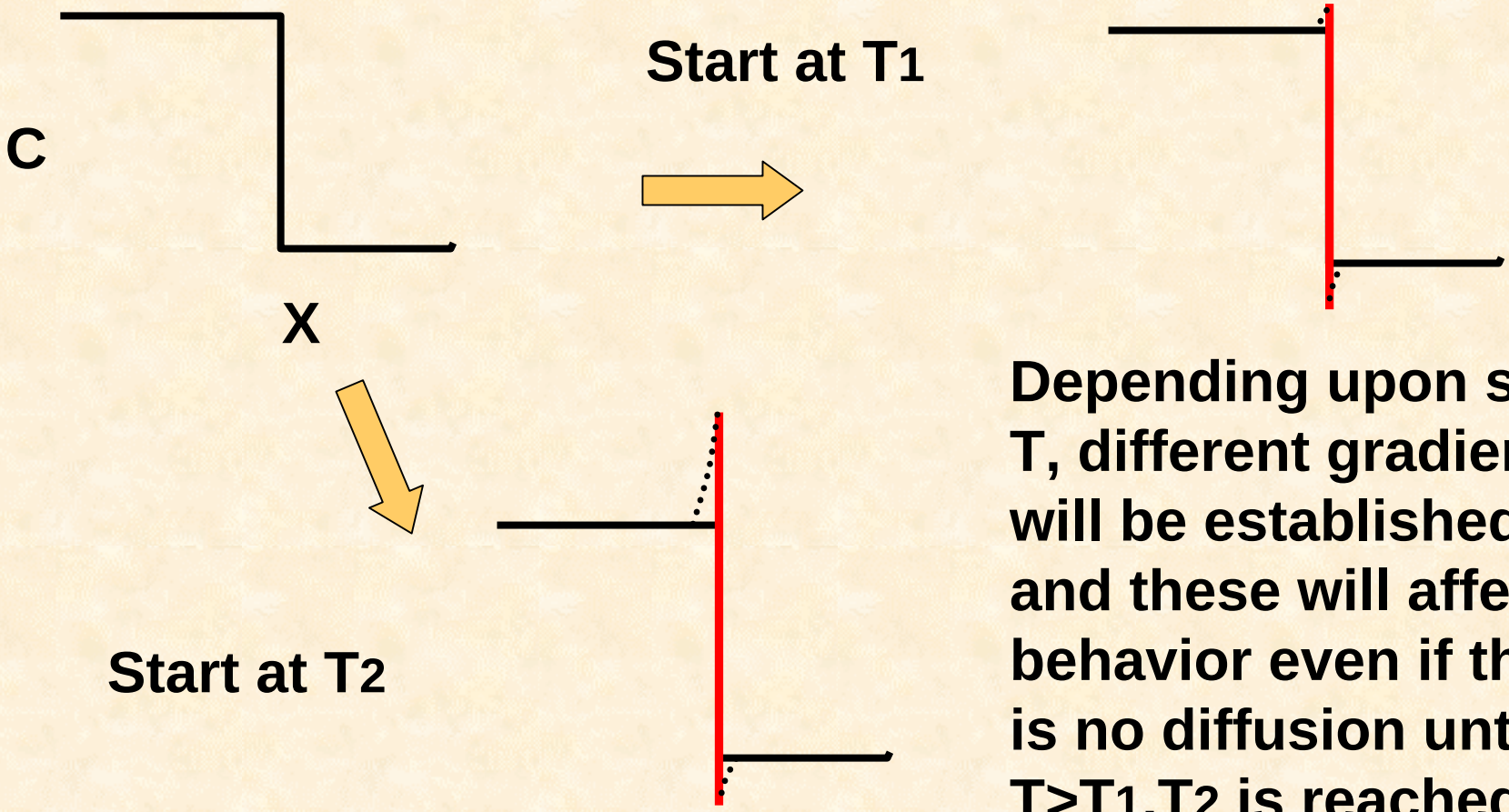
In Another Study, Simulation Start Conditions Had a Profound Influence

- **Transient ferrite dissolution and growth was measured in-situ**
- **Diffusion under para-equilibrium interface constraints could reproduce the time scale for the transformation**
- **The start temperature had a strong influence on the extent and nature of the transformation**



Reference: Palmer, Elmer, Babu, and Vitek, Austenite Formation and Decomposition, eds Damm and Merwin, TMS, 2003, p177

Seemingly Unimportant Changes in Start Conditions Can Be Important



Depending upon start T, different gradients will be established, and these will affect behavior even if there is no diffusion until $T > T_1, T_2$ is reached


UT 68
UConn 67
Jan. 8, 2005

Summary – Part 1

- **Multicomponent diffusion calculations were carried out to simulate the ferrite-austenite transformation in steel**
- **The path toward equilibrium was often indirect, with growth followed by dissolution or vice versa**
- **The results are understood if one considers the diffusional fluxes at the interface**
- **The same indirect behavior will occur in any system in which diffusion rates in the phases under consideration are significantly different**

Summary - Part 2

- **Caution must be observed when setting the simulation conditions**
- **Interface constraints must be chosen correctly (ortho-equilibrium, para-equilibrium, or something else)**
- **In addition to the criticality of the simulation cell size, changes in initial gradients and start temperature may have important consequences**
- **All of these aspects must be considered when simulating multi-component diffusion problems**