A Study of Austenite Precipitate Growth in Duplex Stainless Steel

A Research Performance Evaluation
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Introduction
As new experimental and characterization techniques are developed and improved, long-standing materials questions that have long been the subject of scientific debate are being revisited and answered. Such questions have surrounded the mechanism of solid-state phase transformation in ferrous systems for many years. Famous experimental and theoretical works produced such well-known metallurgists as Clarence Zener, Mats Hillert, Hubert Aaronson, and Rohit Trivedi (among many others) have now become the basis for the application of a variety of new techniques that aim to shed new light on a number of topics in this field. In the following presentation of a current study, several aspects of the physical metallurgy of phase transformations are reviewed and a variety of methods are examined in the context of austenite precipitation from ferrite in a duplex stainless steel.

Current State of Knowledge
The velocity of an interface during a phase transformation can be summarized in the following general equation:

\[ v_{\text{Interface}} = f(\text{Thermodynamics, Diffusion, Interface Structure}) \]  

(1)

Each of these variables represents an important aspect of the phase transformation: the velocity of the interface represents the kinetics of the transformation; thermodynamics provide the driving force for the transformation to take place; long-range diffusion of substitutional and interstitial alloying elements, and also of vacancies (self-diffusion) must occur in order to maintain equilibrium in any multi-component system; energy is required in order to create and maintain an interface of a particular shape and structure.

Thermodynamics and Diffusion
The foundation for obtaining each of these variables is relatively straightforward. The thermodynamics of austenite decomposition into ferrite in iron-carbon alloys have been studied and well-documented for many years and are reviewed in a pair of papers by Aaronson et al. [1,2] and later re-examined by Shiflet et al. [3]. This method can be applied to the reverse reaction, i.e. austenite precipitation from ferrite [e.g. 4], and to reactions involving other elements. Diffusion data for most common alloying elements
in an iron system are readily available and can be found in most current materials-based metals handbooks. Due to the multi-component nature of the duplex stainless steels which are the basis for this study, these variables may become exceedingly complicated, but computer software like Thermo-Calc and DICTRA* may be employed in order to make evaluation possible.

Kinetics

The first widely accepted model for ferrite precipitate growth from austenite in iron-carbon alloys was first proposed by Zener [5] and later modified by Hillert [6] as

$$\nu \frac{\rho}{D} = \frac{1}{a} \cdot \frac{\Omega}{1-\Omega} \quad \text{where} \quad \frac{\Omega}{1-\Omega} = \frac{x^{x/\alpha} - x^{x/\gamma}}{x^{x/\gamma} - x^{x/\alpha}}$$

(2)

Here, the thermodynamic driving force is represented by the supersaturation, $\Omega$, which is dependant on the initial composition of the austenite ($x^{x/\gamma}$), composition of austenite at the interface ($x^{x/\alpha}$), and composition of the growing ferrite ($x^{x/\alpha}$). This driving force is taken up by the requirement for diffusion of alloying elements to the interface ($D$) and by the curvature of the growing interface ($\rho$). Trivedi [7] further added to this model by incorporating interface kinetics and surface tension in the case of precipitate plates and needles, resulting in a much more complicated relationship:

$$\frac{1}{\sqrt{\pi p \cdot e^p \cdot erfc(\sqrt{p})}} = \frac{1}{\Omega_0} + \frac{v}{v_c} \cdot S_1 + \frac{\rho}{\rho_c} \cdot S_2$$

(3)

where $p$ is the Peclet number, i.e.

$$p = \frac{\nu \rho}{2D}$$

(4)

$\Omega_0$ is a critical supersaturation that depends on the equilibrium composition of austenite at a flat interface

$$\Omega_0 = \frac{\epsilon x^{x/\alpha} - x^{x/\gamma}}{\epsilon x^{x/\alpha} - x^{x/\alpha}}$$

(5)

$\rho_c$ is a critical radius of curvature at which $\Omega$ and $v$ become zero, $v_c$ is a critical velocity at which all driving force is dissipated at the interface, while $S_1$ and $S_2$ are complicated functions of $p$ that have been solved graphically. Some simplifications of the Trivedi relationship have been provided by Hillert [8] in a review of these models with regard to diffusion and interface controlled growth. Each of these models goes further towards solving the general equation first discussed, by incorporating aspects of thermodynamic driving force, transport kinetics, and interface shape/precipitate

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morphology. Evidence has been provided, however, as first proposed by Aaronson [9] in his ledge growth theory, that in many circumstances an interface can only propagate by means of even more complicated processes that involve interface structure at the atomic scale. These ledges are the first of a number of similar interface defects that have been discovered which create strain energies, and require additional activation energies, during growth. Significant work [e.g. 10,11,12,13] has been completed in incorporating these processes into growth models for ledged interphase boundaries.

Classically, transformation kinetics have been studied through dilatometry [14,15]. Experimental studies have also focused on studying the final as-transformed structures [16,17]. Recent advances in hot-stage confocal microscopy have resulted in a number of studies of solid-state transformations in iron and its alloys [e.g. 18, 19], including recent studies done by the present author [20, 21]. These studies presented real-time kinetic and morphological observations and included an extensive review of previous work done in the field of austenite formation from ferrite during heating.

Interface Structure

The interface structure determines the interfacial energy that results from broken bonds and surface tension, may include strain energies that result from lattice mismatch between the parent and precipitate phase (which often result in the formation of defects), and will also determine what kind of activation energies (in addition to those associated with long-range diffusion) will be required for the migration of atoms across and/or defects along the interface boundary which are required for it to move. The investigation of this structure at the atomic scale has become increasingly important in a comprehensive analysis of precipitate growth. The Transmission Electron Microscope (TEM) has been used to study interphase boundary structure in many alloy systems including Fe alloys [e.g. 22,23], and specifically dual-phase stainless steels [23,24,25]. These studies have been able to further characterize phase boundaries in terms of coherency [e.g.24,25,26], invariant lines [e.g.26,27,28], dislocation arrays [e.g.29,30,31], growth ledges [e.g. 26,32,33] (as well as any associated terraces and kinks), and a newly described type of interfacial defect called a ‘disconnection’ [e.g. 34,35,36]. The theory described in these papers has been summarized in the following paragraphs relating to interface formation, structure, and migration.

The orientation relationship between parent and precipitate phases during solid-state phase transformations has been widely studied; Dahman [37] has compiled a survey of known OR’s in the FCC/BCC system, which is summarized here. Two of these OR’s which have received the most attention, especially in the case of diffusional transformations in iron alloys, are those first proposed by Kurdjimov and Sachs (K-S) in 1933 [38], and concurrently by Nishiyama [39]and Wasserman [40] (N-W) in 1934. Both assume that a closest-packed plane—{111} in FCC and {110} in BCC—in the parent and precipitate matrix will remain parallel. The K-S OR requires that the close-packed directions in those planes—<110> in FCC and <111> in BCC—be aligned as well. A rotation of 5.26° around the normal to the closest-packed planes results in the N-W OR, in which a <211> FCC direction lines up with a <110> BCC direction. The K-S and N-W OR’s are represented in Figures 1a and 1b by overlaying a <111> projection of
the FCC lattice onto a <110> projection of the BCC lattice, and rotating appropriately to line up the desired directions. These figures indicate two more sets of parallel directions in each OR: <211> FCC/<211> BCC in K-S and <110>FCC/<100> BCC in N-W. A third OR, proposed by Pitsch [41], is obtained by rotating from K-S around the parallel <110>FCC/<111>BCC directions until a set of <100>FCC/<110>BCC directions become coincident (this has also been referred to as the inverse N-W OR). A closer examination of the overlays indicates that there exists 4-fold symmetry about the closest-packed plane normals for the N-W OR (The same exists in Pitsch, though not shown here), while only 2-fold symmetry for K-S. An analysis of the different variants of parallel planes/directions in each OR indicates that there are 4 possible configurations of the N-W and Pitsch OR’s, while there are 8 possible configurations of the K-S OR. Thus one might expect that, ceteris paribus, one would find the K-S OR twice as often as the N-W or Pitsch OR. Of course, other factors—the most important being the ratio between lattice parameters of the FCC and BCC matrices—also affect the relative likelihood of each OR in a particular system. One other OR of note is that of Greninger and Toriano (G-T) [42] which is intermediate between K-S and N-W, at a rotation of about 2.5 degrees from each around the close-packed plane normals.

The OR, however, provides only a small part of the information needed to characterize an interface. All solid phase interfaces can be initially characterized in terms of coherency, a measure of how well atoms of one crystal line up with a neighboring crystal at the boundary between them. Howe et al [25] and Christian [26] provide an excellent basis for a summary of the current understanding of interface structure. In a coherent interface, atoms on either side of the interface have exactly the same planar structure and spacing, such that each atom at the interface can bond with an atom on the other side. Coherent interfaces have a relatively low energy and are generally immobile. In partly coherent interfaces, there is a misalignment of these planar structures and/or a difference in lattice spacing which causes discontinuity and results in misfit-compensating defects [37] that may require varying degrees of energy to maintain. Incoherent interfaces do not have any long range order and have the highest energy of the three. While the two neighboring crystals need not have different structure to be characterized in this way—grain boundaries in a polycrystalline material, for example—this study will focus on boundaries between the FCC and BCC phases of iron.

In order to determine the coherency of an interface we must also know the orientation of the habit plane; that is, the actual plane along which the parent and precipitate phases meet. Habit planes can be described as rational or irrational, depending on whether or not the indices of the plane are integer values. Generally, high index habit planes can be reduced to a system of terraces, ledges, and/or kinks made of low index surfaces. Certain irrational habit planes can also be simplified in this way, using some patterned sequence of these structures. Terraces, ledges, and kinks can also result from misfit at an interface. Screw dislocations in either of the neighboring crystals can form steps at an interface in order to relieve tilt misfit relative to a habit plane; if such dislocations cross as a result of tilt misfit in both axis of a habit plane they result in kinks. Edge dislocations can relieve misfit strains due to twist or differences in lattice parameter. If the dislocation exists in the habit plane, it is referred to as a ‘transformation dislocation’.
Such dislocations are similar to misfit dislocations resulting from lattice mismatch during epitaxial growth of a thin film on a substrate. During migration of an interface, these dislocations become mobile; when two dislocations with burger’s vectors of opposite sign meet, they are annihilated. The result of this annihilation is called a ‘disconnection’. This is an energetically favorable event, as it further relaxes lattice strain on both sides of the interface. If the transformation disconnection has both dislocation and ledge character, it is referred to as a structural ledge. In general, a partly coherent interface will be surrounded by arrays of dislocations in the parent and precipitate matrix, composed of terraces, bounded by ledges (structural or otherwise) and kinks, and containing arrays of misfit dislocations and transformation disconnections. If the density of defects increases to the point where the spacing between dislocations required for full relaxation of an interface approaches the dislocation core size, the interface becomes incoherent (i.e. completely relaxed).

When there is no coherency, an interface needs only to be in thermodynamic equilibrium, and atoms need only to jump across the boundary and join the crystal structure on the other side for migration to take place. Such transformations are generally referred to as ‘reconstructive’, that is to say that atoms from one phase with one structure reform across the interface as a second phase with a different structure. Atoms do not form bonds across the interface, and because activation energies for atoms to make such a jump is relatively low the migration rate in an alloy is usually controlled by long range diffusion in the parent or precipitate phase. The growth direction of such an interface is not constrained by structural features. As previously mentioned, incoherent interfaces require the most energy to form due to the lack of bonds.

Partially coherent interfaces require less energy to form than incoherent interfaces because fewer bonds have been broken. However, structural ledges that have been relaxed by the formation of misfit dislocations and transformation disconnections in order to increase coherency among as many of the atoms across an interface as possible cannot migrate easily. These interfaces require the motion of steps and kinks along the habit plane, as well as the long-range diffusion of alloying elements to maintain thermodynamic equilibrium, in order for growth to occur. The motion of steps and kinks may also require climb of screw dislocations, and so diffusion of vacancies to and from the interface may also become important. Also, as a result of the orientation of such defects and the preferential habit planes in which they exist, growth occurs in certain directions at a much faster rate and the precipitates that form in such a manner will have characteristic shapes such as plates and laths.

**Objectives**

To the knowledge of the author all known *in situ* studies of solid-state phase transformations in various iron alloys have been limited in the sense that the growing interfaces, particularly during ferrite to austenite transformations, could not be retained for structural analysis at ambient temperature because of grain growth during high-temperature annealing and/or complete decomposition of austenite during cooling. On
the other hand, any *a posteriori* studies have relied on the transformation of austenite to martensite during a rapid quench, leaving a ferrite plus martensite microstructure and retaining no growth interfaces. In order to determine an orientation relationship (OR) of ferrite precipitates with the surrounding (prior) austenite matrix or (prior) austenite precipitates with the surrounding ferrite matrix, it is necessary to extract the austenite orientation in a secondary manner based on martensite grain orientations [e.g. 43]. Conveniently, interface structure and OR in duplex stainless steels, which are preserved upon quenching, can be studied directly through high resolution microscopy and diffraction [44, 45, 46] after high temperature kinetic observations. Therefore, the objectives of this study are to

1. Compare and analyze the observed kinetics, morphology, and interface structure of a growing precipitate with respect to the thermodynamics and transport requirements associated with the transformation.

2. Produce important evidence that could lead to the improvement of current models for solid state precipitate growth.

**Approach**

In order to achieve the objectives set forth, a proper material must be chosen and a variety of experimental techniques must be employed and mastered. Therefore, an introduction to duplex stainless steels, and a clear explanation for their applicability to this study is provided. High temperature confocal microscopy is employed to measure directly the kinetics of an evolving microstructure. Electron microscopy, electron diffraction analysis, and quantitative x-ray analysis are essential for the subsequent characterization at multiple scales of resolution.

**Material**

Dual-phase (or duplex) stainless steels are a relatively new grade of material which exhibit an excellent mix of the toughness and workability of austenitic grades with the higher strength of ferritic grades that result from a 50/50 mixture of the two phases. These steels also reduce costs by exhibiting excellent pitting resistance at a much lower nickel content. The duplex microstructure is obtained by a employing a careful mix of high chromium (18-28 wt%) and nitrogen (0.05-0.35 wt%) with low to moderate nickel (2.5-8 wt%). Kinetic data (i.e. CCT, TTT diagrams) [47] for these alloys indicate that a quench rate greater than 5 K/s from the two-phase $\gamma + \delta$ region below the solution temperature can prevent deleterious intermetallic ($\sigma, \chi$), and chromium-rich secondary ferrite ($\alpha'$) precipitation during cooling. While these properties are important from an application standpoint, they also provide an interesting method by which to study the nature of the high temperature ferrite to austenite phase transformation. The 2205 duplex stainless steel used in this study was supplied in the form of a rolled and annealed, industrially supplied sheet about 2mm thick. The exact chemical composition of the sample is provided in Table I, along with the ASTM composition specifications for this particular duplex grade. Duplex steels are generally solution annealed, after hot-rolling,
at a temperature such that an equal amount of austenite and ferrite are present. The material used in this study is no exception, and careful polishing of the surface reveals a relatively even mixture of each phase. Phase fraction diagrams, which indicate the amount of each phase expected to be present as a function of temperature, were created using Thermo-Calc software. In order to simplify these diagrams to some extent, some minor alteration to chemistry or suspension of certain complex equilibrium phases has been allowed. In Figure 2(a), the number of possible precipitate phases is reduced by eliminating the trace amounts of carbon, sulfur, and phosphorous. In Figure 2(b) all of the trace elements are included, but all of the solid phases other than austenite and δ-ferrite/α-ferrite have been suspended—this is essentially a metastable phase diagram. It is expected that the experimentally observed temperature for transformation, during significantly fast heating/cooling rates when only austenite and ferrite are present, should follow closely the phase fraction diagram in Figure 2(b). During extended isothermal holds, however, the diagram in Figure 2(a) should provide a better prediction of how much and at what temperature each phase will form. This will also provide adequate warning with regard to minimum temperatures at which undesirable intermetallics, which would ruin our preserved two-phase structure and composition, are not be expected to form.

Growth Kinetics
Transformation kinetics are measured experimentally through the use of a Confocal Scanning Laser Microscope (CSLM) with a hot stage. The CSLM also allows the precipitate morphology (e.g. tip radius, aspect ratio, interface shape) to be observed during the transformation and quantified. The principle of its operation has been detailed in a number of published studies [e.g. 18-21,48]. Confocal optics, shown in Figure 3a, enable the detection of a strong signal from the focal plane while decreasing the intensity of signals not in the focal plane. A screen with a pin hole deflects any signals that originate at locations above or below than the focal point, or on any surface which is not perpendicular to the laser, and thus an image is created, with a ~5-10 µm depth of field. The depth of field results from the variation of signal strength with elevation, roughness, or inclination, and is based primarily on the topography of the surface being viewed. Because this depth of field is fairly narrow, very small changes in elevation, inclination, or roughness will cause noticeable changes in signal strength. Thus the CSLM becomes an adequate, if not ideal, tool for observing the growth of precipitates in which any of the following processes occur: (i) surface deformation caused by the displacive nature of a phase transformation [e.g. 49,50], (ii) thermal grooving at free surfaces [51], (iii) surface diffusion leading to smoothing of the surface [52], (iv) local dilatometric changes due to differences in density between two phases, and perhaps (v) changes in absorption or scattering of laser radiation resulting from a change in optical properties inherent to phases involved in a transformation. Sample are prepared for experiments by a series of grinding and polishing steps, from 320 grit SiC down to 1 µm diamond particles, designed to provide an extremely flat initial surface that allows any subsequent topographical changes to be easily observed.

The hot stage attached to the CSLM consists of a gold-plated, elliptoid shaped furnace (shown in Figure 3b). Radiation from a halogen lamp at the lower focus is concentrated
on the sample, which is located at the upper focus of the ellipsoid. Because the laser radiation used to form the image is much more intense than thermal radiation from the sample, and because the pin hole mentioned earlier is also able to deflect out of phase radiation that does not originate from the laser, a clear image of the surface can be obtained. The temperature is measured by a thermocouple placed near the surface of the sample. The response of this thermocouple is also used to control the intensity of the heating lamp, and the temperature profile during an experiment can be programmed as desired.

A vacuum pump and gas delivery system are used in tandem to evacuate the furnace of undesired gases before an experiment and provide a constant atmosphere of desired composition during an experiment. An atmosphere of flowing helium gas is capable of cooling the sample from the annealing temperature at greater than 10 K/s throughout the critical temperature region and can thus preserve the high temperature microstructure. The gas used in this study is grade 5.0 He, and has been passed through a gas cleaning system as follows: one steel tube filled with silica desiccant to remove any moisture and three steel tubes wrapped with heating tape and ceramic fiber insulation; one filled with copper turnings (T~700ºC) and the next two filled with magnesium chips (T~600ºC). The furnace chamber is repeatedly evacuated and refilled with the purified He gas from the gas cleaning system, which was subsequently allowed to flow for 1 hour. The oxygen potential was measured in the inlet and outlet gas streams by a ceramic oxygen sensor in order to ensure that appreciable oxygen leaks were not present. Generally a constant (to within one order of magnitude during an experiment) 

\[ P_{O_2} < 10^{-15} \text{ atm} \]

is maintained. The flow rate during an experiment is on the order of 1 L/min to ensure adequate cooling rates can be achieved when necessary.

The sample is then subjected to a programmed thermal profile while an image of the surface was continuously recorded in video recorder at a rate of 30 frames per second. Samples are initially heated at a rate of 10 K/s to a soaking temperature of 1300ºC (1573 K), where the phase diagram indicates a fully δ-ferrite region, and held for 3 minutes. This is followed by a rapid quench (~20 K/s) to a variety of temperatures, ranging from 1100ºC down to 900ºC, and an isothermal hold for up to 30 minutes during which austenite is expected to precipitate from the ferrite matrix. The heating lamp is then turned off, and samples return to ambient temperature within approximately 45-60 seconds. Due to the large size (~1-2 mm) of the δ-ferrite grains formed during the high temperature soak, individual grains can be identified with the naked eye and marked with a scribe to locate observed regions for subsequent characterization. The recorded videos of the surface are subsequently digitized, analyzed, and from which still images can be extracted using MGI VideoWaveTM software.

**Microstructural Characterization**

In order to characterize the crystallography of the final microstructures, an EBSD system [53] was used after the CSLM experiments to characterize the transformed microstructures. Samples are further prepared for observation in the OIM (after CSLM experiments) through a series of polishing steps, from 3µm diamond paste down to .03 µm colloidal silica. The samples are then etched by immersing in an \( \text{H}_2\text{O}-50\% \text{ HCl} \)
solution for 20 minutes. The EBSD system used in this study is composed of a Philips XL-20 SEM, a digital camera and lens which collects electron diffraction patterns, and TexSEM™ OIM data collection software. Scan files obtained are analyzed with TexSEM™ OIM analysis software. For this study, the analysis software is used to produce inverse pole figure (IPF) color maps of an entire surface, and various pole figures of individual points from such a map. The collection software is capable of differentiating between multiple phases, and thus comparisons of selected pole figures can be obtained for any set of parent/precipitate phase points. In certain cases, the IPF maps are cleaned up using Adobe™ Photoshop software, for illustrative purposes. No colors are changed, only noise has been deleted and replaced with the surrounding color. Photoshop is also used to analyze multiple images: IPF images are superimposed onto confocal stills, and selected pole figures from points in precipitate and parent phase can be overlaid to check for common points.

An SEM equipped with EDX/WDX system and using QuantMap™ software is used to measure partitioning of alloying elements between phases. The sample is not prepared further after a CSLM experiment, so that topographical clues can be used to locate specific precipitates and boundaries during this analysis. The QuantMap program produces a series of images which show relative amounts of each element across a surface, and provides full compositional analysis data at an individual point chosen from the SEM image of the surface.

Preliminary Results

In-Situ Observations and Analysis of Kinetic Data

During heating of the 2205 sample from ambient temperature to the high temperature anneal, a number of interesting processes were observed. While dark and light regions of nearly even amounts were faintly visible on an as-polished sample when it was first placed in the microscope (Figure 4a), these regions became much more apparent as the temperature increased (Figure 4b). As the sample is heated beyond the solution annealing temperature (at which an even mixture of ferrite and austenite are expected) and ferritization should occur, the light regions eventually consume the darker regions (Figure 4c). As a result of these observations, it is concluded that the light regions are ferrite and the dark regions are austenite. When the sample is fully ferritized and the temperature approaches 1300ºC, coarsening of the ferrite grains begins to occur (Figure 4d). Coarsening is a very rapid process, and thermally etched grain boundary grooves may only last for a second or two. During the hold at 1300ºC, and once the coarsening process has slowed down to some extent, these grooves, and apparently the grain boundaries they represent, are observed to migrate visibly across the surface at a relatively constant rate, as shown in Figure 5(a-d). Boundaries are long and smooth, and generally had very little curvature. In a previous work [2] on a low alloy, medium carbon and sulfur containing steel, the grain boundaries could not be observed as they migrated. They were only observed in stationary positions, although during coarsening stages they did jump from place to place. Boundaries were also much more jagged in those steels, and could be highly curved. This was suggested as being due to pinning of a boundary at
non-metallic inclusions, and/or at the groove itself. When boundaries could become unpinned, they would rapidly move to a new position (no grooving was visible during this migration), and become pinned again at which time new grooves would appear. As a result of the visibly mobile boundaries, it is concluded that there are few, if any, non-metallic inclusions in the current alloy. Coarsening was thus able to continue until the sample was cooled to the solution annealing temperature, and nearly equilibrium-shaped grain sizes of over 1mm across were often observed.

As a sample was cooled from the high temperature soak, the first visibly apparent changes to the surface were fine precipitates with some directional orientation which varied from grain to grain. A series of still images in Figure 6(a-d) shows these precipitates in three neighboring ferrite grains. These precipitates are easily located in an SEM micrograph of the surface after a CSLM experiment. They seem to appear only on the very surface of the sample and are very thin. Particle are too thin to be identified using EDX analysis, but show up quite brightly which would suggest that they are building up charge in the microscope. Generally metals are good conductors and dissipate charge quickly so these are suspected to be non-metallic particles, likely oxides. These particles do not seem to have any effect on subsequent precipitation, and so have not been studied further. However, their directionality does suggest they prefer certain orientations and may in fact have a rational OR with the ferrite surface.

As the sample is cooled to the solution annealing temperature, nucleation and growth of austenite precipitates begins. Ferrite grain boundaries seem to be the primary location at which the precipitates nucleate. Two distinct forms of austenite precipitates are observed to grow, as shown in Figure 8: (a-b) show allotriomorph type precipitates while (c-d) show widdmannstätten-like laths. While the allotriomorphs have smooth, curved interfaces with the parent matrix and fairly random shape, all the laths growing from a particular grain boundary seem to be oriented almost identically, and have the same shape. Along the grain boundary from which these laths grew, there also seems to be a long, thin precipitate directly on the grain boundary, which seems grow slightly into the grain below this boundary. The presence of this grain boundary precipitate ‘film’, followed by laths growing from the same boundary, suggests that the w-s austenite laths are of secondary, rather than primary, nature.

The growth of both types of precipitates have been tracked and quantified, as shown in Figure 9. Growth rates of both laths and allotriomorphs follow a parabolic decay, which is indicative of diffusion-limited growth. The observed lengthening kinetics of the laths is significantly faster than the interface migration rates of the allotriomorphs.

Implications of the Composition Profile
Because the geometry of the allotriomorph suggests that they have incoherent interfaces with respect to the parent grain, while the lath shape suggests a partially coherent boundary growing by a ledge mechanism, one might expect that the allotriomorphs would grow faster if only interface mobility was the controlling factor. Thus some additional information about the composition of the parent and precipitate phases would be useful to see if partitioning has occurred, i.e. long-range diffusion is necessary for
growth. Figure 10 contains an SEM image of some austenite precipitates in a ferrite grain, and a collection of EDX quantification maps that show relative amounts of important alloying elements in the same region. It is apparent from these maps that significant partitioning of chromium, nickel, and molybdenum occurred during austenite precipitation in this alloy. Table II shows an average composition of the austenite allotriomorphs, the austenite laths, and the remaining ferrite. These averages are obtained from composition data at about 50 points in each type of region in order to ensure accuracy.

A few implications result from this data. First, because the laths grow directionally, and the total area of mobile interfaces (steps) is small compared to the incoherent allotriomorph boundaries, that a similar volume of material transformed in either precipitate results in a significantly different displacement of the respective boundaries. Mobile boundaries at the tip of a lath can thus move towards areas of greater supersaturation, and avoid significant losses of driving force due to transport requirements. It also appears that of the major alloying elements, Molybdenum is the only one which seems to vary significantly between allotriomorph and laths. This might suggest that diffusion of the molybdenum may in fact be the rate controlling factor if the transformation is limited by long range substitutional transport. In any case, the requirements for thermodynamic equilibrium cannot be simplified in this multi-component system, because no para-equilibrium or partial equilibrium situation seems to exist.

Determination of Orientation Relationships from Crystallographic Data

Figure 11 shows a pair of inverse pole figure color maps of polished (a) cross-section and (b) near-surface regions of 2 different samples that were transformed at 1050°C for 20 minutes and quenched. Figure 12(e) contains a different, smaller region of the same surface as 11(b). Several austenite precipitates, and the ferrite grains in which they have precipitated, have been labeled in these figures. Two distinct types of Widmanstätten laths, indicated as \( \gamma_2 \) and \( \gamma_6 \) in the near surface images of 11(b)/12(e), are observed; primary (initiating directly from a grain boundary) and secondary (initiating from a allotriomorph film at a grain boundary), respectively. Two types of allotriomorph-type precipitates also appear; those similar to \( \gamma_1, \gamma_3, \) and \( \gamma_4 \) which seem to evolve towards a jagged sawtooth-like shape along a boundary, and those similar to \( \gamma_5 \) and (especially) \( \gamma_7 \) which appear to form more of a film-like layer along a boundary with no jagged edges of any kind. Similar precipitates appear cross-sectional image in 11(a), although it becomes apparent that the lath-shaped precipitates are passing through the grains at a wide variety of angles relative to the plane of polish, as indicated by a wide variation of the apparent intragranular austenite between smallish ovals and long slender needles of similar width. Some apparent intragranular austenite also appears in the near-surface image, indicating that some laths have originated from grain boundaries or boundary films below the plane of observation and grown upwards, terminating once they reach the surface.

Tables III(a) and (b) present a set of orientation relationships between the austenite precipitates and their parent ferrite grains as indicated in the IPF maps. These OR’s have
been determined by overlaying pole figures from points within each respective austenite and ferrite region in such combinations as to indicate which, if any, of the previously detailed OR’s exist. Figure 13 shows an example of the method by which it is determined if an OR (a) does or (b) does not exist. If the any pair of small closed circles, which indicate poles in the upper hemisphere, overlap, a set of those planes are considered to be a match. If any pair of open circles, which represent poles in the negative hemisphere, overlap, and no closed circles overlap in the same overlay, then a set of planes are considered to be a near match. If any two of the three sets of parallel planes/directions suggested by the K-S or N-W OR’s, or both of the parallel planes/directions required for Pitsch, are considered to match, then that OR is chosen. If all three of the required parallel planes/directions are near matches and no other OR is an exact match (i.e. all three match), then that OR is indicated as a near match. Good agreement was reached between each austenite precipitate and a nearby ferrite grain in every instance that was attempted. It is readily apparent from these tables, and the corresponding IPF maps, that the K-S OR exists in nearly every case, and that for saw-tooth like allotriomorphs and primary laths, the OR is with the grain into which the precipitate grows. In the case of film-like allotriomorphs, it is difficult to know into which grain the precipitate has grown. In the case of secondary laths, the OR appears to be with the grain neighboring the one into which it grows, and the one which has an OR with its parent allotriomorph. However, in this case both the the film-like allotriomorph and secondary laths seemed to have a near N-W OR with the neighboring grain, which may have allowed a unique situation to exist. In only one other case did precipitates have a OR with two neighboring ferrite grains. The light purple laths ($\gamma_2$) in Figure 11(b) appeared to have a Pitsch OR with the light purple grain ($\alpha_1$) and a K-S OR with the dark purple ferrite grain ($\alpha_3$). This seems reasonable, considering that laths of a similar color appear to grow into the light purple ferrite grain, at a significantly different angle to the grain boundary.

The series of CSLM still images shown in Figure 12(a-c) correspond exactly to the IPF map shown in (e), as indicated by the overlay in (d). This series of images, while as a singularity do not result in any conclusions, do display the possibility for precipitates grown in a confocal experiment to be compared to crystallographic data at a later time; producing many such comparisons for analysis will be a fundamental basis for furthering this study.

**Future Work**

Much of the future work necessary for completion of this project is intended to improve the characterization of interface structure, which so far has been limited to a brief orientation relationship analysis. Overlaying pole figures is tedious and may be unreliable. An attempt will be made to improve accuracy and speed by using a computer program to automate the process. Such a program might incorporate texture-like analysis of individual precipitates and parent matrix, and then use the ‘average’ orientations on either side of an interface to quickly obtain the best OR fit and reduce error. A large number of correlated CSLM/OIM kinetic and crystallographic data can then be produced.
from repeated kinetic experiments under controlled conditions. A Focused Ion Beam (FIB) milling process will likely be employed in tandem with the OIM in order to carry out accurate serial sectioning of samples and determine the actual habit planes in a three dimensional structure. TEM analysis will provide more accurate crystallographic data, and, more importantly, allow an atomic scale examination of the interface and the dislocation arrays surrounding it. These interface structures can then be compared directly to kinetic and morphologic data to see if any correlations exist. Such correlations would then be the basis for improving current models. Based on the multi-component segregation observed in this alloy, and because complex diffusion fields exist whenever growth ledges are present, Thermo-Calc and DICTRA will be used to calculate the composition and transport data needed for the models. In either case, these calculated values will be compared to measured composition profiles to ensure accuracy.

References


47. Courtesy of JMatPro software: Thermotech Ltd./Sente Software Ltd., Surrey Technology Center, UK.


Table I: Composition (in wt%) of 2205 alloy used in this study, as well as the ASTM composition range allowed for this alloy.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2205(sample)</td>
<td>22.41</td>
<td>5.67</td>
<td>3.29</td>
<td>0.72</td>
<td>0.45</td>
<td>0.17</td>
<td>0.022</td>
<td>0.044</td>
<td>0.0004</td>
</tr>
<tr>
<td>2205(ASTM)</td>
<td>22-23</td>
<td>4.5-6.5</td>
<td>3-3.5</td>
<td>0.14-0.20</td>
<td>0.030</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II: Average composition of austenite precipitates and parent ferrite grain after CSLM experiment, obtained by SEM/EDX QuantMap analysis.

<table>
<thead>
<tr>
<th></th>
<th>Iron</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Molybdenum</th>
<th>Silicon</th>
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<tbody>
<tr>
<td>γ lath</td>
<td>68.67</td>
<td>20.24</td>
<td>7.90</td>
<td>2.58</td>
<td>0.63</td>
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<tr>
<td>γ allotriomorph</td>
<td>69.66</td>
<td>20.27</td>
<td>7.95</td>
<td>1.77</td>
<td>0.36</td>
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<tr>
<td>α parent</td>
<td>66.55</td>
<td>24.57</td>
<td>4.73</td>
<td>3.54</td>
<td>0.60</td>
</tr>
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</table>

Table III(a): Apparent orientation relationship between selected austenite precipitates with selected ferrite grains on polished near-surface shown in Figures 11(b) and 12(e)

<table>
<thead>
<tr>
<th></th>
<th>γ1</th>
<th>γ2</th>
<th>γ3</th>
<th>γ4</th>
<th>γ5</th>
<th>γ6</th>
<th>γ7</th>
</tr>
</thead>
<tbody>
<tr>
<td>α1</td>
<td>K-S</td>
<td>Pitsch</td>
<td>K-S</td>
<td>none</td>
<td>K-S</td>
<td>near N-W</td>
<td>near N-W</td>
</tr>
<tr>
<td>α2</td>
<td>none</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>K-S</td>
<td>K-S, near N-W</td>
</tr>
<tr>
<td>α3</td>
<td>-</td>
<td>K-S</td>
<td>none</td>
<td>K-S</td>
<td>none</td>
<td>-</td>
<td>none</td>
</tr>
</tbody>
</table>

Table III(b): Apparent orientation relationship between selected austenite precipitates with selected ferrite grains on polished cross-section shown in Figure 11(a).

<table>
<thead>
<tr>
<th></th>
<th>γ1</th>
<th>γ2</th>
<th>γ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>α1</td>
<td>None</td>
<td>K-S</td>
<td>none</td>
</tr>
<tr>
<td>α2</td>
<td>K-S</td>
<td>none</td>
<td>K-S</td>
</tr>
</tbody>
</table>
Figure 1(a): Overlay of (111) FCC surface (red, white, and pink circles represent atoms in the plane, 0.577*a above the plane, and 1.155*a above the plane, respectively) with a (110) BCC surface (black and grey circles represent atoms in the plane and .707*a above the plane) in the K-S configuration.
Figure 1(b): Overlay of (111) FCC surface (red, white, and pink circles represent atoms in the plane, 0.577*a above the plane, and 1.155*a above the plane, respectively) with a (110) BCC surface (black and grey circles represent atoms in the plane and .707*a above the plane) in the N-W configuration, indicating the rotation of 5.26° from the K-S configuration.
Figure 2: Selected simplified phase fraction diagrams for 2205 duplex stainless steel; in (a) trace amounts of phosphorous, sulfur, and carbon are ignored, while in (b) all phases except ferrite and austenite have been suspended.
Figure 3: Schematic of (a) confocal optics and (b) elliptical furnace used as hot stage in CSLM
Figure 4: Evolution of steel surface during heating, showing: a) as-rolled, polished surface b) re-crystallized ferrite (light regions) and austenite (dark regions) c) ferritization of entire surface, d) coarsening of δ-ferrite grains.
Figure 5: Images (a)-(d) show migration of δ-ferrite grain boundaries during soaking at 1300°C.
Figure 6: Series of CSLM images (a)-(d) show directionally-oriented precipitation of non-metallic precipitates on the surface of a sample during cooling to a solution annealing temperature.
Figure 7: SEM images of an unpolished surface of a sample solution treated at 1050°C, showing austenite precipitates in a ferrite matrix. Image (a) shows grain boundary allotriomorphs and a Widmänstetten lath tip, while image (b) shows a group of parallel laths. Both images indicate directional nature of non-metallic surface precipitates.
Figure 8: CSLM still images showing (a) - (b) austenite allotriomorphs and (c) - (d) Widmänstatten type austenite laths precipitating at δ-ferrite grain boundaries.
**Figure 9:** Growth kinetics of austenite precipitate laths and allotriomorphs at 1050°C and laths at 900°C.
Figure 10: SEM EDX composition quantification maps of area in (a), indicating partitioning between austenite and ferrite of (c) Chromium, ranging from $\sim 17 - 28$ wt%, (d) nickel, ranging from $\sim 2 - 10$ wt%, (e) molybdenum, ranging from $\sim 1 - 5$ wt%. Silicon (f), showed no partitioning at $\sim 0.5\%$. Partitioning of solute elements also resulted in some variation of iron content (b), ranging from $\sim 64 - 73$ wt%.
Figure 11: Inverse pole figure color maps of (a) cross-section area and (b) polished near-surface of samples solution treated at 1050°C. Resolution is 1 micron, both images are at same scale.
**Figure 12:** Images (a)-(c) show a CSLM sequence of Widmanstätten-type austenite precipitates during solution treatment of 1050°C, (d) and (e) show the corresponding crystallographic orientations on an EBSD inverse pole figure map with color key (f).
Figure 13(a): A set of overlaid pole figures used to determine the orientation relationship between an austenite precipitate ($\gamma_1$) and an adjacent ferrite matrix ($\alpha_1$). Ferrite points are red, austenite points are grey, circles represent points in the negative hemisphere, points which ‘match’ are indicated by arrows, and points deemed a ‘near match’ are surrounded by black ovals.
Figure 13(b): A set of overlaid pole figures showing no rational orientation relationship between an austenite precipitate ($\gamma_1$) and a second adjacent ferrite matrix ($\alpha_2$). Ferrite points are red, austenite points are grey, and circles represent points in the negative hemisphere. No matches or near matches exist.