In-situ investigation of the oxidation kinetics of Fe-12Cr-2Si using time-resolved transient grating spectroscopy

by

Cody Andrew Dennett

B.S. Engineering Physics, Cornell University (2014)

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering at the

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Abstract

The design and validation of new alloys for engineering applications is limited by the speed at which materials may be tested. In particular, there exist few methods by which the thermal, mechanical, and structural properties of materials may be monitored in conditions that are dynamically changing their microstructure. These conditions, such as heat treatments, radiation exposure, or corrosive environments, are common when material performance needs to be validated. To offset this lack of capability, new non-destructive experimental tools must be developed to facilitate on-line, real-time testing of materials undergoing some type of evolution. In this thesis, a flexible, all-optical methodology known as dual heterodyne phase collection transient grating spectroscopy is developed for this purpose. This method adapts a traditional spectroscopic technique sensitive to thermal and mechanical properties for real-time use. A formalism is also developed to quantify both elastic and thermal transport properties of materials with second-scale resolution. These new tools are then used to study the short-timescale oxidation kinetics of Fe-12Cr-2Si, a model alloy with oxide layer formation properties similar to large classes of Fr-Cr alloys. By monitoring the effect of thin oxide layers on surface thermal transport, there exists a pathway to continuously determine the thickness of a tens of nanometers thick growing oxide layer in real-time. Despite the lack of clarity in the particular set of experimental results presented here, the potential for the methods developed in this thesis is large. In-situ materials testing of this type may allow for a drastic increase in the pace of materials development by reducing the need for post-evolution, destructive materials testing between each design iteration.

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Chapter 1

Introduction

One overarching limitation in standard materials testing capabilities can be seen as the motivation for a large research project of which this work is just a part. This limitation is the lack of flexible, nondestructive methods by which material evolution may be monitored during dynamic processing. For material systems undergoing heat treatment, radiation exposure, electrical cycling, or corrosion, relatively few methods exist for continuous characterization of evolving material properties. In particular, the direct measurement of both thermal transport and elastic mechanical properties of material systems undergoing some kind of evolution cannot, in general, be monitored in real time. Rather, materials are often subjected to processing techniques and then destructively tested afterwards to determine their performance. For materials development purposes, this scheme is often time consuming, expensive, and by its nature limits the composition space of materials that are able to be tested. These testing schemes are also ill-suited to monitoring incipient material behavior such as breakaway oxidation, radiation induced void swelling, or deposition layer delamination. Phenomenon such as these only occur after some fixed incubation time which is not known a priori. These drastic changes material microstructure and system mechanics most often also correspond to drastic changes in thermo-mechanical properties.

Developing new methods by which continuous non-destructive characterization may be carried out is a problem of general interest for the field of materials development and processing. Particularly, if these tools are non-contact in addition to non-destructive, one single test apparatus might be used for a wide variety of testing environments. Towards this goal, we are developing a methodology known as transient grating spectroscopy (TGS). Through optical generation and characterization of surface acoustic waves (SAWs) on opaque media, both the elastic and thermal performance of material systems may be monitored. In prior implementations, this method has been used to study primarily static material systems, most notably thin film and layered structures. As a low-power all-optical technique, this type of testing is both non-destructive, and non-contact. However, traditional
implementations of this type of experiment have not been suited to the study of dynamically evolving material systems or to study both thermal transport and elastic properties concurrently. To use TGS for both dynamic systems and concurrent thermo-mechanical characterization, we have developed new optical and processing configurations which allow for time-resolved characterization.

Although this methodology is under development generally, in the work presented here we focus on a particular application of the technique. This application is the study of short-timescale oxidation processes in an Fe-Cr-Si model alloy system. Fe-Cr alloys are generally of great interest for their mechanical strength and corrosion resistance and are some of the most ubiquitously used materials in modern industry. Corrosion resistance in these systems is imparted through a thin, passivating layer of Cr$_2$O$_3$ which forms and inhibits further corrosion. Enriching Fe-Cr alloys with either Al or Si has been shown to impart an extra layer of protection on the surface, due to the formation of Al$_2$O$_3$ or SiO$_2$ layers between the primary oxide layer and the metal. In particular, Fe-Cr-Si alloys have been candidates of interest for use in lead-bismuth eutectic cooled nuclear reactors, as Si additions are appropriate for this system and the extra SiO$_2$ layer can be protective against chemical attack. The model alloy of choice from this system in the work presented here is Fe-12Cr-2Si.

The protective properties of this alloy are, in large part, determined by the short-timescale oxide layer formation kinetics. We have designed experiments to study these layer formation processes through the use of time-resolved TGS. As the TGS method is sensitive to surface characteristics, the presence of a thin oxide layer on the surface of a metallic substrate will alter the measured acoustic and thermal performance. The deviation in the response of an oxidized material from that of a bare substrate can be used to determine the grown oxide layer thickness. In this work, we develop a high-temperature oxidation test stand such that in-situ monitoring of samples being oxidized is possible. The combination of this testing facility and time-resolved TGS allows for continuous characterization of the thermal and elastic properties of these materials as the under oxidation.

We begin this work in Chapter 2 by describing the alloy Fe-12Cr-2Si and its corrosion characteristics, noting the corrosion behavior in air as a useful proxy for the behavior in other systems. The alloy’s developmental history is explored and we note several characteristics which make it a good material of choice for first-of-a-kind in-situ oxidation testing. Chapter 3 focuses on the TGS methodology. This chapter first describes prior implementations of the experimental apparatus, details the physics of acoustic wave generation and detection, and discusses how the characteristics of the TGS response depend on the surface layering of samples under investigation. We will define an ‘effective thermal diffusivity’ for multi-layers samples, focus on it as the parameter of interest in these studies, and motivate its expected changes as oxide layers are grown. In principle both the thermal and elastic characteristics measured using this technique will change as a function of surface layer formation. However, as changes in thermal transport properties have been explored less in the literature, we focus our efforts there. Chapter 3 also presents a new implementation of the TGS
technique which we call dual heterodyne phase detection transient grating spectroscopy (DH-TGS). This development provides the modifications to the technique which make time-resolved property monitoring of dynamic systems a possibility.

Chapter 4 details the parameters of the in-situ oxidation experiments and the flexible test stand constructed for this purpose. Using this test stand, which has the capability to reach high temperatures in either vacuum or a controlled cover gas environment, near-continuous monitoring of Fe-12Cr-2Si samples is possible as surface oxide layers are growing. This facility is not coupled to the optical configuration used for DH-TGS testing such that the apparatus remains flexible for future testing with different test configurations. Finally, Chapter 5 presents the results of the in-situ oxidation experiments as well as post-exposure chemical and layer thickness analysis. These post-exposure tests include both Raman spectroscopy and white light reflectometry and allow us to more clearly interpret the in-situ DH-TGS measurements in these initial tests. We also note several features of the dataset collected here that have been left for future work. This chapter concludes with a critical analysis of both the results of the tests conducted for this thesis and a discussion of the implications of this work for future experiments on dynamic materials systems.
Chapter 2

The Fe-12Cr-2Si material system

Fe-Cr alloys are some of the most prolifically utilized materials in modern industry. Where high-temperature operations are common, corrosion resistance is a must to ensure safe and reliable systems. The addition of chromium to iron-based alloys allows for the generation of dense, passivating Cr$_2$O$_3$ scales which protect the base alloy from continued corrosion [1]. This protection is imparted by drastically reducing the rate of Fe transport through the scale to the surface in comparison with iron oxide layers. In systems which undergo not only oxidation but also chemical attack, the formation of passivating scales is necessary to stabilize the base metal for use. Specifically, examples of such environments with aggressive heat transfer fluids are common and occur in nuclear power systems [2], concentrated solar energy systems [3], and many others.

The possible oxide layers which will form on Fe-Cr alloys are sketched in Fig. 2-1. The presence of each type of oxide layer is not guaranteed and depends sensitively on temperature, oxygen partial pressure, and chromium alloying composition. Upon exposure to high temperature, the time dependence of this layer formation is determined in large part by the free energy of formation of a given oxide species. This layering process is often complex and can be influenced by minor alloying additions. A schematic description of these types of layer formations is given in [4]. However, chromium bearing oxides have a marginally lower free energy of formation and will therefore be able to form at lower oxygen potentials. This generally leads to the presence of a chromium-rich oxide close to the metal/oxide interface and iron-rich oxides above [5]. In systems at lower temperatures or chromium compositions, the iron-chrome spinel layer, Fe(Fe$_x$Cr$_{2-x}$O$_4$), may form preferentially instead of the denser, slower growing Cr$_2$O$_3$. This layer is somewhat protective, but does not slow Fe transport to the same degree as Cr$_2$O$_3$ [1].
2.1 Characteristics of Fe-Cr-Si alloys

For some applications the formation of Cr$_2$O$_3$ protective layers is not enough to inhibit Fe transport to the surface layer, allowing net corrosion of the base metal to continue [1]. In these cases it is of interest to promote the formation of further protective oxide layers. The canonical choices for alloying elements to form these additional scales are Al and Si, as the oxides that they form, Al$_2$O$_3$ and SiO$_2$, can form thin layers that greatly inhibit Fe and Cr transport and completely passivate the oxide in question [5]. Additionally, Cr$_2$O$_3$ vaporizes above 900°C, necessitating the addition of another protective layer for operation at even higher temperatures [6]. However, both Si and Al additions can be detrimental to the stability and mechanical properties of iron-based alloys [7,8]. To reduce the overall amounts of Si or Al necessary form protective scales, these elements may be alloyed in small amounts in addition to significant Cr alloying [5].

The kinetics of protective SiO$_2$ and Al$_2$O$_3$ layers that form in these ternary, Fe-Cr-(Si,Al), alloy systems is often described as a ‘secondary getter’ process [9]. The free energy of formation for SiO$_2$ and Al$_2$O$_3$ are both lower than that of Cr$_2$O$_3$ [10]. However, if alloyed in small enough amounts the primary oxide layer formed at the metal/oxide interface, on short timescales, will be a chromium-rich oxide, as in the case of the pure Fe-Cr system. As oxidation continues, this quickly-formed chromium-rich barrier acts as an oxygen getter, lowering the oxygen potential in the metal under the oxide layer. This reduction in oxygen in the metal matrix ensures that little precipitation of SiO$_2$ or Al$_2$O$_3$ occurs. Instead, oxidation occurs at the metal/oxide interface of either Al or Si. In the case of Si, significant enrichment near the interface layer may occur as Si is relatively mobile in the metal matrix. In the case of Al, diffusion to the interface is highly dependent on grain boundary
diffusion as bulk matrix diffusion is slow \[5\]. A schematic of this process is shown in Fig. 2-2, which also includes a grain boundary transport mechanism for Si.

Of the two choices of alloying elements for this additional protective scale, Al is often preferable to Si. \(\text{Al}_2\text{O}_3\) has a significantly lower free energy of formation than \(\text{Cr}_2\text{O}_3\) \[10\]. Therefore, when present in sufficient amounts, it is easier to form a non-porous, protective \(\text{Al}_2\text{O}_3\) oxide scale than a \(\text{SiO}_2\) oxide scale. Additionally, for high Al alloying compositions, \(\text{Al}_2\text{O}_3\) may form preferentially to the \(\text{Cr}_2\text{O}_3\) scale found on Fe-Cr alloys, imparting passive protection faster than if the formation occurs through the secondary getter mechanism \[5\]. For these reasons, the Fe-Cr-Al alloy system has found significantly more use than the Fe-Cr-Si alloy system and has been studied more widely. However, the Fe-Cr-Si system has been developed as a material system of greater interest in the study of corrosion resistant materials for several particular systems. One such system is lead-bismuth eutectic (LBE) cooled nuclear reactors \[11,12\].
2.2 Development of Fe-12Cr-2Si

We will now briefly discuss the design parameters in [12] which lead to the particular alloying composition choices of the Fe-12Cr-2Si stock that is used as the material basis for the remainder of this thesis. In [12], a weld overlay method is used to coat structural components with a corrosion-resistant coating for use in LBE systems. The structural basis used in this composite is chosen to be F91 (Fe-9Cr-1MoNbVW). This choice was made based on a variety of criteria including performance in LBE, phase stability, irradiated material response, and compatibility with ferritic Fe-Cr-(Al, Si) coating layers. Despite the general high performance of Fe-Cr-Al alloys, previous studies had shown that amount of Al necessary to form protective scales in an LBE environment were very high, in the range of 4-15% (all alloying compositions specified in weight percent) [11]. The primary detriment in Al concentrations this high came from the lack of weldability. As the composite production technique under consideration in that work is weld-overlaying, Fe-Cr-Al alloys are poor choice for this application.

The alloying compositions of Cr and Si were chosen to promote the formation of both SiO$_2$ and Cr$_2$O$_3$ protective scales at 700°C in variable oxygen environments and ensure the stability of the base metal matrix. At 500°C, Cr is only miscible in an Fe matrix up to around 10% [13]. Beyond this concentration and in the temperature range from about 500 to 825°C, intermetallic σ-phase formation has been noted in a wide variety of stainless steels [14]. Extensive σ-phase precipitation has been shown to allow fast cracking pathways, the presence of which would be severely detrimental to a thin, corrosion protection coating [12]. To reduce the total amount of σ-phase present, the alloy designed for protection in LBE was chosen to have 12% Cr. At this level, Cr will still form Cr$_2$O$_3$ passivating layers for protection, but will keep σ-phase precipitation to a minimum. As Si alloying reduces the mechanical performance of stainless steels, especially under irradiation [15], the Si content was chosen at 2% to be as low as possible to while still forming a continuous SiO$_2$ scale below the chromium-bearing oxides. This alloying composition is similar to several engineering steels, particularly the 400 series stainless steels, comparisons to which will be made throughout this work.

2.3 In-situ oxide growth determination

The alloy Fe-12Cr-2Si was chosen as the alloy of choice for the studies conducted in this thesis for several reasons. Although it has been developed for a particular purpose, Fe-12Cr-2Si can be taken as a material fairly representative of the oxidation behavior of a large class of Fe-Cr and ternary alloys. Generally understanding the composition, thickness, and formation order of oxide layers on engineering alloys is important in determining both the short- and long-timescale performance of alloys in corrosive conditions. In practice, high temperature systems expected to undergo particularly
harsh chemical attack may need to be preconditioned before use to ensure a passivating layer has fully formed before operation can begin [16]. Detailed knowledge of the protective scale formation kinetics for alloys currently in use allows for optimization of this procedure, with potential for large cost savings.

To study these fast kinetic processes, we will apply a non-contact, non-destructive methodology to monitor the surface layer elastic and thermal transport properties of Fe-12Cr-2Si undergoing oxidation. This methodology, which will be described in detail in Chapter 3, uses an active measurement spot size several hundred microns in diameter. For the initial studies performed here, we also sought to use a material with a large grain size. As surface grain boundaries can possibly affect the transport properties that are being measured, eliminating their influence through the use of large-grained materials was a clear choice. The grain size of the ferritic Fe-12Cr-2Si alloy used in this work is several mm’s, making it well suited for this application [12]. Finally, we sought to use a low-addition alloy, as opposed to a true engineering alloy with many minor alloying elements, to simplify the kinetic processes governing the oxidation we observed. Oxidation experiments on alloys in this composition space from the literature have mostly been conducted at temperatures higher than those used in this thesis. Experiments at similar temperatures have been carried out by only a few authors, most notably [9], although these studies used much longer exposure times than considered here. Studies carried out on similar composition Fe-Cr alloys, without Si, for times and temperatures close to those used here prove to be the most useful comparisons [17].

In this work, oxidation characteristics will be studied in dry air conditions. Although not likely the conditions in which materials with careful tailored oxidation characteristics will be utilized, these conditions serve as a useful baseline. Most directly, these studies might be compared to the case of system preconditioning, as described above. Additionally, work in the Fe-Cr-Al alloy system has also shown that passive layer formation occurs in largely the same morphology in dry air conditions as in steam conditions [18,19]. In the simplest terms, however, air oxidation is the easiest by which to validate a new methodology of continuous characterization of passive film growth and is thus an obvious starting point.

The outcomes of the work presented in this thesis are designed to have broader implications than the behavior that we observe on this particular material. We seek to design diagnostic methods by which the growth of thin layers, oxides or otherwise, can be monitored in near-real time. For the case of oxides, this capability would greatly accelerate the pace of development and testing of new, oxide layer engineered materials. As with most steel performance characteristics, oxide layer formation is sensitive to minor alloying elements [10]. The ability to rapidly and iteratively test materials with changes in minor alloying for protective scale formation properties in a variety of environments would be a powerful tool for material development.
Chapter 3

Transient grating spectroscopy and dual heterodyne collection

In this chapter we describe the primary experimental methodology used in this thesis, transient grating spectroscopy (TGS). Much of Section 3.1 and Section 3.3 are drawn from [20], which at the time of submission of this thesis has been accepted for publication in *Applied Physics Letters*. Broadly, TGS is a non-contact, non-destructive, photoacoustic methodology which can be used to measure thermal and elastic mechanical properties materials under investigation [21–24]. For almost two decades, TGS has been implemented using an optical heterodyne detection technique in an arrangement described in [21]. This methodology has been used to study the acoustic and thermal transport properties of a wide variety of systems including thin-film semiconductors [24], microsphere lattices [25], and suspended silicon films [26], among many others [23]. It has also been applied to study the magnetic properties of thin films [27], the electronic properties of 2D semiconductors [28], and transport properties in high-\(T_c\) superconductors [29]. Similar methods have been used for grain mapping in polycrystalline metals [30]. Recently, TGS has been shown to be a useful tool in evaluating the effects of irradiation in metallic systems [31–33].

However, although there is great variety in the types of material systems for which TGS has been used, these systems are all static in the sense that the properties of the materials under investigation are not changing as a function of some time-dependent forcing. Of late, there has been increased interest in using the TGS methodology to study thermo-mechanical properties which are dynamically changing as a result of material forcing such as heat, layer deposition, or irradiation [34,35]. Although variations of TGS experiments have been described in the past which report short collection times, such as [36,37], these systems focus solely on monitoring changes in the acoustic response of materials on short timescales. Developing methods which allow for the concurrent monitoring of both elastic and thermal transport properties in dynamically changing systems is of great interest.
The chapter begins in Section 3.1 with a description of the physical processes utilized in the TGS methodology. Section 3.2 describes the difference between the 'amplitude grating' and 'phase grating' responses which can be probed using TGS and describes a new informed fitting method which can be used to determine thermal transport properties though the phase grating response. Section 3.3 describes the design and implementation of a new experimental methodology, dual heterodyne phase collection TGS (DH-TGS), that allows for complete TGS measurements to be made on very short timescales. DH-TGS allows for second-resolution time-resolved data to be collected for both thermal and acoustic parameters of interest. As the focus of this thesis is on the growth of thin oxide layers on materials at high temperature, Section 3.4 describes how the thermal and elastic material responses in TGS measurements are affected by the film layering structure of the material under investigation. This section introduces the concept of an 'effective thermal diffusivity,' which will be the parameter of interest for the studies presented later in this thesis. The goals of the experimental campaign described in Chapter 4 are designed to use this effective thermal diffusivity as the parameter from which a grown oxide layer thickness can be determined.

3.1 Transient grating material excitation

TGS is a type of pump-probe spectroscopy which relies on the generation and monitoring of a periodic ‘material excitation’ on the surface of a sample of interest. The generation of a periodic excitation is accomplished by pulsing the surface of a sample with a periodic laser intensity grating. This grating is generated by crossing, in both space and time, two short laser pulses at the sample surface to generate an optical interference pattern. The wavelength of the excitation, \( \Lambda \), is uniquely determined by the wavelength of the laser used to pulse the surface and the angle at which the two beams cross

\[
\Lambda = \frac{\lambda_e}{2 \sin (\theta/2)} = \frac{2\pi}{q},
\]

where \( \lambda_e \) is the wavelength of the excitation laser, \( \theta \) is the beam crossing angle at the surface, and \( q \) is the grating wave vector, which will be an important parameter in describing material responses to this type of excitation [38]. A schematic of this process is shown in Fig. 3-1. The transient grating technique is often used on both transparent and opaque materials [24], however the work in this thesis will focus solely on opaque materials, or the ‘reflection geometry’ as it is sometimes referred to. Hence we will only be concerned with the generation of material excitations on the surface of samples, and not through their bulk.
3.1.1 Excitation generation

In practice, this material excitation is generated using a single pulsed laser source and a compact optical geometry as shown in Fig. 3-2. A single pulsed laser source is passed through a volumetric diffraction grating tuned to diffract most of the incident light into the ±1 diffraction orders [21]. The transmitted beam, and all other diffraction orders, are spatially filtered, leaving only two co-planar pump paths. These pump pulses are passed through a pair of achromatic doublets, $L_1$ and $L_2$, which first collimate, then re-focus the pump pulses at the sample surface. The diffraction grating used for this purpose is referred to as the ‘phase mask,’ as the optical arrangement described can also be considered an imaging system for the mask onto the sample surface. If the phase mask grating spacing is $\Lambda_0$, then $\Lambda$ at the sample surface is fixed by

$$\Lambda = \frac{MA_0}{2},$$

(3.2)

where $M$ is the magnification ratio of the $L_1/L_2$ lens system given by $M = f_2/f_1$, where $f_i$ are the focal lengths of the imaging system lenses [21]. Common excitation spot sizes are in the range of several hundred microns and common excitation wavelengths are in the range of 1-10 $\mu$m.

The periodic laser intensity grating pulsed onto the surface will rapidly increase the local electron temperature, which, given sufficient electron-phonon coupling, will rapidly increase the phonon temperature in a periodic profile as well [39]. This laser pumping has the effect of both launching two, counter-propagating acoustic waves on the surface as a result of stress generated by rapid thermal expansion, as well as generating a non-equilibrium thermal profile on the surface [24,38]. This excitation is manifested as surface displacement and/or transient changes in the reflectivity.
The change in reflectivity is a good indicator of the time-dependent temperature of the surface excitation [24].

3.1.2 Excitation detection

To interrogate the dynamics of this excitation, a third, probing, laser beam is diffracted from the excited material grating. The first order diffraction of this probe from the surface is directed into a photodetector, such that the amplitude of the response oscillates with the frequency of the material excitation. The probing laser is controlled such the spot size at the sample surface is smaller than the excited region, as is shown in Fig. 3-3. In TGS experiments to date, a fourth laser beam, generated from the same laser source as the probe, is made spatially coincident with the diffracted signal and used as a reference oscillator, allowing the diffracted probe signal to be heterodyne amplified. In this configuration, the measured signal intensity has the form

\[ I_S(t) = I_R + I_D(t) + 2\sqrt{I_R I_D(t)} \cos \phi, \]  

(3.3)

where \( I_R \) is the reference oscillator intensity, \( I_D(t) \) is the diffracted signal intensity, and \( \phi \) is the heterodyne phase difference between the reference and diffracted beams [21]. The functional depen-
Transient grating spectroscopy is a technique which measures thermomechanical properties by inducing and monitoring surface acoustic waves.

Figure 3-3: Pump and probe beams are spatially overlapped on the sample surface to monitor the excited material response. Pump excitation spots used in experiment are normally several hundreds of microns in diameter.

dence on time reflects the time-dependent nature of the material excitation, which will subsequently be discussed in greater detail. As $I_R$ is constant and usually of much greater amplitude than $I_D(t)$, the result is an overall amplification of the time-dependent signal of interest. In general, spatially ensuring the overlap of the diffracted signal and the reference oscillator is difficult. However by passing a single probing laser through the same phase mask used to generate the material excitation, as shown in Fig. 3-2, the spatial overlap of the signal and reference oscillator are ensured [21]. Geometrically, the specular reflection of the reference oscillator and the first order diffraction of the probe beam will be coincident in this configuration. The heterodyne phase is controlled by placing a highly parallel optical flat in the path of the probing beam path at a slight angle to control the path length difference between the probe and reference oscillator. Fig. 3-2 also includes a neutral density (ND) filter in the reference oscillator path to ensure that the reference beam does not saturate the photodetector. Both probe beams are vertically separated from the probe paths to allow for phase and intensity control of the probe beam paths. The location of all beam paths in the plane of lens $L2$ are indicated in Fig. 3-2 as well.

To recover large amplitude signals suitable for quantitative analysis of the acoustic and thermal transport properties, it is common practice to record traces at both $\phi = 0^\circ$ and $\phi = 180^\circ$. These two signals can be subtracted from one another to recover a total signal amplitude

$$I_S^{\text{tot}}(t) = I_S^0(t) - I_S^{180}(t) = 4\sqrt{I_R I_D(t)}.$$ (3.4)

In addition to further amplifying the recorded signal intensity, taking a set of measurements in this manner allows for the removal of any systematic noise, such as the impulse response of the photodetector or other electrical noise present near the experiment, from signals that are used for
analysis. It is this principle, the need for signal collection at multiple heterodyne phases, which becomes the time-limiting factor for traditional implementations of TGS experiments. As only signals at a single heterodyne phase can be collected at a time, a complete measurement may either be time-resolution limited by a mechanical actuation time (for short collection times) or by the desired signal-to-noise ratio in the resultant collected response (for materials where long collection times are necessary). For metallic samples, an average collection time would be on the order of several minutes for a response characterized at two heterodyne phases.

### 3.1.3 Components of the TGS response

Although a useful illustration of the principle of heterodyne amplification, Eqs. (3.3) and (3.4) are a simplification of the process which only account for a general periodic material excitation from which the probing laser can diffract. In reality, as mentioned above, the material response of opaque materials will generally be comprised of:

1. A component due to changes in the complex reflectivity of the sample, $r^* (t) = r_0 \left[ 1 + r'(t) + i r''(t) \right]$, whose time dynamics scale as the temperature profile of the surface and

2. A component due to surface displacement, $u(t)$, which is generated by periodic thermal expansion.

A detailed analysis in [24], which first considers an incident plane wave diffraction from a periodic material excitation comprised of both of the reflectivity and surface displacement components followed by a mixing of that first diffraction order with a specularly reflected reference oscillator, concludes that the total heterodyned signal intensity has a form

$$I_S(t, \phi) = t_r I_{op} R_0 \left[ r'(t) \cos \phi - (r''(t) - 2k_p u(t) \cos \beta_p) \sin \phi \right],$$

where $t_r$ is the attenuation factor of the reference beam due to the neutral density filter, $I_{op}$ is the initial intensity of each of the probe and reference oscillator beams, $R_0 = |r_0|^2$ is the reflectivity of the sample, $k_p$ is the optical wave vector, $\beta_p$ is the angle of incidence of the probe beams onto the sample surface, and $\phi$ is the heterodyne phase. This expression is valid in a regime where the reference oscillator intensity is much greater than the diffracted signal intensity, \{ $t_r \gg r'(t), r''(t), k_p u(t)$ \}, which is true in TGS experiments. The form of this expression indicates that by setting the heterodyne phases in experiment to $\phi = 0$ or $\phi = \pi$, the real component of the reflectivity change, $r'(t)$, can be isolated. This selection of phases is referred to as the ‘amplitude grating’. If the phase is chosen to be $\phi = -\pi/2$ or $\phi = \pi/2$, the ‘phase grating’ may be selected, which is comprised of a combination of the imaginary part of the reflectivity, $r''(t)$, and the surface displacement, $u(t)$. Following a pulsed transient grating excitation, the resultant material excitation will thermally decay, reducing the in-
tensity $I_S(t, \phi)$ as a function of time for all values of $\phi$. In addition, a periodic acoustic oscillation may be superimposed on this decaying profile for certain choices of $\phi$.

As the component of the material excitation due to thermal expansion and acoustic wave propagation, $u(t)$ is the dynamic which includes information about the elastic mechanical properties of materials under investigation. These surface acoustic waves (SAWs) have phase velocities determined by the fourth order elastic constants, $C_{ijkl}$, and density for a general anisotropic crystalline material [40]. For isotropically elastic materials, or materials whose grain size is much smaller than the excited region on the material in question, the SAW velocity is well described by a polynomial fit to Rayleigh’s equation,

$$c_R = \sqrt{\frac{E}{2\rho(1+\nu)}} \left(0.874 + 0.196\nu - 0.043\nu^2 - 0.055\nu^3\right),$$  \hspace{1cm} (3.6)

where $c_R$ is the SAW (or Rayleigh wave) velocity, $E$ is the Young’s modulus, $\rho$ is the density, and $\nu$ is the Poisson’s ratio [41]. This expression is a good approximation for $c_R$ for all physical values of $\nu \in [-1, 0.5]$. The root term on the right hand side of the above expression is the bulk shear wave velocity. The polynomial expression on the left is always less than one, indicating that SAWs on isotropic materials will always have a velocity slower than that of bulk shear waves. For either isotropic or anisotropic materials, the surface layering structure of materials under investigation will also affect the phase velocity of the acoustic response [23]. From measurements of the phase grating response conducted with a known grating spacing, $\Lambda$, $c_R$ can be determined to great precision by finding the dominant frequency in the power spectrum of the collected signal, $f_{TG}$. The SAW speed is then simply

$$c_R = \Lambda f_{TG}.$$ \hspace{1cm} (3.7)

Fig. 3-4 shows both the recorded phase grating signal as well as the power spectrum of that signal for an {001} oriented single crystal of pure aluminum with the SAW polarization oriented along the (100) crystal direction.

To be able to continuously collect information about both the thermal and elastic material properties of samples being investigated under dynamic conditions, the phase grating response is more useful than the amplitude grating response. However, as we will discuss next, the functional dependence of the thermal response of the reflectivity and surface displacement are not the same. This mismatch complicates the procedure of determining thermal transport parameters from the phase grating response.
Figure 3-4: Sample results from transient grating excitation with $\Lambda = 4.82 \, \mu m$ along the (100) direction of $\{001\}$ oriented single crystal aluminum. The SAW response is superimposed over the decaying thermal grating as a function of time. The inset shows the filtered power spectrum of the response with a clear peak at the SAW frequency. Figure sourced from [35].

3.2 Amplitude and phase grating thermal transport

To use the TGS technique to monitor the thermal transport properties of bulk materials under investigation, we must first construct an appropriate model for both the surface temperature profile and the surface displacement profile as a function of time. Consider a two-dimensional semi-infinite half-space defining a surface (at $z = 0$) on which a periodic transient grating will be projected.

We define the positive $\hat{z}$ direction into surface. The surface temperature profile resulting from a $\delta$-function grating excitation can be found by solving the thermal diffusion equation

$$
\rho c_v \frac{\partial T}{\partial t} - k_x \frac{\partial^2 T}{\partial x^2} - k_z \frac{\partial^2 T}{\partial z^2} = Q(x, z, t),
$$  

where $\rho$ is density, $c_v$ is the heat capacity, $T$ is the temperature, $k_x$ and $k_z$ are the thermal conductivity components parallel and perpendicular to the surface, respectively, and $Q(x, z, t)$ is the absorbed heat density [24,22]. This equation can be solved for an infinite periodic surface excitation of the form

$$
Q(x, t) = Q_0 \cos(qx)\delta(t),
$$  

where $Q_0$ is a laser intensity, $q$ is the grating wave vector as defined in Eq. (3.1), and $\delta(t)$ is the Dirac delta function, by using a Fourier transform technique for both spatial and temporal components of the response [22]. Appropriate boundary conditions for the problem are given by

$$
\frac{\partial T}{\partial z}(z = 0) = 0,
$$

$$
T(z = \infty) = T_{\text{bulk}},
$$

(3.10)
where $T_{\text{bulk}}$ is the initial equilibrium temperature of the system. Solving the system in this manner returns a form for the surface temperature profile

$$T(z = 0, x, t) = \frac{A}{\sqrt{\alpha_z t}} \cos(qx) \exp(-\alpha_x q^2 t), \quad (3.11)$$

where $A$ is an amplitude, and $\alpha_z$ and $\alpha_x$ are the cross- and in-plane thermal diffusivities given by $\alpha_i = k_i / \rho c_v$, respectively. This form reveals that, following excitation, the temperature grating, and therefore the grating in transient reflectivity change, decays with dynamics governed by

$$\{r'(t), r''(t)\} \propto \frac{1}{\sqrt{t}} \exp(-\alpha_x q^2 t). \quad (3.12)$$

Note that the cross-plane thermal diffusivity appears in a term only governing the amplitude of the response. Experimentally recorded traces are normally sensitive only to the in-plane thermal diffusivity, as shown in the expression above \[24\].

To find the surface displacement profile resulting from the same periodic, short-pulse excitation, we must also consider the equation of thermoelasticity, written for isotropically elastic materials as

$$(1 - 2\nu) \nabla^2 \mathbf{u} + \nabla(\nabla \cdot \mathbf{u}) = 2(1 + \nu)\alpha_{th} \nabla T, \quad (3.13)$$

where $\nu$ is the Poisson’s ratio, $\mathbf{u} = (u_x, u_z)$ is the two dimensional displacement vector, and $\alpha_{th}$ is the thermal expansion coefficient. This equation may be solved for the same excitation, coupled to the solution for the temperature dynamics, under the boundary conditions

$$\sigma_{zz}(z = 0) = \sigma_{xz}(z = 0) = 0$$
$$u_x(z = \infty) = u_z(z = \infty) = 0, \quad (3.14)$$

where $\sigma_{zz}$ and $\sigma_{xz}$ are the surface stress components, using the same Fourier domain solution for both components of the surface displacement \[22\]. The surface displacement dynamics are recovered through $\partial u_z/\partial x$, which at the surface takes the form

$$\frac{\partial u_z}{\partial x}(z = 0) = B \sin(qx) \exp \left( -q^2 (\alpha_x - \alpha_z) t \right) \text{erfc} \left( q\sqrt{\alpha_z t} \right), \quad (3.15)$$

where $B$ is an amplitude and erfc($x$) is the complimentary error function defined by

$$\text{erfc}(x) = \frac{1}{\sqrt{2\pi}} \int_x^\infty dt \exp(-t^2). \quad (3.16)$$

Note that although we have written an expression for $\partial u_z/\partial x$, the dynamics of the $u(t)$ will be the same as the response is periodic in $x$. Most commonly, we will be interested in systems with
approximately isotropic thermal diffusivity, \( \alpha_x = \alpha_z = \alpha \), such that the displacement response dynamics of interest can be captured by

\[
u(t) \propto \text{erfc}(q\sqrt{at}). \tag{3.17}
\]

This approximation is appropriate for bulk systems with cubic symmetry, but may fail for systems with hexagonal symmetry \([42]\). Comparing Eq. (3.12) and Eq. (3.17), it is clear that the dynamics of the two processes governing the heterodyned signal response, Eq. (3.5), are different. However, both are strongly dependent on the thermal diffusivity of the sample under investigation and have a characteristic thermal decay time of \( \tau = 1/q^2\alpha \). Therefore, in principle, the decay in signal intensity associated with the decay of either grating should be able to be fit to measure \( \alpha \) from a TGS measurement. In the analysis presented above, we have neglected the time-dependent acoustic wave propagation component of the displacement response. The component can be added back into the analysis by including \( \partial^2u/\partial t^2 \) term to the left hand side of Eq. (3.13) \([43]\). However, the acoustic wave period realized in experiments is normally much greater than \( \tau \), such that the processes are separable. In these cases, the high frequency imposed oscillations do not affect the character of the thermal transport processes described above.

### 3.2.1 Thermal diffusivity measurements from the amplitude grating

As TGS measurements are most often completed as a set, at complimentary heterodyne phases, the total signal used for analysis is given as the difference of Eq. (3.5) at two different heterodyne phases such that

\[
I_{\text{tot}}(t) \propto \left( r'(t)(\cos \phi_1 - \cos \phi_2) - (r''(t) - 2k_p\nu(t)\cos \beta_p)(\sin \phi_1 - \sin \phi_2) \right).
\tag{3.18}
\]

By selecting \( \phi_1 = 0 \) and \( \phi_2 = \pi \), a purely amplitude grating can be selected, and the resultant material response will depend only on the reflectivity dynamics. Assuming that the imposed grating spacing is known, experimental data of this type can be fit to the simple expression

\[
I(t) = A \frac{\nu}{\sqrt{t}} \exp(-q^2\alpha t) + B, \tag{3.19}
\]

where \( A \) and \( B \) are again amplitude constants, to measure values of \( \alpha \) for a given sample. Note that the constant offset term is included to account for any baseline voltage produced by a photodetector used in experiment. Fig. 3-5 shows an example of measurements taken using this method from the literature, and many studies have used this methodology to measure the thermal diffusivity of system such as thin film or suspended semiconductors \([24,26]\).

However, this methodology has two major drawbacks. This procedure intrinsically relies upon
Instead of constructing a complete TGS measurement from signals collected at \( \phi_1 = 0 \) and \( \phi_2 = \pi \), a purely phase grating response can be selected by constructing a complete signal from measurements collected at \( \phi_1 = -\pi/2 \) and \( \phi_2 = \pi/2 \). Again, assuming that the grating spacing is known, from
Figure 3-6: Calculated reflectivity and displacement decay profiles for $\alpha = 6$ mm$^2$/s and $\Lambda = 3.1$ µm. The total signal is taken as the displacement response minus the reflectivity response to be representative of a total collected phase grating signal. The relative amplitude of the reflectivity and displacement signals was chosen to illustrate the characteristic shape often seen in experiments.

Eq. (3.5), data of this type should fit the form

$$I(t) = A \text{erfc} \left( q\sqrt{\alpha t} \right) - \frac{B}{\sqrt{t}} \exp(-q^2 \alpha t) + C,$$

(3.20)

where $A$, $B$, and $C$ are constants. The challenge of reliably fitting to a form like this, with two functional dependencies decaying at different rates, is illustrated by Fig. 3-6. Assuming that the physical factors that control the relative amplitudes are such that the reflectivity and displacement components contribute to the composite signal with opposite sign and that the contribution due to imaginary transient reflectivity change is smaller than the contribution due to displacement, then the total profile of the thermal decay will characteristically take on the shape shown here.

Previous studies seeking to use a pure phase grating response to measure the thermal diffusivity of samples under interrogation have only been able to do so in the case where the total reflectivity contribution is negligible. In this case, as in [32], profiles are fit exclusively to the $\text{erfc}(\cdot)$ form appropriate for the displacement grating response (with an imposed SAW oscillation). The authors of that work justify their assumption by noting that measurements made in the amplitude grating configuration showed very little response. Having a large imaginary component to the transient reflectivity change and a small real component is unlikely, so fitting to the pure displacement signal is justified in this case. Unfortunately, the classes of materials that exhibit a phase grating response purely due to the displacement grating are small. Particularly, it has been noted in the material system of interest for this thesis that the presence of a thin, less conductive oxide film on the surface increases the reflectivity contribution to the phase grating signal. Fitting these data to a pure
displacement response would incur significant systematic error.

However, for these phase grating responses which include a noticeable reflectivity contribution, the thermal decay curve can, in principle, be fit to a model which includes only a single extra parameter (describing the relative intensity of the reflectivity and displacement gratings) than the model used to fit amplitude grating data. In particular, for a range of heterodyne phases, a phase-insensitive fitting procedure may be used to determine a best-fit value for thermal diffusivity. Consider conducting a TGS measurement with the intent of collecting phase grating data at both \( \phi_1 = -\pi/2 \) and \( \phi_2 = \pi/2 \). In practice, setting the heterodyne phase in experiment close to these values is relatively simple. The acoustic oscillations due to the displacement grating should be maximized at both of the phases indicated above. Therefore, by using the real-time Fourier transform capability that most modern oscilloscopes include, the phase can be tuned to maximize the power in the acoustic oscillation peak. Using this procedure, measurements are recorded at phases \( \phi_1 = -\pi/2 + \delta_1 \) and \( \phi_2 = \pi/2 + \delta_2 \). Assuming that \( \delta_i \ll \pi/2 \), Taylor expanding Eq. (3.18) to first order shows that the composite signal is given by

\[
I(t) = a \left[ u(t) + br'(t)(\delta_1 + \delta_2) - cr''(t) \right] + D
= A \left[ \text{erfc} \left( q\sqrt{\alpha t} \right) - \frac{(C - B(\delta_1 + \delta_2))}{\sqrt{t}} \exp(-q^2\alpha t) \right] + D
= A \left[ \text{erfc} \left( q\sqrt{\alpha t} \right) - \frac{\beta}{\sqrt{t}} \exp(-q^2\alpha t) \right] + D,
\]

where \( a, b, c, A, B, C, D, \) and \( \beta \) are all constants. The constant of note in the final form is \( \beta \), the ratio in amplitudes between displacement decay and reflectivity. Note that this form is identical to Eq. (3.20) even though the heterodyne phase is not set to capture the pure phase grating response. If the parameter \( \beta \) can be fit accurately, then the form presented here is insensitive to the precise value of the heterodyne phases at which the two measurements were collected. Therefore, TGS measurements whose general shape is characteristic of the form shown in Fig. 3-6 may be fit with Eq. (3.21) to recover a value for the thermal diffusivity. The free parameters in this fit are \( A, D, \beta \) and \( \alpha \).

In practice, naïvely using a standard non-linear least squares fitting algorithm to find a best fit value for thermal diffusivity from phase grating TGS data may not always provide a representative value. Two factors inhibit this process. The presence of an imposed acoustic oscillation is not taken into account in Eq. (3.21) and can negatively affect the fitting accuracy. Additionally, for some values of \( \alpha \) and \( \beta \), a naïve fit will tend to ignore the hump present in the response at short times by minimizing \( \beta \) to zero. A fit of this nature clearly represents a local minimum and will not return a proper value of \( \alpha \). To combat this effect, we can pre-compute initial guesses for \( \beta \) and \( \alpha \) by noting that there is a location in Eq. (3.21) at which the profile has a maximum. The location of this
maximum can be found by solving
\[ \frac{\partial I(t)}{\partial t} \bigg|_{t_0} = 0, \tag{3.22} \]
to find \( t_0 \), the location of the maximum. A simple analytical solution to this equation can be found, yielding
\[ t_0 = \frac{\beta}{2} \left[ \frac{q\sqrt{\alpha}}{\sqrt{\pi}} - \beta q^2 \alpha \right]^{-1}. \tag{3.23} \]
This expression tells us that the location of the maximum in the characteristic phase grating profile is uniquely determined by a known value, \( q \), and the two parameters that need to be fit. As there is a discontinuity in the expression for \( t_0 \), we note that the maximum appropriate value of \( \beta \) for this form to hold is
\[ \beta_{\text{max}} = \frac{1}{q\sqrt{\pi\alpha}}. \tag{3.24} \]
Eq. (3.23) can also be inverted to provide an expression for \( \beta \) as
\[ \beta = \frac{q\sqrt{\alpha}}{\sqrt{\pi}} \left[ q^2 \alpha + \frac{1}{2t_0} \right]^{-1}, \tag{3.25} \]
which is practically useful because the parameter \( t_0 \) can be found by simply seeking the maximum in experimentally recorded profile and represents a new parameter by which to infer information about the best-fit values of \( \beta \) and \( \alpha \) for a given measurement.

With this form in hand, we have constructed a method by which we can pre-compute approximate values of \( \beta \) and \( \alpha \) to provide a non-linear least squares minimization method a good initial guess. The algorithm works as follows:

- Perform a naïve fit to the trace with a form that only includes the \text{erfc}(\cdot) decay to get an initial, incorrect, estimation of \( \alpha \).
- Find \( t_0 \) from the trace by taking the absolute maximum of the profile.
- Calculate an initial value of \( \beta \) from this bad estimate of \( \alpha \) and the value of \( t_0 \) using Eq. (3.25).
- Re-fit the data to the form of Eq. (3.21), by fixing \( \beta \) to the calculated value and varying only \( \alpha \).
- From the new value of \( \alpha \), re-compute \( \beta \) holding the found value of \( t_0 \) fixed.
- Iterate on the above procedure until the values of \( \beta \) and \( \alpha \) stop changing.

For an idealized thermal decay which includes no acoustic oscillations, this procedure should converge to the true values of \( \alpha \) and \( \beta \). However, as \( u(t) \) also includes an imposed surface acoustic wave, it is likely that a value close, but not equal, to the true value of \( t_0 \) will be found from the profile. Therefore, we describe the outputs of this procedure as \( \alpha_0 \) and \( \beta_0 \) and use them as initial guesses in
a fit of a measured phase grating response to Eq. (3.21), allowing all four of the parameters $\alpha$, $\beta$, $A$, and $D$ to vary. In practice, the number of iterations needed to converge on values of $\alpha_0$ and $\beta_0$ using the above procedure is fairly small. The number of iterations in the pre-computation step has been fixed to ten for all data in this thesis analyzed using this method. Every individual measurement checked had $\alpha_0$ and $\beta_0$ converge by iteration four or five. As we provide a good initial guess of the best-fit parameters, the search range in the $\alpha$ and $\beta$ parameter space in the final fitting step can be fairly narrow. For the experimental results presented here, best-fit parameters are found within the ranges $0.5\alpha_0 < \alpha < 1.5\alpha_0$ and $0.5\beta_0 < \beta < 1.5\beta_0$. This range is limited by experimental constraints which will be discussed in Section 5.1.

The efficiency and accuracy of this methodology will be discussed in Chapter 5 of this thesis. However, at least in principle, this framework provides a method by which both the thermal and acoustic components of TGS signals can be measured simultaneously. To be able to monitor changes in these properties in near-real-time, further development of the traditional TGS technique as described in previous sections needs to be carried out.

### 3.3 Dual heterodyne phase collection TGS

In this section, a modification to the optical arrangement for heterodyne amplified TGS experiments is presented which allows for the simultaneous collection of two signals with differing heterodyne phases, hereafter referred to as dual heterodyne TGS (DH-TGS). Throughout this section, we revert to the simplified notation of Eq. (3.3) and thus describe a material excitation of interest comprised of a surface displacement response maximized at heterodyne phases denoted $\phi = 0^\circ$ and $\phi = 180^\circ$.

#### 3.3.1 Optical arrangement and experimental parameters

The DH-TGS optical arrangement for a reflective sample is shown in Fig. 3-7(a). Similar to previous experimental configurations, the generation of the excitation grating on the sample under investigation is accomplished by passing a short pulsed laser through a phase mask, which is optimized to diffract most of the light into the $\pm 1$ orders. All other orders are spatially filtered and the two pump paths are recombined at the sample using an imaging system of cemented achromatic doublets, $L_1$ and $L_2$. The wavelength of the intensity grating projected onto the sample is given by $\lambda = M\lambda_0/2$, where $\lambda_0$ is the wavelength of the phase mask and $M$ is the magnification ratio between $L_1$ and $L_2$ [21]. In this implementation a matched pair of doublets is used for $L_1$ and $L_2$ such that $M = 1$.

To record two heterodyne phases concurrently, two additional laser paths are added to the standard TGS implementation as a probing beam and reference oscillator pair. All of the probing beams are generated from the same continuous wave laser source. Prior to incidence onto the phase mask the probe path is split using a non-polarizing 50:50 beam splitter ($BS$). The transmitted leg of this
Figure 3-7: (a) Top-view block schematic of the DH-TGS optical geometry showing paths from laser sources to detectors. BS - beam splitter, L1 & L2 - achromatic doublets, ND - neutral density filter, PA1 & PA2 - phase adjustment flats, APD1 & APD2 - silicon avalanche photodiodes. (b) Beam arrangement in the plane of lens L2, just before the sample surface. The positions below the dotted line represent the reflection and diffraction of the reference oscillator and probe beams from the sample surface.
probe is focused coincident with the pump source onto the phase mask at an angle $\theta_1$ (out of the plane of the page in Fig. 3-7(a)) such that between $L1$ and $L2$ there is a vertical separation of the pump and first probing paths. The reflected probing beam from the beam splitter is re-directed such that it, too, is coincident onto the phase mask as the same spot as the pump, but with incoming angle $\theta_2 > \theta_1$ such that the vertical separation between the second probe paths and the pump is greater than that of the first pair. For both probes, the $\pm 1$ diffraction orders are again retained while transmitted beam and higher orders are blocked. The vertical placement of each of the six beampaths in the plane of $L2$ is shown in Fig. 3-7(b).

Between $L1$ and $L2$ the two reference oscillator beams are passed through a neutral density filter ($ND$) to avoid saturating the photodetector downstream. Both probing paths are passed through a first phase adjust flat (PA1) which is used to uniquely control the heterodyne phase of $I_{180}^S(t)$. The extremal probing path is passed through a vertically separated, second phase adjust flat (PA2), which adds an additional path length difference and uniquely controls the phase of $I_0^S(t)$. The phase adjustment flats are a matched set and have extremely high ($< 5$ arcsec) parallelism. Upon reflection and diffraction from the sample surface, the spatial coincidence of the reference oscillator and the diffracted signal for both probing paths is guaranteed by the optical geometry. In the reflection geometry, both signals pass back through $L2$. As these paths are now vertically separated below the plane of the pump paths, they can be picked off, separated, and directed into two fast silicon avalanche photodiodes (APD1 and APD2). The path lengths between the sample surface and APD1 and APD2 are managed such that the two signals are aligned in time when recorded on a digital oscilloscope.

The primary advantage of the optical arrangement described above over previous implementations of the technique is time resolution. The pumping laser in these types of experiments is commonly operated with a repetition rate in the single kHz range. Each measurement, therefore, is taken as an average over hundreds to thousands of laser pulses to reduce system noise. Previously, a complete measurement of both heterodyne phases could be time resolution limited either by the signal collection time (in a case where many averages are taken) or by the mechanical action necessary to change the heterodyne phase (in the case where only a few averages are needed). By recording both of these phases independently, the time resolution of the system becomes, in all cases, limited by the collection time necessary to achieve a desired signal-to-noise ratio. Some disadvantages include a more complicated compact optical arrangement and a reduction in probe power intensity as a fixed probe laser source is spread across two paths.

All of the DH-TGS experiments using an optical arrangement as described above are carried out for this thesis using a passively Q-switched, 532 nm, solid-state laser with a pulse length of 300 ps, repetition rate of 1 kHz as a pump laser source with a spot size of 210 µm, and pulse energy at the sample surface of 2.38 µJ. The probe laser source is a 785 nm, CW diode laser modulated to a
repetition rate of 1 kHz with a 20% duty cycle, a power at the sample surface of 4.7 mW for both probe/reference oscillator pairs, and a spot size of 175 μm. The probe laser is RF modulated to the frequency of the pump to reduce sample heating. The silicon avalanche photodetectors used have a 3 dB bandwidth of 1.0 GHz and manual external gain adjustment. Their outputs are concurrently recorded on a dual-band 5 GHz bandwidth digital oscilloscope.

3.3.2 System characterization – acoustic measurements

In metallic samples investigated using this technique, $I^{\text{tot}}_S(t)$ has two features of interest, a damped acoustic oscillation overlaid on a non-exponential thermal decay curve, as described in Section 3.2. A filtered power spectrum of $I^{\text{tot}}_S(t)$ can be used to identify the dominant frequencies of the surface acoustic wave (SAW) oscillation induced by the imposed transient grating. These power spectra can be used as one measure of the quality of the recorded signal. To determine a representative minimum collection time, a series of measurements is carried out on a {001} oriented sample of 99.99% pure, single crystal tungsten varying the number of traces collected in a single measurement from 10 to 50000. These measurements are carried out using an imposed grating wavelength of $\Lambda = 5.50 \, \mu$m. The time-dependent signals for a 250 trace averaged measurement are shown in Fig. 3-8. The long-timescale oscillation in $I^0_S(t)$ and $I^{180}_S(t)$ is systematic noise due to the photodetector impulse response which is removed in the composite signal, $I^{\text{tot}}_S(t)$. The filtered power spectra for each measurement are given in Fig. 3-9. Given the repetition rate of the pump laser, the sampling rate of the oscilloscope, and the communication time between the oscilloscope and the acquisition computer,
the total collection time of these measurements ranged from 0.550 seconds to 743 seconds (12.5 minutes). As the collection time is increased, the signal-to-noise ratio of the identifiable acoustic peaks in the spectrum is increased, as is expected.

Table 3.1 shows statistics for each collection time, including the signal-to-noise ratio as well as the 95% confidence interval of the peak position parameter from a Gaussian fit to the spectrum. As there is often a DC component retained in the power spectrum from slow thermal decay, the signal-to-noise ratio is calculated over the noise floor from 0.7 to 1.3 GHz as the DC component is clearly separable from the acoustic peak of interest. The entries in Table 3.1 are the average values given from three measurements of the same record length. For measurements averaging 10 and 25 laser pulses, identifiable peaks in the power spectrum were not always apparent above the noise floor. From this series of measurements, based solely on the consistency of the appearance of peaks in the acoustic spectrum, a minimum temporal resolution of between one and ten seconds is observed with the current data collection scheme. Note that the time required to collect a given number of traces shown in Table 3.1 is higher than expected given the pump laser repetition rate of 1 kHz.
<table>
<thead>
<tr>
<th>Collection Time (sec)</th>
<th>Traces Averaged</th>
<th>Signal-to-Noise Ratio</th>
<th>Peak Position Error ($\times 10^5$ Hz)</th>
<th>% Peak Position Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.550</td>
<td>10</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.770</td>
<td>25</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1.14</td>
<td>50</td>
<td>3.73</td>
<td>5.3</td>
<td>0.109</td>
</tr>
<tr>
<td>1.85</td>
<td>100</td>
<td>6.55</td>
<td>3.7</td>
<td>0.076</td>
</tr>
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<td>4.19</td>
<td>250</td>
<td>9.97</td>
<td>3.0</td>
<td>0.061</td>
</tr>
<tr>
<td>7.92</td>
<td>500</td>
<td>11.8</td>
<td>2.5</td>
<td>0.051</td>
</tr>
<tr>
<td>15.5</td>
<td>1000</td>
<td>14.1</td>
<td>2.2</td>
<td>0.043</td>
</tr>
<tr>
<td>38.5</td>
<td>2500</td>
<td>15.0</td>
<td>2.1</td>
<td>0.042</td>
</tr>
<tr>
<td>75.7</td>
<td>5000</td>
<td>20.7</td>
<td>1.7</td>
<td>0.035</td>
</tr>
<tr>
<td>149</td>
<td>10000</td>
<td>22.9</td>
<td>1.8</td>
<td>0.037</td>
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<tr>
<td>374</td>
<td>25000</td>
<td>24.8</td>
<td>1.6</td>
<td>0.034</td>
</tr>
<tr>
<td>743</td>
<td>50000</td>
<td>26.3</td>
<td>1.6</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristics of power spectra from $I_S^{tot}(t)$ at varying collection times on single crystal tungsten. The signal-to-noise ratio is calculated as $SNR = 10 \log_{10}(P_s/P_n)$ where $P_s$ is the peak signal power and $P_n$ is the maximum noise power in the range 0.7 to 1.3 GHz. The percent peak position error is the Gaussian fit error divided by the peak position value.

For example, a 1000 trace collection take 15.5 seconds compared to an expected $\sim$1 second. Factors influencing this disparity include the talk-time between the oscilloscope and the data acquisition computer, graphics updating on the oscilloscope, and real-time averaging operations being carried out on the oscilloscope. Further optimization of these parameters may be possible to further reduce the time necessary to collect a fixed number of traces.

Using this implementation of a TGS experiment, the thermal and acoustic properties of specimens subject to some external driving force can be monitored. Drivers such as temperature [45], voltage [46], or irradiation exposure [47] can cause drastic changes in the elastic and thermal transport properties of materials under investigation. As a simple proof of principle experiment, a series of DH-TGS measurements is carried out on a $\{111\}$ oriented sample of single crystal aluminum subject to a temperature ramp between 50 and 250°C. Measurements were taken with $\Lambda = 4.78$ µm, using 1000 trace collections on a 20 second interval over a period of about 30 minutes. If acoustic peaks are identified in the power spectrum at dominant frequencies $f_{TG}$, then the surface acoustic wave (SAW) speed for each measurement can be calculated as $c_{TG} = \Lambda f_{TG}$ since the imposed grating wavelength is calibrated before each experiment, as in [35]. Fig. 3-10 shows the variation in SAW speed with temperature as measured on single crystal aluminum. The apparent linear decrease in $c_{TG}$ over this temperature range is consistent with SAW speeds calculated from temperature-dependent elastic constants of aluminum [48,40]. Validation testing is carried out on simple metallic single crystals because their TGS responses are simpler to analyze than polycrystalline Fe-12Cr-2Si, as we will show later.

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Figure 3-10: Change in SAW speed, $c_{TG}$, as a function of temperature for \{111\} oriented single crystal aluminum. Each data point is a 15.5 second collection recorded on 20 second intervals. Red circles indicate points taken on the heating cycle, blue triangles the cooling cycle, and the dashed line is the expected SAW speed based on [48].

3.3.3 System performance discussion

In general, collecting traces of $I^{\text{tot}}_S(t)$ of with a signal-to-noise ratio sufficiently high enough in the time domain to accurately fit thermal transport parameters requires a longer collection time than that required to identify the primary excited acoustic oscillations as discussed here. The difference in these time scales can vary widely between different material systems. As the ability to accurately fit time dependent thermal diffusivity data from DH-TGS measurements is overall goal of this work, a more complete discussion of the results and challenges of this procedure applied to the oxidation of Fe-12Cr-2Si will be provided in the following sections.

A comment is required concerning the difference in the angles $\theta_1$ and $\theta_2$ which control the vertical separation of the two probe paths in Fig. 3-7(b). In practice, these two angles should be set as close as possible to each other while maintaining the ability to independently control the heterodyne phase of each path. The lenses $L1$ and $L2$ used in the current iteration of this experiment are achromatically, but not aspherically, corrected doublets. A small spherical aberration present in the lens system causes a focal length shift between the two probing paths. The overlap volume of the two pump beams is large enough with the spot sizes used here to allow for simultaneous collection of both $I^S_0(t)$ and $I^{180}_S(t)$ with careful positioning of the sample surface in the beam path direction. Upon initial alignment, the photodetectors must be tuned to compensate for differences in signal amplitude occurring due to lens aberration as well as differences in intrinsic gain. The response amplitudes can be matched by setting the heterodyne phase to $\phi = 0^\circ$ for both probe paths, taking the real-time Fourier transform of the photodetector response on the acquisition oscilloscope, and
manually tuning the photodetector gain such that the SAW peak in the transform of each detector has the same power. Future implementations of this technique should utilize both achromatically and aspherically corrected lens systems for $L1$ and $L2$ to reduce the sensitivity to this aberration.

The removal of any long-timescale systematic error by subtracting $I_{S}^{0}(t)$ and $I_{S}^{180}(t)$ to find $I_{S}^{tot}(t)$ provides several improvements in the analysis of elastic properties through the measured acoustic response. As signal intensity measured on the photodetectors is intrinsically shot-noise limited, the method proposed here relying on the upstream splitting of the same probe laser source to create both probing paths should, in theory, not result in an improvement in the overall acoustic signal intensity compared to a single-phase collection using the same probe laser source. However, as the reference oscillator needs to be attenuated to avoid saturating the photodetector, splitting the probe laser source allows for the ratio of reference oscillator intensity to diffracted signal intensity, $I_R/I_D(t)$, to be increased across two detectors compared to the single detector in traditional TGS experiments. Additionally, the power spectra of short time scale collections with traditional TGS experiments which do not correct the systematic component of $I_{S}^{tot}(t)$ may be more complicated to analyze in the low frequency region. This complication becomes detrimental for measurements at long acoustic wavelength or for particularly compliant materials.

In contrast to the acoustic analysis, the determination of the thermal transport properties from $I_{S}^{tot}(t)$ relies on model fitting as described in Section 3.2.2, for which the removal of systematic error by subtracting $I_{S}^{0}(t)$ and $I_{S}^{180}(t)$ is a necessary step. Given this requirement and the presence of a systematic component to the captured signals, which is common, DH-TGS allows for thermal transport properties to be measured on much shorter time scales than traditional experiments.

### 3.4 Thermal and elastic response of multi-layered materials

There is one final component of the investigation of materials using the TGS methodology which must be discussed given the goals of the project at hand. We are attempting to use this methodology to determine the thickness of a thin surface oxide layer grown on a metallic substrate. As such, a discussion of the thermal and elastic responses of multi-layered systems exposed to transient grating excitation is necessary to motivate the use of the technique for this particular purpose. The acoustic and thermal components of the multi-layered material response are most often, much as the case for bulk materials, considered separately. The primary focus of this section will be the multi-layer thermal response and the elastic response will be discussed briefly at the end. The thermal portion of the multi-layered response is the less well documented of the two and thus the one we seek to elucidate in this work.
3.4.1 Multi-layer thermal response

To motivate the use of TGS to study the thermal properties of thin surface coatings, it is first necessary to note the thermal penetration depth of the technique. The type of laser energy deposition used in the transient grating process is extremely local, on the order of the optical skin depth of about 10 nm for metals \([39, 49]\). As such, the thermal excitation associated with the imposed transient grating will only penetrate a finite depth into the surface of the material under investigation. Considering a two-dimensional thermal diffusion length-scale of \(L_{th} = \sqrt{4 \alpha \tau}\) and noting the characteristic thermal diffusion time for the single-layer thermal problem, we find a characteristic thermal penetration depth

\[
L_{th} = \frac{\Lambda}{\pi} = \frac{2}{q},
\]

where \(\Lambda\) is again the imposed transient grating wavelength and \(q\) is the grating wavevector \([22]\). Probing the thermal properties of thin surface layers using this technique is therefore reasonable, as wavelengths normally used in TGS experiments are in the range 1-10 \(\mu m\). For surface layers of thickness \(L\) with \(qL \gg 1\) on a substrate, the thermal response will appear unchanged from the bulk response of the coating layer material. For \(qL \ll 1\), the response will be dominated by the substrate material without contribution from the surface layer. However, for intermediate thicknesses, the response becomes a function of the thermal characteristics of both the layer and substrate material.

This multi-layer thermal response can be solved using the same framework as described in Section 3.2 by including multiple layers coupled by appropriate inter-layer boundary conditions. For a system with a surface layer (1) atop a substrate (2), the surface and infinite depth boundary conditions described in Eq. (3.10) and Eq. (3.14) still apply. Additional inter-layer thermal boundary conditions include

\[
k_{z,1} \frac{\partial T_1}{\partial z} = k_{z,2} \frac{\partial T_2}{\partial z},
\]

\[
k_{z,1} \frac{\partial T_1}{\partial z} = \frac{1}{R_1} (T_2 - T_1),
\]

where \(T_i\) are the temperatures of the layers at the interface location and \(R_1\) is the thermal resistance between the two layers. Elastic inter-layer boundary conditions are

\[
\sigma_{zz,1} = \sigma_{zz,2},
\]

\[
\sigma_{xz,1} = \sigma_{xz,2},
\]

\[
u_{x,1} = \nu_{x,2},
\]

\[
u_{z,1} = \nu_{z,2}.
\]

This system of equations cannot, in general, be solved analytically. However, they can be solved numerically using the same Fourier transform technique as used for bulk systems \([22, 50]\). We will
not detail the process here, and refer the reader to the sources cited for a detailed description of the solution procedure.

The important concept to take away from this discussion is that of an ‘effective thermal diffusivity.’ Originally introduced in [22], this parameter is constructed as follows. Even though the general multi-layer thermal response to transient grating excitations does not take the same simple form as the bulk reflectivity or displacement response, experiments made on two-layer structures can be fit to these simple forms to learn something about the thermal diffusivity of both the surface film and the substrate material. This concept is demonstrated in Fig. 3-11 which shows the measured thermal diffusivity of a two-layer model system comprised of a more conductive film atop a less conductive substrate [50]. As described above, it is the product $qL$ which determines which of the two thermal characteristics will be probed in detail, and for intermediate regimes the measured effective thermal diffusivity will be between the values of the film and substrate. It is important to note that the literature has largely used this parameter only by fitting pure displacement grating responses of two-layered systems to the erfc($\cdot$) forms, and using the fit value of $\alpha$ from that process as the ‘effective thermal diffusivity’ [22,50,51]. In principle, since the thermal penetration depth is the same for both reflectivity and displacement gratings, using the effective thermal diffusivity as fit from the total phase grating response as described in Section 3.2.2 should be no different.

Much of the previous literature, as in Fig. 3-11, considers the case of a thin, highly-conductive coating placed on a less conductive substrate. This configuration is of practical interest since placing thin metallic layers atop insulating materials is an effective way to increase the level of excitation generation from a transient grating impulse. However, recent work has also confirmed the principle with a poorly conducting layer atop a highly conducting substrate. This is the case as described
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thermal diffusivity (mm²/s)</th>
<th>Temperature (°C)</th>
<th>Thermal diffusivity (mm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>7.50</td>
<td>23</td>
<td>1.263</td>
</tr>
<tr>
<td>130</td>
<td>7.23</td>
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</tr>
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</tr>
<tr>
<td>430</td>
<td>5.65</td>
<td>800</td>
<td>0.809</td>
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<td>526</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>4.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>3.73</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Temperature dependent values of thermal diffusivity for 403 SS and Cr₂O₃, which is expected to be one of the oxide layers formed. 403 SS has a nominal composition Fe-12Cr-1Mn-0.5Si-0.15C, close to the model alloy being used here. Data are spaced unevenly in temperature as they originate from different sources.

In [51], where depth dependent thermal transport properties of thin diamond films atop silicon substrates are investigated. This will be more similar to the case we are interested in for oxidation experiments, as 403 stainless steel (a commercial alloy similar in composition to Fe-12Cr-2Si) has a thermal diffusivity of about 7.5 mm²/s at room temperature [52] and Cr₂O₃ and FeCr₂O₄ both have thermal diffusivities of about 1 mm²/s [53,54]. Table 3.2 shows temperature dependent values for thermal diffusivity for both 403 SS and Cr₂O₃ over the temperature range of interest for this thesis.

In [50], a multiple parameter minimization technique is developed which is able to fit values for both the film and substrate thermal diffusivity as well as a film thickness when provided with thermal dispersion data like those in Fig. 3-11. However, the goals in this thesis are somewhat simpler. From the measurement of the thermal diffusivity of a bare, un-oxidized substrate, and from previous measurements of the bulk thermal diffusivity for the various oxide layers present, a cost-function minimization of only the film thickness parameter should be able to be constructed. This function would need to use the applied grating spacing and measured effective thermal diffusivity as inputs. Such a method would allow for the calculation of the thickness of the film to be made as the effective thermal diffusivity changes with film growth. As we will detail in Chapter 4, the excitation grating selected for these experiments will be as small as is reasonably possible to capture the effect of thin, surface oxide layers. Due to constraints of time, creating the numerical framework to solve this particular minimization problem is beyond the scope of this thesis. But, the literature shows that similar solutions do exist, so this component of the analysis should be a tractable future problem for this type of analysis.
3.4.2 Multi-layer acoustic response

For completeness, we will provide a short description of the multi-layer acoustic response generated using TGS. The acoustic properties of film-substrate systems have been well-studied in the literature and a compact overview of first-generation applications of these techniques can be found in [23]. Solving for the acoustic propagation modes present in a film-substrate, or in a general multi-layer system, involves solving the elastic wave equation

$$\frac{\partial^2 u_j}{\partial t^2} = \frac{C_{ijkl}}{\rho} \frac{\partial^2 u_k}{\partial x_i \partial x_l},$$

(3.29)

where $x_i$ are the Cartesian coordinates, $u_i$ are the components of the displacement vector, $C_{ijkl}$ are the fourth-order elastic constants, and $\rho$ is the material density for the particular layered system under consideration. Several methods exist by which to calculate the response of general anisotropic layered systems, including [40] and [56]. The generated acoustic modes observed in experiment also depend on the adherence of the film to the substrate [23]. Note that in the discussion of multi-layer thermal transport above, and in the experiments carried out in this thesis, the surface films are assumed to be well-adhered to the substrate materials.

Similar to the case of thermal transport, an acoustic penetration depth can be discussed. This depth is found simply to be the excitation wavelength, $\lambda$, such that a depth-resolved acoustic response can be characterized in a manner similar to the depth-resolved thermal response as described above. Again, if the film thickness is much greater than the penetration depth, the properties measured using TGS will be reflective only of the film and if the film is much much thinner than the penetration depth, only the properties of the substrate will be reflected. Note that as the thermal penetration depth is a factor of $\pi$ smaller than the acoustic penetration depth, the measured thermal transport properties will be more sensitive to thin surface layers than the acoustic response. Variations of solving the inverse problem, recovering film thickness from measured acoustic responses with known layer compositions, exist, see in particular [56]. Again, we will not attempt to solve the inverse problem here. Rather, we simply motivate that by using the phase grating response and measuring both the thermal and elastic characteristics of a sample as a function of processing time, multiple methods may be applied to recover information about film thickness and/or material property changes.

3.5 Summary

In this chapter, we have provided an overview of the transient grating spectroscopy (TGS) methodology. Traditional TGS experiments carried out on static material systems can be analyzed to determine both thermal and elastic transport properties. The implementation of optical heterodyne
amplification allows for either amplitude or phase grating responses to be probed. The amplitude grating response is generated solely by the decay of the excited reflectivity grating, whereas the phase grating response is comprised of both the reflectivity and surface displacement gratings. Since the reflectivity grating only contains information about thermal transport properties, we would like to use the phase grating response to monitor dynamic material systems such that both elastic and thermal properties are retained. To this end, we develop a pre-computation method which is able to fit a value for the thermal diffusivity from the phase grating response despite the more complicated thermal decay profile in comparison with the amplitude grating response.

In addition, the new method of dual heterodyne phase collection TGS (DH-TGS) is presented. By constructing an optical arrangement in which two TGS measurements made at complementary heterodyne phases are collected simultaneously, we show that the total collection time for complete TGS measurements can be reduced to a function of the desired signal-to-noise ratio and the system repetition rate. This allows for the near-continuous characterization of both the thermal and elastic properties of dynamic material systems undergoing some external forcing. Time and temperature dependent TGS measurements are made on single crystal aluminum subject to a heating ramp using this new methodology to test its efficacy.

Finally, the response physics of multi-layered systems to transient grating excitation are outlined and the concept of an effective measured thermal diffusivity is introduced. We motivate that the inverse problem, using a measured effective thermal diffusivity to calculate the thickness of a less-conductive oxide layer atop a metal substrate, is solvable based on current literature. However, solving that problem for the data collected in this study is outside the scope of the thesis. Rather, we simply motivate that the experimental development carried out for this project provides a reasonable pathway to determining oxide layer thicknesses continuously as a function of exposure.
Chapter 4

*In-situ* oxidation experimental parameters and apparatus

In this chapter, we will describe in detail the sample parameters and experimental methodology used for *in-situ* oxidation testing with DH-TGS. One of the major advantages of this methodology is the flexibility to test materials under a wide variety of conditions. As the technique is non-contact and non-destructive, many configurations of the test stand used for sample control are possible. The only requirement for TGS testing is optical access to the sample surface under investigation with a working distance from the final lens of the imaging system, $L_2$, set by the focal length of that lens. As the apparatus used in these tests was designed to be compact, that working distance is only 7.5 cm, requiring samples to be fairly close to the TGS optics. Several test stand configurations including rotating stages [35] and simple heating stages [20] have been used with this experimental apparatus in the past. For the *in-situ* oxidation tests carried out for this thesis, a test stand with high temperature, vacuum, and cover gas control was developed to control the temperature and oxidation parameters for each sample under investigation.

This chapter begins in Section 4.1 by describing the characteristics of the Fe-12Cr-2Si samples used in this study. Section 4.2 discusses the development and performance of the test stand designed and built to carry out these experiments. The parameters at which experiments are conducted are limited not by the test stand itself, but rather by the characteristics of the material system at high temperature. Finally, Section 4.3 presents both the sample matrix tested and delineates the particular procedure used to conduct all of the tests in this thesis.
4.1 Sample preparation

All of the Fe-12Cr-2Si used for this thesis were sourced from materials left over from another set of experiments [12,2]. The alloy was made as a custom melt for those experiments, with the composition specified to the manufacturer. Following production, the chemical composition of the procured plate was measured using inductively coupled plasma mass spectroscopy (ICP-MS). The results of this analysis show a final composition close to the specified amounts, with the chromium content slightly above specification [12]. From the remainder of the plate, 1/16” thick coupons were cut using wire electrical discharge machining (wire EDM) in dimensions of 3/4” × 3/8”. As coupons of this size are larger than the button heater used in the test stand (see Section 4.2) these coupons were sectioned using a low-speed diamond wafering saw to the dimensions 1/4” × 3/8”, such that each coupon produced three samples. A total of 21 samples were produced using this method.

TGS requires that all samples under investigation have a mirror finish so the probing laser used to monitor the induced material excitation does not diffusely scatter from the surface. To meet this requirement, all 21 samples produced were mechanically polished in parallel. The procedure followed in mechanical polishing was informed by instructions for ferritic steels in the Buehler, Inc. polishing guide. As following these steps directly did not produce the desired finish, the following detailed procedure was used for all samples tested:

1. De-burr samples by hand with 400 grit SiC sandpaper.
2. Mount all 21 samples to polishing head plate using high-shear-strength epoxy (Crystalbond).
3. Mechanical polishing using auto vector head polisher. All samples run at 150 rpm with a 40 N total load with complimentary head and platten spinning directions.
   - (a) 2:00 minutes, 70 µm diamond grinding disk.
   - (b) Ultrasonic clean mount and samples in water.
   - (c) 18:00 minutes, 9 µm diamond suspension.
   - (d) Ultrasonic clean mount and samples in water.
   - (e) 5:00 minutes, 3 µm diamond suspension.
   - (f) Ultrasonic clean mount and samples in water.

Table 4.1: Composition in weight percent of Fe-12Cr-2Si used in this thesis as measured by ICP-MS. Note that the oxygen content measured in these experiments was removed due to the dependence of that measured value on the cover gas used in experiment. Data sourced from [12].

<table>
<thead>
<tr>
<th>Fe</th>
<th>Cr</th>
<th>Si</th>
<th>W</th>
<th>Mo</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>V</th>
<th>S</th>
<th>P</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.6493</td>
<td>13.1086</td>
<td>1.9975</td>
<td>0.1736</td>
<td>0.0006</td>
<td>0.0002</td>
<td>0.0058</td>
<td>0.0190</td>
<td>0.004</td>
<td>0.0029</td>
<td>0.0005</td>
<td>0.0416</td>
</tr>
</tbody>
</table>
(g) 3:00 minutes, 50 nm alumina suspension.

(h) Ultrasonic clean mount and samples in water.

4. Remove samples from polishing plate with heat and acetone.

5. Ultrasonic clean samples in acetone and alcohol.

6. Manually clean surfaces with cotton swab and acetone or cotton swab and alcohol if necessary.

Following cleaning, some water spots were noted on the surface of about half of the samples. These spots are likely mineral deposits from the tap water used in the mechanical polisher. After some initial oxidation testing showed non-uniform oxide formation where these water spots were present, the remainder of the samples were cleaned using cotton swabs and reagent grade water, followed by a swab of alcohol to speed drying. The samples chosen for exposure testing were generally those with the fewest obvious surface defects. Polishing the samples in parallel was necessary to ensure uniform processing in the sample matrix, but left some samples with obvious surface scratches on otherwise mirror surfaces. These small defects are in principle not a hindrance to TGS testing. The sample surface area is much larger than the pump laser spot size used in experiment, so the surface scratches can be avoided by appropriate positioning. Nevertheless, choosing samples with fewer surface defects is an obvious way to avoid unintentional diffuse reflections from the surface.

One additional Fe-12Cr-2Si coupon was individually mounted and polished for grain size analysis. Ideally, we would like to carry out *in-situ* DH-TGS experiments on materials with grain sizes larger than the laser spot size to avoid the effect of grain boundary scattering of the induced acoustic propagation. Previous work suggests that the grain size of the sample used here is quite large. To confirm this, the selected sample was stained by swabbing with Kalling’s reagent #2 (5 g CuCl$_2$, 100 cc HCl, 100 cc ethyl alcohol) for 30 seconds. Optical microscopy confirmed that the grain size was on the order of the size of the samples themselves. A sample micrograph is shown in Fig. 4-1. Fewer than ten grains were present in the stained coupon (the size of three samples). From this, we cannot define an average grain size for the samples, but we can safely note that it is unlikely that an excitation spot will happen to be placed at a grain boundary. In practice, we also confirm that we test surface spots far from grain boundaries by exploring the sample surface before testing and choosing a location with largest intensity response. We observe that near to grain boundaries, and surface scratches, the recorded intensity decreases noticeably.

Although placing the experimentally measured spot in this manner is preferable in terms of recorded signal intensity, we do then notice effects of an anisotropic single crystal response. Crystal anisotropy in cubic systems will not affect the thermal transport properties as the conductivity tensor remains diagonal in these systems [42]. However, it will affect the observed acoustic wave velocities [40]. In this sense, we expect the surface acoustic wave frequencies measured on each
of the samples under investigation to vary as we do not \textit{a priori} have any information about the orientation of each grain of material investigated. However, this concern is minor in the studies we are conducting for this thesis, as we will primarily be concerned with using measured thermal diffusivity as a path to monitoring surface oxide layer thickness.

### 4.2 Test chamber design and parameters

One of the most powerful advantages of TGS as a non-destructive testing technique is the ability to monitor both thermal and elastic properties of material without physically contacting the sample under investigation. The non-contact nature of the technique allowed for a great deal of flexibility in designing the experimental test stand to explore time- and temperature-dependent oxidation characteristics. To this end, a five-axis motion controlled, vacuum and controlled cover gas chamber was constructed around a high power density button heater. This test stand was centered around a 3” side length, six-way vacuum cube used as the primary sample chamber. A front-view schematic of the test stand is shown in Fig. 4-2, where ‘front’ designates the portion of the chamber facing the incident laser beam path. Similarly, a top-view schematic of the same test stand is shown in Fig. 4-3. Optical access to samples for the pump and probing lasers is ensured through the use of highly parallel optical vacuum viewports. These viewports are anti-reflection coated in the
4.2 Test chamber design and parameters

Figure 4-2: Front view schematic of high temperature vacuum/controlled gas fill test chamber designed for in-situ TGS oxidation testing. Labeled components include (1) $\hat{x}$-$\hat{z}$ translation and planar rotation stage, (2) $\hat{z}$ translation stage, (3) $\hat{y}$ scissor lift, (4) ConFlat flange mount adapter, (5) sample chamber, (6) heater/sample linear rotation actuator, (7) top viewport window, (8) laser access anti-reflection window, (9) button heater with heat shield and sample clips, (10) sample, and (11) to vacuum/gas control system.

range 650-1050 nm to ensure that back reflections do not inhibit the interpretation of the measured heterodyne signals.

4.2.1 Motion control

Five-axis sample motion control is achieved through the use of a combination of standard optomechanical components and vacuum compatible actuators. In general, it is helpful but not strictly necessary to ensure that the face of the sample is normal to the direction of the incident laser beams in TGS experiments. If both pump and probing lasers are well-focused at the sample surface, the same optical configuration necessary for transient grating excitation and heterodyne signal amplification will be realized even if the sample is not normal to the incident lasers. However, if successive samples are significantly off-set from normal, then a substantial amount of re-alignment of the post-sample beam path needs to be carried out for each sample (primarily the pointing of the heterodyne signal into the small active areas of the photodetectors). In practice, having five-axis control allows for the positioning of samples at the appropriate position and rotation to use the same down-stream optical path every time a new sample is aligned. The only degree of freedom not included in this test
4.2 Test chamber design and parameters

\( \hat{x}, \hat{y}, \hat{z} \).

Figure 4-3: Top view schematic of high temperature vacuum/controlled gas fill test chamber designed for in-situ TGS oxidation testing. Labeled components include (1) incident TGS laser path through anti-reflection window, (2) sample chamber, (3) heater/sample linear rotation actuator, (4) top viewport window, (5) sample thermocouple feedthrough, (6) heater power feedthrough, (7) vacuum pressure gauge, (8) in-line valve, (9) moisture trap, (10) in-line valve, (11) to room air, (12) vacuum valve, and (13) to vacuum pump.
stand, rotation normal to the incident laser direction, is unduly complicated due to the constraints of space.

As shown in Fig. 4-2, two stages of linear translation in the \( \hat{z} \) direction are provided. This linear direction is the most important in the experiment, as the surface of the sample under interrogation must be placed precisely where the two pump beams cross. The position can be found in practice by moving close to a known approximate position and then optimizing by monitoring the amplitude of the signal in real time on the acquisition oscilloscope. The \( \hat{x} \) and \( \hat{y} \) positioning allows for selection of the portion of the sample surface to be measured. Due to the clips holding the samples to the surface of the heater as described in Section 4.2.3, only about half of the 1/4" × 3/8" sample surface is free to be measured. This is still far more area than strictly necessary for the spot size of the transient grating excitation used in these experiments. An additional amount of translation in the \( \hat{x} \) direction is provided by the linear/rotation actuator onto which the sample heater is mounted. For certain pump laser crossing angles the planar distance between the two beams may be close to the size of the window. Therefore, the \( \hat{x} \) degree of freedom in the actuator was included so the sample could be translated in this dimension without restricting the free aperture of the laser access window. This allows for the window to be centered on the laser beampath in the \( \hat{x} \) direction with the bottom stage and fixed there.

Besides aiding in positioning of the sample, the viewport on the top of the chamber indicated in Fig. 4-2 and Fig. 4-3 is the sample exchange access for the test stand. As noted previously, the working distance for the DH-TGS setup used in these experiments is fairly short. This distance makes sample exchange impossible through the laser access window, leaving the top viewport as the only option. The rotational degree of freedom in the actuator allows the heater face to be rotated 90° from the active test position to a vertical position for sample exchange. The top window vacuum seal uses a Viton gasket, as opposed to the majority of seals which use copper gaskets, so the window can be removed and replaced easily.

### 4.2.2 Vacuum and controlled gas operation

A major goal in constructing this test stand was to be able to evacuate the sample chamber to rough vacuum, for two purposes. For this study, we were interested in controlling the amount of time a sample had been exposed to oxidizing conditions at a particular temperature. As we will show in Section 4.3.3, ramping the temperature of the chamber up to the desired exposure conditions takes a significant amount of time. Control of the gas content in the chamber during the heating period was necessary to minimize the amount of un-controlled oxidation taking place during this period. Additionally, it is often of interest to make TGS measurement outside of ambient conditions. For certain material systems, the TGS excitation process can also excite an acoustic wave in a small region of air close to the sample surface [21]. This additional acoustic component can inhibit the
interpretation of thermal and acoustic data from TGS experiment. Therefore, the vacuum control of the chamber will be a feature of interest in both this and future studies.

Mechanical construction of the sample chamber was accomplished with vacuum-compatible components. As is shown in Fig. 4-3, the sealed portion of the test stand is connected to a dry scroll vacuum pump. This pump has an ultimate pressure of 5 mTorr, and the best performance of the chamber (after pumping down and waiting overnight for out-gassing to complete) has been noted at 7 mTorr. A dry scroll pump was selected to both minimize vibration and to remove liquids as protection for optical components in the case of pump failure. The pump is connected to the primary gate valve with a long, flexible hose to further minimize the amount of vibration imparted to the optical table on which the experiment is placed. With these connections no significant degradation in signal quality while the chamber is actively being pumped, allowing DH-TGS measurements to be made at any time.

Also shown in Fig. 4-3 is the controlled gas feed line. For the experiments in this thesis, the controlled gas line is comprised of a vent to room air through a moisture trap designed to take water content down to below 20 ppb. The humidity in the room where these experiments are conducted is not well controlled. Therefore, to ensure that all samples were exposed in equivalent conditions, the chamber back fill for oxidation trials was always done through the moisture trap. The oxidation observed in these experiments can therefore be designated a ‘dry air’ oxidation. Additionally, not shown in Fig. 4-3, the test stand includes another backfill value straight to room air. This feature is useful to preserve the desiccant in the dry air fill line as long as possible; for many routine operations dry air is not necessary.

4.2.3 Temperature control

For high-temperature sample control, a high power density resistive button heater was purchased from Heat Wave Labs. The heating element consisted of a precious metal resistive unit encased in alumina. The button heater is mounted in a refractory metal heat shield, which includes a series of clips around the perimeter of the exposed heater face. These clips are used to press samples directly onto the surface of the heating element. The metals under investigation are good thermal conductors, affixation to the heater face with these sample clips is enough to ensure adequate thermal contact. The rear of the heat shield is attached to the linear/rotation actuator by a custom designed adapter made of high-strength steel. Thus, motion of the sample under investigation is accomplished by rotation or translation of the entire heating element. The power leads for the heating element are passed through the vacuum barrier at rear of the chamber as shown in Fig. 4-3. The heating element itself is rated up to 850°C in oxygen containing environments and up to 1200°C in vacuum. However, the test stand is never taken above 600°C for practical reasons, which will be described in Section 4.3.1.
Temperature feedback is accomplished through a type K thermocouple spot welded to one of the sample clips. As we are interested in measuring the temperature of the surface of the sample, placing the thermocouple in this manner ensures at any given time we read back the temperature of the sample itself and not the heating element. The thermocouple feedthrough is located on the same flange as the heater power feedthrough at the rear of the chamber. The sample temperature is recorded on an Omega Platinum series control unit, which is in turn controlled through a USB interface on system data acquisition computer. Power to the sample heater is provided by a variable voltage and current power supply rated up to 200 W. Operationally, the applied power rarely exceeds 35 W. As the resistance of the heating unit changes as a function of temperature, the voltage and current limits on this controller must be manually changed as a function of temperature. Not limiting the applied current at low heater temperatures can lead to over-current operation and damage the heating unit. In the future, an adaptive control algorithm might be implemented to control this process automatically. Cooling is provided only by radiative losses, in vacuum, or conductive/convective processes, in air. The temperature control process is carried out with a simple on/off setpoint. This method was found to be more consistent than smarter PID controls due to the low cooling rate.

4.3 Oxidation testing parameters and procedure

A standard set of test procedures is used for each of the in-situ oxidation tests carried out for this thesis. The particular parameters used for these tests were not established until the DH-TGS experiment and test stand were complete and tested. At the outset, the goals were simply to choose exposure conditions at as high a temperature as possible using the shortest collection times possible. Some initial testing was carried out using ex-situ TGS testing on Fe-12Cr-2Si samples which had been oxidized for times up to 80 minutes at 810°C in an open air furnace. Post-exposure measurements on these samples indicated that oxide layers of approximately 100 nm had been grown after 80 minutes exposed at 810°C. The ex-situ TGS testing of these samples proved inconclusive, but the parameters used in those experiments provided rough guidelines for the range of parameters used in this study. Many of the parameters chosen for the tests carried out for this work are limited by the high and low temperature TGS response of Fe-12Cr-2Si.

4.3.1 Grating spacing and temperature selection

To select the optimal grating spacing for in-situ oxidation measurements, the behavior of the effective thermal diffusivity as sketched in Fig. 3-11 was used as a guiding principle. The oxide layer grown on these samples was expected to be thin, 100 nm or less. As phase grating measurements will return effective thermal diffusivity measurements more sensitive to thin surface layers at smaller values
of \( \lambda \), we sought to use a small grating spacing as possible in these experiments. The minimum possible grating spacing is limited by two factors. The primary factor is the high-frequency cutoff of the photodetectors used in experiment. The photodetectors used in this DH-TGS experiment have a bandwidth of 1 GHz. By making a series of measurements at room temperature, we determine that smallest possible wavelength usable for these experiments is 3.1 \( \mu \)m. Fig. 4-4 shows a filtered power spectrum of the phase grating response of one of the Fe-12Cr-2Si samples measured with \( \lambda = 3.1 \mu \)m. The SAW frequency is this case is almost at the 1 GHz detector cutoff. Measurements made at the at the next available grating spacing, \( \sim 2.7 \mu \)m, returned a SAW frequency above the cutoff frequency and hence with a significantly reduced amplitude.

Keeping the SAW frequency below this cutoff is of interest for several reasons. Although we are not measuring the response of these materials at room temperature during the oxidation process, we will also attempt to measure the pre- and post-exposure response at room temperature in addition to those measurements made at high temperature. Therefore, it is of interest to make sure that the experimental parameters chosen are appropriate for room temperature as well as high temperature, where the SAW response is at a lower frequency as the material softens. Even though the acoustic response of these materials is not the primary interest of the study conducted here, useful information about the oxide layer growth process may be encoded in that response as well. It is therefore of interest to try and retain that information if possible. Finally, Eq. (3.5) described the intensity of the surface displacement response as modified by a term of the form \( \cos \beta_p \), where \( \beta_p \) was the incidence angle of the probe beams onto the sample surface. As smaller and smaller grating spacings are selected, the angle of incidence of the probe beams becomes closed to \( \pi/2 \), decreasing the amplitude.

Figure 4-4: Filtered power spectrum of Fe-12Cr-2Si response at 21°C with \( \lambda = 3.11 \mu \)m. The measured SAW frequency is very close to the 1.0 GHz photodetector cutoff, indicating that using smaller grating spacings is not possible.
of the measured response. This effect also provides a lower limit on the grating spacing selected in experiment.

The phase mask used in our DH-TGS experiment has several grating spacings which can be selected by exposing different regions of the mask to the incident pump and probe lasers. These gratings all have specified nominal spacings. However, the wavelength of the actual transient grating projected onto materials is sensitive to the placement of all of the optical components used in the imaging system. To calibrate the actual grating spacing used in these experiments, a series of measurements is made on a single crystal, {001} oriented piece of pure tungsten. As tungsten is the most elastically isotropic metal [57], we can use the measured surface acoustic wave frequency, \( f_{TG} \) and a calculated value for the Rayleigh wave speed in tungsten from Eq. (3.6) to discover the actual projected grating spacing. The theoretical acoustic wave speed in tungsten is calculated by using an aggregate of elastic constant values from the literature with Eq. (3.6) to find \( c_W = 2665.9 \text{ m/s} \) [58–60]. The calibrated grating spacing is found to be \( \Lambda = c_W / f_{TG} = 3.1091 \pm 0.0025 \mu \text{m} \). This value is used in the fitting and analysis of all \( \textit{in-situ} \) data collected.

The maximum exposure temperature for these experiments is limited by the temperature-dependent reflectivity of Fe-12Cr-2Si. As the reflectivity of these samples decreases upon increasing temperature, the intensity of the collected signal is reduced. Past experiments on ferritic steels, as well as many other metallic systems, confirm this trend [61]. A series of tests at \( \Lambda = 3.1 \mu \text{m} \) in vacuum show that at about 600°C, the total signal intensity becomes too small to continuously collect using DH-TGS. Therefore, two temperatures were selected for \( \textit{in-situ} \) experiments, 550°C and 500°C.

### 4.3.2 Sample matrix

For both exposure temperatures, samples are exposed for varying lengths of time. Although thermal and mechanical properties are monitored continuously throughout the exposure, our analysis includes post-exposure testing of samples exposed for different lengths of time to directly correlate the measured change in thermal performance with oxide layer thickness. Table 4.2 lists all seven samples that were exposed as part of this study. For each temperature, exposure times of 1, 2, and 4 hours were carried out. Additionally, the two-hour 550°C exposure was repeated to test a hypothesis which will be described later. These times were chosen to be longer than exposure times used for previous samples at 800°C as the oxide layer formation rate is lower at lower temperatures.

### 4.3.3 Testing procedure

A standard procedure is used for each \( \textit{in-situ} \) oxidation run. Samples are placed into the test stand one day before \( \textit{in-situ} \) testing and allowed to pump down to vacuum overnight, for at least 12 hours. Placing samples under vacuum for so long before oxidation testing ensures that minimal residual gas will be released during the sample temperature ramp. This proscription was not followed only
Table 4.2: Matrix of samples exposed in this study. Each sample is continuously monitored using DH-TGS during its exposure.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Exposure temperature (°C)</th>
<th>Exposure time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>550</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>550</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>550</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>550</td>
<td>4</td>
</tr>
</tbody>
</table>

for sample #4. The exposure time was short for that sample, and its testing was carried out in the same day as one of the other samples. We noted significantly more out-gassing as that sample was brought up to temperature compared to samples which had spent a night under vacuum. Samples are affixed to the heater surface using the clips described previously, with the clip containing the thermocouple placed near the center of each sample. This placement allows for about half the sample surface area to be measured, if so desired, and was chosen to ensure good thermal contact between the thermocouple and the sample.

Laser spot positioning is carried out at room temperature in vacuum. An ideal sample position is found by locally exploring the free surface of the sample and monitoring the response in real time on the acquisition oscilloscope. Once the optimal sample position is found, that position is fixed for the duration of the experiments. Before heating, baseline measurements are collected on each sample in vacuum, at room temperature. These collections are long averages, collecting 5000 trace average measurements (75-second collections) with ten batches of measurements. This data provides a well-characterized background for each sample. Heating is carried out in 50° C intervals. Between each interval the pressure in the chamber is allowed to pump back down below 10 mTorr to control the amount of residual gas present. Heating from room temperature to 500 or 550°C in this manner takes around one hour per sample. The recorded temperature profile for sample #5 is shown in Fig. 4-5. As the oscillation about the temperature set point was repeatably observed to be about 4°C, the temperature set point on the controller was set to 502°C for 500°C exposures and 552°C for 550°C exposures to ensure that the average temperature over the exposure time was the desired value.

For samples exposed at 500°C, baseline, in-vacuum measurements are collected using the same parameters as the room temperature baseline measurements (ten 75-second collections) once the sample is brought up to temperature. For the samples exposed at 550°C, high-temperature baseline measurements were collected at both 500° and 550°C. The time spans during which these baseline
Figure 4-5: Temperature history profile for sample #5 exposed at 550°C for two hours. The red region on the plot indicates a baseline series of measurements collected at 500°C in vacuum and the blue region a baseline series of measurements collected at 550°C in vacuum. The green region indicates region over which the sample was exposed to dry air at high temperature. The small spike before the in-situ collection begins is caused by air backflow into the sample chamber.

measurements are collected is marked in Fig. 4-5. Following these measurements, the gate valve to the vacuum pump is closed and the chamber is vented with dry air through the moisture trap. This back fill initially causes a spike in the temperature readout, followed by a slight cooling of the sample as cool room air comes into contact. The recovery time to full temperature is monitored and found to be on the order of one minute or less. The chamber is filled over the course of 1-2 minutes to avoid shocking the actuator and moving the sample position. For all samples, despite the slow fill rate, minor positioning adjustments were made once the chamber had recovered to full room pressure. Hence the DH-TGS monitoring begins a few minutes after the air backfill is complete for all samples.

In-situ DH-TGS measurements are carried out using 1500 trace averages continuously throughout the exposure time. These collections take approximately 17 seconds each and are repeated on a 30 second interval. The repeat interval was chosen as a precaution to provide a small window of time for measurement adjustment between collections should something unintended occur. Most often these small adjustment included tuning of the heterodyne phase as small changes in sample positioning occur with temperature, as will be discussed in greater detail in Section 5.2. Thus, for a four hour exposure, approximately 480 individual batches of DH-TGS measurements are recorded as oxidation is taking place. During exposure, the chamber pressure is kept at equilibrium by leaving the dry air fill line open.

Once the proscribed length of time for a given test is reached, the set point temperature of the controller is set to 10°C, below room temperature. The dry air fill line is closed, and the samples are
allowed to cool naturally. Post-exposure measurements are taken for each sample at temperatures in the range of 30-40°C, as allowing samples to naturally return to room temperature takes an unduly long time. These post-exposure measurements are again carried out with the same long averaging parameters used for initial baseline measurements.

4.4 Post-exposure testing

Post-exposure testing is conducted to determine the chemical compositions and thicknesses of grown oxide films. Surface oxide chemical composition is determined using Raman spectroscopy [62]. Oxide layer thicknesses are determined using white light reflectometry [63]. Finally, a small amount of scanning electron microscopy is conducted to investigate the surface morphology of the exposed samples. Direct imaging does not prove especially illuminating, but sample images will be presented and general comments on the oxide morphology discussed.

4.4.1 Raman spectroscopy

Raman spectroscopy relies on inelastic scattering of incident monochromatic light from low frequency vibrational modes present in a material system of interest. Incident monochromatic laser light, typically in the visible spectrum, will excite virtual states at an energy corresponding to that of the incident light, \( E_0 = h\nu_0 \) [62]. If the virtual state decays back to the ground state of the system, a photon will be emitted at the same wavelength as the incident light through the process known as Rayleigh scattering. If the virtual state instead decays back to an excited vibrational mode with energy \( E_v = h\nu_v \), then emission will occur at lower energy \( E_f = h(\nu_0 - \nu_v) \). This process is Stokes scattering, and causes a wavenumber shift \( \Delta k = \nu_v/c \) from the incident light. The opposite process may also occur, where an already excited state is promoted to a virtual state by an incident photon and decays back to the system ground state, causing the emitted photon to have more energy than the incident photon. This process is denoted anti-Stokes scattering and is much less common for materials at room temperature. The scattered light from the sample under investigation is focused and collected in a spectrometer through a monochromator tuned to reject the large intensity of elastically scattered light.

The Raman peaks of a material, observed as intensity as a function of wavenumber shift, may be used as a fingerprint to identify its chemical composition. As the Raman spectra of the oxides expected on these materials are present in the literature, the measured Raman spectra from our samples can be compared to the expected lines to determine the dominant oxide layer present [64–68]. Raman spectra in this thesis are collected primarily using a 532 nm excitation wavelength, a spot size of 433 nm, and approximately 10 mW laser intensities without filtering. The instrument was calibrated before use with a silicon wafer baseline and an expected, well-known 520.7 cm\(^{-1}\)
Results are consistent with ellipsometric measurements on the substrate steels used in the present study. The approximate composition and structure of the crystallites and film layers are known from prior work [1], but the optical properties have not previously been reported. The present calculations are made under the assumption that the optical properties of the iron-rich crystallites and top layer are close to those of magnetite (Fe$_3$O$_4$) and the optical properties of the oxide are close to those of chromite (FeCr$_2$O$_4$). Figure 11 shows the predicted (solid line) and measured (circles) specular reflectivity for polished stainless steel surfaces. Simulation curves are for various surface roughness parameters from 0 nm (top curve) to 100 nm (bottom curve) in steps of 10 nm. The best simulation of the observation is found assuming an average surface roughness of 35 nm.

### 4.4.2 White light reflectometry

The measurement of thin-film thickness using white light reflectance techniques has been in use since at least the 1960s [63]. In these methods, the reflectance spectra of a broadband visible light source (400 to 800 nm) incident onto a substrate-film system are measured to determine properties of the films. If, for example, the complex indices of refraction are known for both the substrate and the film, then the film thickness can be determined by iteratively solving the Fresnel equations for the layered system to find a best-fit value for the given optical properties. In these types of experiments, the feature of greatest interest, and the most useful in determining the film thickness, is the curvature in the reflectance spectrum and the location of the minima [70].

In these experiments, a broadband white light source is shone at normal incidence onto samples of interest through a bundled multi-mode fiber optic cable. Reflected light is collected through a single multi-mode fiber at the core of this bundle and passed into a simple USB powered spectrometer. Exposure spot sizes are about 1 mm in diameter, small enough to be placed on individual grains of oxidized Fe-12Cr-2Si samples. To calculate film thicknesses, the substrate wavelength-dependent index of refraction is used from [72]. The steel investigated in that study was a 13.5Cr ferritic stainless steel with only minor additional alloying elements and was the closest characterized case we are able to find in the literature. Literature on optical constants for the oxide layers expected...
to form on these alloys is sparse, but some data are available [71, 73]. Fig. 4-6 shows the calculated complex index of refraction of FeCr$_2$O$_4$ from powder reflectivity measurements made in [71]. The calculation for film thickness is carried out assuming a constant index, so literature dispersion values, when provided, are averaged in the range of 400 to 800 nm to provide a single value for calculation of film thickness. This assumption is fair for FeCr$_2$O$_4$ based on the dispersion shown in Fig. 4-6.

4.5 Summary

In this chapter we detailed the preparation and condition of the sample matrix used in this study. The design and parameters of the experimental test stand used for $in$-$situ$ oxidation experiments are also presented. This facility has a working distance compatible with the current implementation of DH-TGS experiment and can provide vacuum, controlled cover gas, and temperature control. For these initial experiments, oxidation exposures are carried out using dry air filtered from ambient room air. The ability to pump samples down to vacuum gives precise control over the exposure parameters as samples may be brought up to temperature in vacuum before being exposed to ambient air pressure. We have also detailed the testing procedure and parameters used for this study. Exposure conditions and test parameters are chosen as a result of material properties and are not limited in this case by the capabilities of the test stand. A total of seven samples are exposed, and the effective thermal diffusivity of each is monitored continuously throughout its exposure at high temperatures.

Finally, several post-exposure test methods are described. White light reflectometry is used to determine the ending oxide film thickness for each exposed sample. The sample matrix is designed to include enough exposure times such that the grown film thickness can be analyzed as a function of time using post-exposure methods as well as the $in$-$situ$ method developed for this work. To most effectively use this white light method, the approximate chemical composition of oxide films should be known. To this end, Raman spectroscopy is carried out on all exposed samples before white light measurements to confirm the composition of the oxide film. Together, the $in$-$situ$ DH-TGS, Raman, and white light measurements provide the necessary information to construct and validate a procedure to determine the grown film thickness continuously throughout an exposure.
Chapter 5

Results and future work

In this chapter, we present the results of the first in-situ oxidation experiments conducted using the newly developed DH-TGS methodology. Two major factors affect the ability to draw quantitative results from the data presented in this chapter. Post-exposure appearance of samples from this matrix revealed that oxidation, specifically the layer thickness and composition, is highly surface grain orientation dependent in this alloy. Millimeter scale grains are all clearly visible to the naked eye on oxidized samples and in some cases the coloration of these oxide scales varies significantly from grain to grain. Secondly, a parameter of the silicon avalanche photodiodes was found to be sub-optimal for these types of experiments directly before the in-situ exposure testing was set to begin. It was not possible to procure replacement parts during the extent of this thesis project such that all experimental data is collected with a known deficiency, which will be described in detail in Section 5.1.

Following this discussion, Section 5.2 presents the primary results of each in-situ exposure carried out. For each sample, data are presented detailing the best fit value of the effective thermal diffusivity as a function of exposure time. Several anomalous features in this data set are identified and discussed in the context of the experimental constraints under which these experiments were conducted. Section 5.3 details all of the post exposure characterization carried out on this sample matrix including visual inspection, scanning electron microscopy (SEM), Raman spectroscopy, and white light reflectometry. Simple visual inspection is the motivation for conducting a second exposure at 550°C for two hours (for both sample #5 and sample #6). This suite of post-exposure characterization techniques provides a complete picture of the ending oxide layer morphology and thickness for all samples. This information elucidates some of the behavior noted in the DH-TGS measurements. Discussion of this suite of experimental results is in Section 5.4. We emphasize that the in-situ DH-TGS results collected here are a useful motivating tool for future experiments of this nature, but are not indicative of quantitative values of effective thermal diffusivity as a function of
oxide layer growth.

With these constraints in mind, Section 5.5 describes some additional analysis that might be carried out on the data set collected for this study. We also delineate several steps moving forward for future studies using the methods developed here, but perhaps on different material systems. Finally, we conclude the thesis in Section 5.6 with a re-statement of the goals for this work and a critical assessment of the realization of those goals.

5.1 Detector low-frequency cutoff

As we described in Section 3.3.1, optical detection for DH-TGS measurements are carried out on a matched pair of silicon avalanche photodiodes. These detectors are sensitive to extremely small changes in light levels, generating a voltage output in response to the heterodyned laser signal from probing lasers incident onto the diode active area. As stated previously, the detectors used in the construction and testing of the DH-TGS experimental apparatus described in Section 3.3 have a bandwidth of 1.0 GHz and a 3 dB cutoff of 1.3 GHz. In particular, the detectors used for this experiment are model number APD210 from Menlo Systems.

While testing the informed fitting method described in Section 3.2.2, a consistent feature of the measured response of un-oxidized Fe-12Cr-2Si in air at room temperature was noted. This feature can best be described as ‘detector droop’ and is shown in Fig. 5-1. As the thermally-induced surface grating decays, these responses were observed to undershoot the 0.0 mV line of the photodetector output before slowly decaying back to 0.0 mV on a timescale of several hundred nanoseconds. This feature of the response is unexpected and problematic. The functional forms for the heterodyne signal intensity of the complete phase grating response as described in Eq. (3.21) strictly decay to zero on long time scales. This form, to which captured signals must be fit, cannot account for the type of droop that we observed consistently in this experiment.

To discover the cause of this droop, a single additional silicon avalanche photodiode from a different manufacturer was borrowed from a collaborator. This photodiode module (C5658) also has a total bandwidth of 1.0 GHz, but is made by Hamamatsu Photonics. This detector was swapped in for one of the detectors in our DH-TGS measurements. We then conducted a series of measurements using this single photodetector in the same manner as traditional TGS experiments. For each spot characterized, phase grating signals are collected at two complimentary heterodyne phases sequentially, adjusting the phase manually between each. A sample of the results from data collected using this detector are also shown in Fig. 5-1. The detector droop present in DH-TGS measurements with Menlo detectors is absent from the response measured on the Hamamatsu detector.

The difference in these detector modules, as is evident from the section heading, is the low-
In this chapter, we present the results of the first in-situ oxidation experiments conducted using the newly developed DH-TGS methodology. The Menlo Systems detectors have a high low-frequency cutoff and consequently do not accurately capture the thermal decay profile for these samples. In comparison, the Hamamatsu Photonics detector has a sufficiently low cutoff to capture a decay profile representative of what is expected from Eq. (3.21).

Figure 5-1: Phase grating response of Fe-12Cr-2Si recorded for $\lambda = 3.11 \mu m$ with 5000 trace collections on two different Si avalanche photodiode modules in air at 20°C. The Menlo Systems detectors have a high low-frequency cutoff and consequently do not accurately capture the thermal decay profile for these samples. In comparison, the Hamamatsu Photonics detector has a sufficiently low cutoff to capture a decay profile representative of what is expected from Eq. (3.21).

frequency cutoff. Although the Menlo detectors have a 1.0 GHz bandwidth, the low frequency cutoff is large, 5.0 MHz. In contrast, the low-frequency cutoff value for the Hamamatsu detector is 0.05 MHz. In previous work using the Menlo detectors, analysis has only been carried out on the acoustic component of measured phase grating signals [35,20]. As acoustic propagation occurs at several hundreds of MHz, these responses are well within the active response range. However, thermal decay profiles with time constants on the order of 50 ns, as we observe on these materials, have significant spectral components below 5.0 MHz. This leads to the failure of the decay profile measured on Menlo detectors, exhibited as signal droop, and proves to be the ultimate limiting factor for the experiments carried out for this thesis.

5.1.1 Detectors with appropriate characteristics

Using a photodetector with a suitable low-frequency cutoff, complete phase grating measurements are carried out on polished, un-exposed Fe-12Cr-2Si using a variety of imposed grating spacings. Fig. 5-2 shows representative data collected using $\lambda = 3.11 \mu m$, the same spacing used for in-situ measurements, as an average of 5000 traces. The fit phase grating profile clearly matches the entire decay profile of the measurement well. Fit values of thermal diffusivity taken on data of this character consistently have a relative 95% confidence interval from the non-linear least squares minimizer on the order of 1%. Note that the response shown in Fig. 5-2 shows very little reflectivity response in the phase grating signal at room temperature. This feature is common on all measurements made on un-oxidized Fe-12Cr-2Si at room temperature.

Ideally, in-situ oxidation data would be collected using the Hamamatsu detectors, or similar modules with low-frequency cutoffs which do not artificially change the shape of the thermal decay profile. Unfortunately, only a single Hamamatsu detector was appropriated from our collaborator.
Orders for multiple detectors of this type were placed as soon as this issue was characterized, however, those modules were not received in time to carry out the remainder of the work that will be presented here.

### 5.1.2 Detectors used for in-situ oxidation experiments

As a result of the practical limitation described above, all the experiments carried out for this thesis use a matched pair of Menlo Systems photodetectors in the configuration described in Section 3.3. As is clear from the comparison in Fig. 5-1, the frequency domain responsivity of these detectors not only modifies the longer-timescale thermal decay profile due to droop, but also significantly changes the apparent short-timescale rate at which the initial thermal decay is occurring. Measured response profiles of this character are therefore challenging to analyze for two reasons. At long timescales, the measured response is no longer accurately represented by a physical thermal decay profile. In particular, as the measured response droops below the zero level, the profile to which we would like to fit it now fails in all cases. To combat this, we may attempt to fit only the portion of the decay profile above the ‘drooped’ area. This choice also proves challenging, as the location of the zero crossing is a function of the effective thermal diffusivity of the sample in question, which is expected to change as a function of oxidation time, and is also a function of the absolute phase at which the experiments are recorded, as we will see later.

The complication at the other extreme, fitting only the shortest time responses, is that signals must be long enough to accurately fit a profile. Another complicating factor is that the location of
the characteristic hump in the phase grating profile, at $t_0$, used for pre-computation of $\alpha$ and $\beta$ in the fitting procedure may also change as a function of temperature and exposure. Even by selecting an appropriate end time for a given measurement using these constraints, fitting Eq. (3.21) to data of this type will find values for thermal diffusivity higher than physical values. This is again a consequence of the low-frequency cutoff hastening the apparent decay even for short times. Another major factor affecting the decision of an appropriate start time for a fit to measured data is the presence of a short initial intensity spike associated with the pump laser. For this reason, fit start times for all measurements must be 300 ps or greater, as this is the duration of the pump pulse. Note that this issue is independent of the low-frequency cutoff complication and has been considered by other authors as well [24].

Given these constraints and complications, the start and end times for all of the fits carried out in the analysis of this data must be optimized individually. To be able to make any comparison between consecutively recorded measurements the fit start and end times are chosen for the pre-exposure, in-situ, and post-exposure measurements on each sample individually. In this way, we are able to make the most meaningful statements about continuous changes in the effective thermal diffusivity as possible. The start and end time used for all three classes of measurements on each samples are denoted in Table 5.1. On inspection, this table has many repeated values. A common set of parameters was manually optimized on much of the data using the minimal fit start time and varying the ending time. Only in cases where fits using these parameters failed were the start and end time parameters modified. In general, fit start times needed to be modified in cases where $\beta$ was large, and caused the short-timescale portion of the signal to be significantly below zero. Fit end times needed to be increased in these cases as well, as larger values of $\beta$ increase $t_0$ and the profile must be fit past this point. The actual measured temperatures for each of the sets of measurements considered are reported in Table 5.1 as well.

A representative thermal profile fit for a sample at high temperature during an oxidation exposure is shown in Fig. 5-3. Compared to Fig. 5-1 and Fig. 5-2, which both show measurements taken at room temperature, the contribution of the reflectivity response is noticeably larger. This is manifested as the clear presence of a rounded over profile at $t_0$. Qualitatively, the thermal decay time is longer than that shown in Fig. 5-1, which is consistent with our expectation that the thermal diffusivity should go down for the oxide-substrate layered system at high temperature as shown in Table 3.2. Compared to the total length of the recorded trace, which is set to be 500 ns for all measurements, the portion of the response which we are able to analyze for transport properties is small. Even in this small range, the fit appears to begin to deviate at the end of fitting region. This behavior captures well the challenges associated with attempting to fit data of this quality with methods designed to fit the entire thermal decay profile.
<table>
<thead>
<tr>
<th>Sample #</th>
<th>Measurement type</th>
<th>Temperature (°C)</th>
<th>Fit start time</th>
<th>Fit end time</th>
</tr>
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<tr>
<td>1</td>
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<td>300 ps</td>
<td>30.7 ns</td>
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<tr>
<td></td>
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<td>1.45 ns</td>
<td>30.7 ns</td>
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<td></td>
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<td>29.6</td>
<td>300 ps</td>
<td>30.7 ns</td>
</tr>
<tr>
<td>2</td>
<td>Pre-exposure</td>
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<td>300 ps</td>
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</tr>
<tr>
<td></td>
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<td>498.5</td>
<td>300 ps</td>
<td>30.7 ns</td>
</tr>
<tr>
<td></td>
<td>Post-exposure†</td>
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<td>300 ps</td>
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</tr>
<tr>
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<td>300 ps</td>
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<tr>
<td>4</td>
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<tr>
<td></td>
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<td>2.50 ns</td>
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</tr>
<tr>
<td></td>
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<td>300 ps</td>
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</tr>
<tr>
<td></td>
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<td>30.7 ns</td>
</tr>
<tr>
<td></td>
<td>Post-exposure</td>
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<td>1.50 ns</td>
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</tr>
<tr>
<td>6</td>
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<tr>
<td></td>
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<td>Post-exposure</td>
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<td>1.45 ns</td>
<td>30.7 ns</td>
</tr>
</tbody>
</table>

†Communication between temperature controller and acquisition computer was lost on the cooling cycle of this measurement. The value reported here is approximate.

Table 5.1: Fit start and end times for all sets of measurements recorded on this sample matrix. Temperatures for each measurement are listed and are provided as an average of the recorded temperature for the duration of each measurement set. The baseline fit end time, 30.7 ns, occurs at 35 ns with respect to the absolute trace start time. There is a 4.3 ns delay between the trigger signal on the measurement oscilloscope and the pump laser pulse. It was the absolute time value which was manually optimized as a baseline parameter.
Figure 5-3: A portion of the phase grating thermal response on sample #5 collected at 550°C about one hour into a two hour exposure with $\lambda = 3.11$ µm on Menlo photodetectors. The signal is fit only in the portion of the curve overlaid with the best-fit profile in red (−−). The fit error from minimization is about 4%, however deviation from the recorded trace is evident near the end of the fit region. The blue (−−−) curves show decay profiles generated by modulating $\alpha$ by ±15% and leaving all other best-fit values constant.

5.2 *In-situ* DH-TGS results

With the caveats of the detector limitations noted, the *in-situ* measurements of effective thermal diffusivity as a function of oxidation time at both temperatures are now presented. Again, these exposures are conducted at varying temperatures in dry air. Recall that each *in-situ* measurement is an average of 1500 traces which take about 17 seconds each to collect. These data are collected on 30 second intervals for the duration of each exposure. This interval was chosen such that small changes in the heterodyne phase control or sample surface placement could be made if the sample happened to move through the exposure as parts of the apparatus relaxed at high temperature. In principle, using the new phase-insensitive fitting methods, these small adjustments should not affect the fit value of the effective thermal diffusivity. However, this feature of the fitting procedure becomes less straightforward with the additional low-frequency cutoff complication.

5.2.1 500°C exposures

Fit values of the effective thermal diffusivity as a function of exposure time are plotted for all three samples exposed at 500°C in Fig. 5-4. The results of pre- and post-exposure measurements carried out at room temperature using the procedure as described in Section 4.3.3 are shown in Table 5.2. At room temperature in vacuum, pre-exposure measurements return values in a range that is somewhat higher than the reference value given for 403 SS in Table 3.2. *In-situ* measurements show initial values for measured effective thermal diffusivity over a fairly large ranges, the values of which are
all higher than those expected from prior results. The spread in absolute value of these quantities and their deviation from the true expected value of $\alpha$ for this model alloy can both be attributed the limitations of the fitting methods we are forced to use with photodetectors of inappropriate characteristics. In addition, several distinct jumps are visible in the measured values of $\alpha_{\text{eff}}$ for sample #2 and sample #3. These jumps are caused by a phase sensitivity issue with the current experiment which will be elaborated more in Section 5.2.3.

However, a general trend can be established from the data shown here. In regions between sudden jumps in the measured value, there is a distinct trend of the measured effective thermal diffusivity decreasing as a function of increasing exposure time. This is the behavior that we expected from the outset, as even at high temperatures we expect the grown oxide scale to have a lower thermal diffusivity than the base metal. This trend is especially clear in the second half of the four hour exposure (sample #3) where no sudden transitions occur. Post-exposure measurements show measured values for thermal diffusivity little changed from the pre-exposure values. However, as the heterodyne phase must be individually set for post exposure measurements after the sample cooling ramp, direct comparisons of these values to the pre-exposure values are difficult to make. The experimental positioning of samples is re-set prior to post-exposure characterization as the samples generally drifted slightly from their ideal alignment after long periods at high temperature.

### 5.2.2 550°C exposures

Fit values of the effective thermal diffusivity as a function of exposure time are plotted for all four samples exposed at 550°C in Fig. 5-5. The results of pre- and post-exposure measurements of the effective thermal diffusivity are shown in Table 5.3. Again, the values for pre-exposure thermal diffusivity have a phase-dependent spread and are all somewhat larger than values for similar alloys in the literature. The initial features of in-situ data are similar to those for the samples exposed at 500°C, with a fairly large spread in the starting point thermal diffusivity. At these temperatures there is again an observable trend in the effective thermal diffusivity as a function of exposure time.
Figure 5-4: Best-fit values of effective thermal diffusivity of Fe-12Cr-2Si samples exposed at 500°C as a function of exposure time. DH-TGS measurements are collected using $\lambda = 3.11 \, \mu m$ as averages of 1500 traces on 30 second intervals. Discrete jumps in the apparent linear decrease in $\alpha_{eff}$ with temperature correspond to manual changes in the recorded heterodyne phase.
Sample #   Pre-exposure $\alpha_{\text{eff}}$ (mm$^2$/s)   Post-exposure $\alpha_{\text{eff}}$ (mm$^2$/s)   Difference
4           8.33 ± 0.22                        7.01 ± 0.16                        −15.8%
5           8.96 ± 0.19                        9.24 ± 0.23                        +3.1%
6           8.93 ± 0.25                        10.21 ± 0.29                       +14.3%
7           8.85 ± 0.38                        8.48 ± 0.34                        −4.2%

Table 5.3: Pre- and post-exposure effective thermal diffusivities for samples oxidized at 550°C. Data are collected as sets of ten measurements, each of 5000 traces. The quoted error includes both the standard deviation between the ten measurements as well as the uncertainty on the fit values for effective thermal diffusivity. The difference column is taken as the difference of the post- and pre-exposure measurements over the pre-exposure value. Although large changes are observed for some samples, this is likely an effect of experimental parameters and not truly a physical change.

Initially, the measured values for the thermal diffusivity appear to linearly decrease with continued oxidation, similarly to samples exposed at lower temperatures. However, for sample #4 there is an uptick in measured effective thermal diffusivity at around 45 minutes. A similar, albeit slower, feature is also noticeable on samples #6 and #7 near the end of their exposures.

Sample #8 deserves special comment. At around 150 minutes and 190 minutes, large gaps in the collected data appear and beyond this point the scatter in the measured values becomes quite large. For this sample in particular, the intensity of the probe laser light incident onto the photodetectors was significantly reduced as the sample continued to oxidize. Around 150 minutes, this intensity became so low that significant adjustment of the sample positioning and heterodyne phase setting was made in an attempt to recover a larger signal intensity. This process was repeated around 190 minutes. The character of the measured profiles in these regions showed significant reflectivity grating contributions, as evidenced by increasing large values of $t_0$. Data in the regions around these two adjustment periods is manually removed during the analysis process. A similar reduction in overall signal intensity is observed in sample #4 during its short exposure, although not to the same extent. Post-exposure examination shows that the coloration of the oxide scales grown on sample #4 and #7 are very similar and distinct from the scales grown on samples #5 and #6. We believe that for samples which experience a significant decrease in signal amplitude, the combination of thicker oxide layers and rougher oxide/metal interfaces caused more diffuse reflection of the probing laser. Note that at 785 nm, the wavelength of the probe laser, chromium-rich oxide films are largely transparent [73], causing the oxide/film interface to have an effect on the specular reflection of the probing lasers.

In contrast to post-exposure measurements on samples oxidized at 500°C, samples exposed at 550°C exhibit significant changes in the measured value of the effective thermal diffusivity. However, these changes do not seem to follow any particular trend with regards to exposure time. It should be noted, as is stated in Table 5.1, that the fit beginning and end times are often non consistent for pre- and post-exposure measurements made on samples exposed at this temperature. This necessity
Figure 5-5: Best-fit values of effective thermal diffusivity of Fe-12Cr-2Si samples exposed at 550°C as a function of exposure time. DH-TGS measurements are collected using $\lambda = 3.11 \mu m$ as averages of 1500 traces on 30 second intervals. Portions of the data for sample #7 are omitted in post-processing as the signal intensity became too low to analyze. Some samples appear to have a slight upturn in the fit values of $\alpha_{eff}$ at longer times, indicating that the composition of the grown oxide layer may be changing.
further complicates the direct comparison of these two sets of measurements.

5.2.3 Phase sensitivity and experimental challenges

Throughout the preceding sections, we have commented briefly on challenges associated with phase sensitivity originating from the low-frequency cutoff characteristics of the photodetectors used for these experiments. In Section 3.2.2, we showed that TGS data collected at heterodyne phases slightly offset from a purely phase grating response should still follow the functional form of Eq. (3.21). This, in principle, allows for some freedom in the setting of the heterodyne phases in experiment. As long as the heterodyne phases for both traces collected in DH-TGS measurements are close to pure phase grating values, the fitting procedure outlined in Section 3.2.2 should still return a physically meaningful value of $\alpha_{\text{eff}}$. This methodology was developed before the completion of in-situ oxidation testing. As a consequence, during in-situ testing on-line modification of the heterodyne phase was sometimes conducted in an effort to keep the highest amplitude acoustic oscillation possible. Overall, the heterodyne phase set by the optical components is extremely stable. But, thermal relaxation of structural components with time or surface layer morphology changes during oxidation are observed to slightly change the sample position and the heterodyne phase at which traces are recorded.

Due to the complication of detector droop, fit values for $\alpha_{\text{eff}}$ for these experiments are not independent of the absolute value of the heterodyne phase at which the measurement is collected. As an illustration of this problem, Fig. 5-6 reproduces the measured values of $\alpha_{\text{eff}}$ as a function of exposure time for sample #3, oxidized for four hours at 500°C. During this in-situ measurement, the intensity of the induced acoustic oscillation was noted to decrease as the exposure continued. In response, at around 92 minutes into the exposure, as indicated by the dashed line on Fig. 5-6, the heterodyne phase was adjusted to increase the intensity of the acoustic oscillation.

Recorded traces on either side of this phase adjustment are shown in Fig. 5-7 to demonstrate the changes in recorded signal induced by this small change in phase. In contrast to most of the DH-TGS traces shown in this work, the scaling on these two plots is left in millivolts as recorded on the acquisition oscilloscope so the amplitudes of the two can be directly compared. The goal in the adjustment carried out at 92 minutes was to increase both the overall signal intensity as well as the intensity of the acoustic oscillation imposed over the thermal decay profile. Comparing Fig. 5-7(a), recorded before the adjustment, to Fig. 5-7(b), recorded after the adjustment, there is a noticeable increase in both the overall signal intensity as well as the intensity of the acoustic oscillation. However, by making this change, the value of $\beta$ in the best fit of these two responses is also changed. Particularly, Fig. 5-7(b) has a lower fit value of $\beta$ that (a), indicating that the response recorded after the phase adjustment contains less of the reflectivity grating dynamic, which is indeed the goal of the adjustment.

In theory, this difference in the relative contribution of the reflectivity versus displacement dy-
Figure 5-6: Reproduction of $\alpha_{\text{eff}}$ versus time for sample #3 exposed at 500°C for four hours. At 91.6 minutes into the exposure, the heterodyne phase is adjusted to increase the signal intensity, causing a jump in $\alpha_{\text{eff}}$. Measurements collected just before the adjustment, at 86.9 minutes, and just after, at 95.9 minutes are shown in Fig. 5-7.

Figure 5-7: Initial 100 ns of recorded in-situ DH-TGS measurements on sample #3 (a) immediately prior to and (b) immediately following phase adjustment. Best-fit values for $\alpha_{\text{eff}}$ and $\beta$ for each measurement are indicated. Modifying the heterodyne phase increased both overall signal intensity as well as the acoustic component of the response.
namics should not change the minimized, best-fit value of $\alpha_{\text{eff}}$. However, detector droop due to the low-frequency cutoff causes the measured values of $\alpha_{\text{eff}}$ to differ significantly. Compared to Fig. 5-7(a), Fig. 5-7(b) has a steeper initial descent in the thermal decay due to a smaller component of the reflectivity response coming in with the opposite sign of this dominant displacement response (see Fig. 3-6 for a schematic of how these two contributions combine). This steeper initial descent will, in absolute terms, reach $1/e$ times the peak intensity more quickly than a measurement with a larger value of $\beta$. As the model cannot accurately account for the complete shape of the thermal decay curve in these measurements, this results in larger values for $\alpha_{\text{eff}}$ being assigned to (b) compared to (a). In short, because of the failure of the measured response to follow the physical description of the thermal decay profile, the methods we employ to fit these thermal profiles lose their degree of phase insensitivity.

The measurement phase sensitivity as described above is evident in many of the in-situ measurements shown in Fig. 5-4 and Fig. 5-5. This sensitivity is also why we cannot directly compare the pre- and post-exposure measurements. All samples tested post-exposure were re-aligned following cooling to maximize the signal response and are not necessarily set to the same absolute value of the heterodyne phase. In general, absolutely setting the heterodyne phase in these types of experiments is difficult, and relies on the use of reference samples [24,44]. Even for very stable optical arrangements, this type of pre-calibration of the heterodyne phase is a major complication for short collection time, in-situ measurements. The degree of phase insensitivity imparted by fitting to the phase grating profile as described in Section 3.2.2 is perhaps a necessary ability for high-resolution time-dependent measurements. As we have seen, for the experimental collections possible with the hardware used for this thesis, phase insensitivity is lost. In these experiments, that issue is coupled with the issue of higher-than-physical values of $\alpha_{\text{eff}}$ being fit to decay profiles due to detector droop. Together, these limitations imply that at best only qualitative results may be taken away from the performance of oxidized Fe-12Cr-2Si measured with DH-TGS here.

### 5.3 Post-exposure testing

Following exposure, each sample is subject to a series of tests using a variety of different methods. Visual inspection is carried out on samples immediately following to their exposure and reveals a significant amount of qualitative information upon which other tests can be based. Several samples are investigated using SEM, but the entire matrix is not imaged in this manner due to the lack of significant features visible. Raman spectroscopy is conducted on all samples on the same grains as investigated using DH-TGS. Finally, the oxide layer composition information is used to inform white light reflectometry measurements of post-exposure oxide film thicknesses. Were the in-situ data of sufficient quality to make quantifiable calculations of grown film thicknesses, these direct
Figure 5-8: Photographs of all Fe-12Cr-2Si samples following exposure. Note the clear difference in oxide layer coloration between samples exposed at 500°C and samples exposed at 550°C. Placement of the sample clips and the surface thermocouple are clearly visible on all samples. The DH-TGS laser spots are placed between the sample clips and the bottom of the sample in all cases. Samples #2, 3, and 6 have surface defects (scratches) caused during post-exposure handling.

measurements of film thickness would serve as a necessary benchmark for qualification of an algorithm used to calculate film thicknesses. These methods together provide information which aids in the interpretation of the results of each exposure.

5.3.1 Visual inspection

Simple visible inspection of samples following oxidation showed a rather striking difference in the grown oxide layer character at different times and temperatures. Fig. 5-8 is a composite photograph of all seven samples exposed for the studies conducted here. The obvious difference in this sample matrix is the end-state color of the grown oxide layer. For samples exposed at short times at 500°C, the surface appears golden in color, taking on purple tints for the longest exposure. For samples exposed at 550°C the oxide scales all appeared blue or purple, depending on the surface grain orientation. In fact, even better than Fig. 4-1, these photographs illustrate the size of the grains in this material. Different grains become highlighted due to anisotropic transport properties of metal ions through the grown oxide scale [74]. Surface grain orientation dependent oxide character and thickness has been observed in Fe-12Cr-2Si before as well [12].

In several of the samples in Fig. 5-8, contact marks left by the sample clips and thermocouple
contact from experimental runs are visible. In fact, on all samples, these marks are visible when viewed at some angle. These markings serve as useful fiducial markers when determining which grain was observed during DH-TGS experiments. For all experiments, laser spots were placed halfway between the bottom of the samples and the clip markers, to the left of center. When designing these experiments, we counted on the large grain size making it unlikely that TGS measurements would be conducted near grain boundaries, and this goal was realized in experiment. Several samples, particularly #2 and #3, show visible surface scratches which were induced unintentionally post-exposure during sample handling. In addition, sample #6 made physical contact with a gloved thumb, the mark of which can be seen in the top left quadrant of the sample. This contact was made both away from the grain which was measured during DH-TGS and following Raman testing so it is not believed to have affected those results. For white light measurements, the spot was clearly placed away from this region on the grain banding the bottom third of the sample.

Initial visual inspection of sample #5 is the motivation for repeating an exposure at the same conditions for sample #6. During the course of experimentation, both the one hour and four hour exposures at 550°C were conducted before either 2 hour exposure. As the character of the oxide layer grown on most of sample #5 is different than that observed on sample #4 or sample #7, we were curious to see if layer character was consistent, or a result of some unintended contamination in the test stand for this trial. Sample #6 clearly shows evidence of oxide layer characters similar to all three other samples from 550°C delineated by a grain boundary. Therefore, this difference can be attributed to the anisotropic transport properties of the thin oxide layer films.

As one final note, on close inspection sample #1 can be observed to have a non-uniform oxide character even within individual grains. As mentioned in Section 4.1, water spots (mineral deposits from the tap water used in the polishing process), were noted on some samples following mechanical polishing. Samples with the most obvious spots are avoided as test candidates, however it became clear with this sample that water non-visible water spots may also play a role in changing the morphology of the oxide layers grown on these materials. Following this sample, which was second in the matrix to be exposed, all samples were re-cleaned with reagent grade water and alcohol as described in Section 4.1. Post-exposure effects of surface mineral deposits were not observed on any samples which were further cleaned in this manner.

5.3.2 Scanning electron microscopy

Low-resolution scanning electron microscopy (SEM) is carried out on two of the samples exposed for this study. In particular, sample #3 (500°C, one hour) and sample #5 (550°C, two hours) are imaged as the oxide layers exhibited distinct characteristics on surface grains of different orientation on these samples. Micrographs captured using a secondary electron detector on a JEOL 5910 SEM using an acceleration voltage of 15 kV are shown in Fig. 5-9 for both samples. For both samples, survey
Figure 5-9: Low magnification SEM images of samples #3 and #5. Oxidized surfaces appeared uniform with a small amount of porosity in the grown oxide layer.

images of this type showed small but noticeable differences in contrast between oxidized grains of different orientations. Grain boundaries are clearly highlighted as they provide fast transport pathways for metal ions during oxidation [5]. Higher-resolution imaging showed that the oxide films on both samples were not perfectly crystalline and had small amounts of porosity present. Imaging of this nature did not prove particularly informative with regards to the compositional differences between films or film thicknesses. Survey images here are presented for completeness. While imaging, cursory energy-dispersive x-ray spectroscopy (EDX) line scans are conducted to see if any differences in film chemical compositions can be noted across grain boundaries. As expected, the penetration of electrons at energies in a range of 10–25 kV is too high to provide quantitative information about the thin surface film composition.

5.3.3 Raman spectroscopy

All exposed samples are investigated using Raman spectroscopy as described in Section 4.4.1. Several literature studies have been conducted on the types of oxide layers that expected to form as oxide layers on Fe-Cr-Si alloys [64–68]. In particular, the oxides that are the most likely to form at the compositions, temperatures, and oxygen potentials studied here are Cr₂O₃, Fe₃O₄, and FeCr₂O₄ [17]. It is the reference Raman shifts of these oxides, then, which should be used as the fingerprints by which to judge the compositions of the films grown here. Note that SiO₂ is not on the list provided above. For the times and temperatures used in these experiments, it is unlikely that we will observe significant SiO₂ at the metal/oxide interface, let alone a continuous protective scale. Table 5.4 provides one set of literature values for the expected Raman shifts for each type of oxide. There is some scatter in the literature with regards to the precise positioning of these peaks, however the values provided here are representative of the set of values found across the literature. Of note is the presence of only a single value for the Raman shift observed for the iron-chrome spinel, FeCr₂O₄.
Table 5.4: Literature values for Raman shifts associated with Cr$_2$O$_3$, Fe$_3$O$_4$, and FeCr$_2$O$_4$ from [68]. Although not expected to form in significant amounts at the moderate temperatures used in this study, shifts for SiO$_2$ are included as well [67].

Some authors have not noted any other peaks in the Raman spectra for the stoichiometric spinel phase [68], while others have noted peaks which cannot be distinguished from those of Fe$_3$O$_4$ [65].

Measured Raman spectra for all samples are shown in Fig. 5-10(a). These data are collected using an excitation laser of 532 nm with the proscriptions delineated in Section 4.4.1. All of the spectra for oxidized samples show similar qualitative features. Namely, a small set of peaks is present in the 530-550 cm$^{-1}$ range corresponding to Cr$_2$O$_3$ formation which takes place at short time scales on all samples. For all samples there is also a broad peak slightly above the region in which the Fe$_3$O$_4$ and FeCr$_2$O$_4$ peaks appear. For samples exposed at short times at 500°C, a minor Cr$_2$O$_3$ peak is distinguishable at 353 cm$^{-1}$.

The large-intensity, broad peak slightly above the literature value for the iron-chrome spinel is the feature of greatest interest to us here. The grown oxide layers appear to be dominated by this peak in all cases. This peak in the Raman spectrum may lie above the expected value for FeCr$_2$O$_4$ due to laser heating. As has been noted by several authors, Fe$_3$O$_4$ undergoes a phase transition to maghemite (γ-Fe$_2$O$_3$) at a temperature around 200°C. Maghemite has a prominent Raman peak at 700 cm$^{-1}$, which is closer to the observed dominant feature of these spectra than the spinel peak [75]. A dependence on the laser power used for Raman measurements on ferrous oxides has been noted in the past [65]. Namely, these authors find that using increasing laser power on Fe$_3$O$_4$ samples will induce a phase transition and modify the observed Raman peaks.

To test whether the observed Raman peaks are affected by either laser heating or the wavelength of the excitation laser, an additional series of measurements is carried out on sample #6 using a 633 nm excitation source. Fig. 5-10(b) shows the spectra measured on this sample varying the intensity of the excitation laser. Measurements at 100% and 10% power are collected for the same times as the 532 nm measurements, but the 1% power measurement is collected for three times longer to increase the total number of counts. Each measurement is collected on a different location within the same grain as was measured with DH-TGS. The spectra show no variation in peak location with laser power. This indicates that the peak above the reference FeCr$_2$O$_4$ peak
Figure 5-10: Collected Raman spectra on oxidized samples for (a) all samples measured with 532 nm excitation and (b) for sample #6 with 633 nm excitation and variable laser intensity. Spectra in (a) are normalized to one constant value, while spectra in (b) are normalized to the peak value in each spectrum. The absolute intensity is smaller for lower laser powers, as evidenced by the decreased signal-to-noise ratio. Reference Raman lines are taken from [68].

are likely not due to phase transitions of heated Fe$_3$O$_4$. It also indicates that there is likely little Fe$_3$O$_4$ present in the grown oxide film. If there was a significant Fe$_3$O$_4$ layer, a dependence on laser temperature is expected and we do not observe that behavior [65,76].

The difference in the position of the observed Raman peak and the literature value for the iron-chrome spinel phase can be explained by the stoichiometric dependence of the spinel lattice parameter and therefore the spinel Raman peak. As the iron content is lowered in the spinel compound Fe$_x$Cr$_{3-x}$O$_4$, the Raman peak around 685 cm$^{-1}$ is observed to shift to higher wavenumbers [68]. Although this spinel structure has only been studied using Raman spectroscopy to the stoichiometric point, FeCr$_2$O$_4$, x-ray diffraction data on samples synthesized with 0.8 < x < 2.2 have shown that the lattice parameter decreases with decreasing Fe content [65]. However, in this study, all samples synthesized with x < 1 also showed a significant fraction of corundum phase, Cr$_2$O$_3$, forming in addition to off-stoichiometric spinel. Based on these prior analyses, we expect the dominant oxide layers formed on samples oxidized here to be sub-stoichiometric iron-chrome spinel phase in addition to a smaller fraction of Cr$_2$O$_3$. We also note that the same work which analyzed synthesized off-stoichiometry spinels shows Raman spectra from naturally oxidized Fe-Cr alloys with peak structures of similar character to those observed here [65].
Table 5.5: Measured oxide layer thicknesses from white light reflectometry. Monotonic growth is observed on grains measured with DH-TGS for 500°C samples, but not for 550°C samples. This can be attributed to differences in oxide composition as noted in Section 5.3.1. An additional measurement on sample #6 on a grain with similar coloration to sample #4 and #7 indicated a layer thickness of 146 ± 5 nm.

5.3.4 White light reflectometry

Following the identification of the dominant oxides present on the exposed samples, white light reflectometry is carried out to measure the grown film thicknesses. The identification of the oxide layer composition is necessary before these measurements may be carried out as the index of refraction of the oxide film should be known to recover a film thickness. White light measurements are made using the procedure described in Section 4.4.2. Following measurements, simulations of the reflectance response of a single layer film-substrate systems are conducted using the thickness of the surface film as a free parameter. This simulation uses a matrix method of solving the Fresnel equations for reflection and transmission on the film-substrate system [77]. For these calculations a full set of dispersion data for both the real and complex components of the refractive index for the substrate are used from [72], while the film is taken to have a constant index. For these measurements we assume that the iron-chrome spinel oxide is the only oxide, and use index data for the stoichiometric oxide to find an average value of the index as \( n = 1.50 \) over the visible range 400–800 nm [71]. Despite the visibly difference in oxide characters between samples exposed at 500 and 550°C, the single dominant spinel phase approximation is the best guess we can make for oxide composition based on Raman measurements.

Table 5.5 shows the measured oxide layer thicknesses from white light measurements. Finding best-fit thickness values is complicated in one major way, as shown in Fig. 5-11. The intensity in the reflectance experimentally measured on these samples was significantly reduced compared to calculations based on the system indices and film thickness. Similar effects have been observed in the literature for oxide layers grown on various substrates, including iron-chrome spinel grown on stainless steel [78]. This reduction in intensity can be attributed to a rough oxide/metal interface, causing diffuse reflection to take place in addition to specular reflection from the film surface and
Figure 5-11: Measured (black, solid curve) and simulated best-fit (red, dashed) white light reflectance measurements on sample #4. For all samples, a difference in the magnitude of the measured and simulated reflectivity is present. We attribute this intensity mismatch to scattering from a rough oxide/metal interface.

metal interface. Some authors have constructed models to account for this type of scattering in the calculation of reflectance curves [71], but software used in the analysis of these measurements did not have this capability.

Despite this complication, oxide layer thicknesses can be assigned based on these measurements with reasonable certainty given the sensitivity of the curvature of the reflectivity response to the film thickness. Best-fit assignments for thickness are made by iteratively simulating a reflectance curve and manually optimizing the film thickness to best match the curvature of the experimental response. As seen in Fig. 5-11, this curvature can be matched very well over the range of measurement, despite the offset in intensity. Noise can be seen at the lower end of the reflectance curve as the intensity of the white light excitation begins to drop significantly near 400 nm.

The data presented in Table 5.5 are illuminating based on visual and Raman classification of the oxide character on each of the surface grains measured. No significant difference in oxide character either from either visual inspection or Raman measurements is present in the series of samples oxidized at 500°C. For these series of samples, the measured oxide layer thickness increases monotonically as a function of exposure time, as is expected. An alternative measurement on sample #3 off of the grain that was monitored using DH-TGS returned a similar oxide layer thickness (109 ± 5 nm) to the grain listed in Table 5.5. However for the series of samples exposed at 550°C, the oxide thickness on samples exposed for two hours are smaller than for the sample exposed at one hour. Visually, the spots under inspection for samples #5 and #6 have much darker and more purple oxide layers compared to the lighter blue oxide layers on sample #4 and #7. In addition, the Raman spectra
in Fig. 5-10 show more intensity in the Cr$_2$O$_3$ peaks relative to the broad spinel peak for #4 and #7 compared to the two hour exposures. In this light, it is not surprising that the measured oxide layer thicknesses are not monotonic on the grains which happened to be analyzed using DH-TGS. For the sake of comparison, an additional white light measurement is carried out on sample #6 on a grain which also shows characteristics of this Cr$_2$O$_3$ enrichment. The measured film thickness on this grain is $146 \pm 5$ nm. This data point would fit in a monotonic trend of increasing oxide thickness as a function of exposure time and suggests that the oxidation rate on similar grains is decreasing as a function of exposure time.

5.4 Comments and Discussion

Taken together, the series of in-situ DH-TGS and other experimental results provide a good qualitative picture of the oxidation process taking place on Fe-12Cr-2Si. The short time oxidation kinetics for alloys with a mid-range chromium composition at moderate temperatures as described in the literature, specifically [5] and [17], are exhibited in these exposures. Initial oxidation will occur as both Cr$_2$O$_3$ and Fe$_3$O$_4$ because the chromium content is not high enough to preclude the formation of iron oxides. The oxide quickly evolves into some form of iron-chrome spinel, as the temperatures we use in this study are not high enough to form only the passivating Cr$_2$O$_3$ scale. For higher temperatures, we observe an enrichment of corundum Cr$_2$O$_3$ in the oxide scale formed primarily of the spinel phase. These features are all exhibited through the Raman spectra of samples investigated post-exposure. Drawing quantitative conclusions from only three data points for post-exposure white light thickness measurements is difficult, but it appears that the oxide layer growth rate is decreasing with time, which is characteristic of parabolic growth of passivating oxide layers. It is of note that although the spinel oxide phase does not inhibit ion transport to the same degree as Cr$_2$O$_3$, it is still somewhat protective, certainly more so than pure iron oxides. At the temperatures and times investigated here, we see no evidence in the Raman spectra of SiO$_2$ formation. Some authors have found SiO$_2$ layers formed near the temperatures investigated here, but only for far longer oxidation times [9].

This picture of the oxidation process taking place on these samples is largely consistent with previous literature on alloys similar to the model alloy studied here. However, one purpose of this work is to try and determine the grown oxide layer thickness continually as a function of exposure time through the use of time-resolved DH-TGS. In reaching that goal, the work presented here is unsuccessful. From the data collected for this study, we are not able to make a determination of the grown oxide layer thickness as continuous function of exposure time. The major challenge in reaching this goal, as we have described in detail, can be attributed to a deficiency in the silicon avalanche photodiodes used to collect DH-TGS measurements in this study. The low-frequency cutoff
of these detectors makes the fitting procedure developed for thermal performance measurement from phase grating TGS responses fail. Modifying the methodology to accommodate signals inclusive of the ‘detector droop’ noted in experiments allows us to monitor the effective thermal diffusivity of oxidized materials to some degree, but we lose both the phase insensitivity which makes the method attractive and the correspondence of measured values to true physical values of thermal diffusivity.

Despite these restrictions, we still observe some of the characteristics of the oxidation process of these samples in the measured in-situ DH-TGS response. In Section 3.4, we stated that the parameter of interest when determining which thermal transport properties are going to be reflected in the measured TGS response (either film or substrate) is the product $qL$, where $q$ is the grating wavevector and $L$ is the surface layer thickness. Post exposure white light reflectometry indicated that the oxide films grown on Fe-12Cr-2Si in this same matrix had thicknesses on the order of 100 nm. For the $3.11 \, \mu m$ grating spacing used in experiments, we find a product $qL \approx 0.2$ for films near the end of their exposures in this sample matrix. This value is precisely in the range in which the measured effective thermal diffusivity should be sensitive to both the thermal diffusivity of the substrate and the film on the surface. Had the experimental measurements been of sufficient quality to calculate film thicknesses, this a combination of grating wavevector and film thickness in this range is where we would like to operate. In that sense, at least, the experiment was carried out in the correct parameter space for its intended goal. It is also of note that the functional dependence of the effective thermal diffusivity in this region of thin films is a non-linear function of film thickness (in Fig. 3-11 we would be at about $L_{th}/L = 10$). Although only small changes in $\alpha_{eff}$ are evident as a function of exposure time in the experiments presented here, this change possibly corresponds to significant changes in film thickness on the short time scale.

For samples exposed at $500^\circ C$ we observe what seems like a linear decrease in $\alpha_{eff}$ as a function of exposure time between jumps corresponding to phase adjustments. The behavior seems consistent with the increase in post-exposure film thickness as a function of time. For samples exposed at $550^\circ C$, we initially observe the same decrease in $\alpha_{eff}$, but this trend eventually levels off. For these samples exposed at higher temperatures, this behavior is consistent with the increased post-exposure $\text{Cr}_2\text{O}_3$ concentration in the oxide film. $\text{Cr}_2\text{O}_3$ forms a more protective film than the spinel, such that the oxide scale growth rate will decrease sooner as the $\text{Cr}_2\text{O}_3$ content increases. A slight uptick in the effective thermal diffusivity after the formation of a protective mixed $\text{Cr}_2\text{O}_3$/spinel layer is also possible. Following complete or partial passivation by $\text{Cr}_2\text{O}_3$ or mixed $\text{Cr}_2\text{O}_3$ and spinel, continued oxidation will occur via transport through the passive layer and oxidation at the surface. This process results in iron-rich oxide formation near the surface of the oxide [1]. Iron-rich oxides, either in the form of $\text{Fe}_3\text{O}_4$, stoichiometric spinel, or spinel with large iron content, are more thermally conductive than chromium-rich oxides, and will tend to increase the thermal diffusivity of the surface oxide layer [79,80]. In addition, at high temperatures the $\text{Cr}_2\text{O}_3$ scale may densify with
continued exposure time, increasing the apparent thermal diffusivity of oxide layer [5]. Either of these processes may be the root of uptick in $\alpha_{\text{eff}}$ at long times in 550°C exposures, however we cannot definitively conclude the mechanism from the work carried out here. To quantitatively determine the enrichment of Fe and Cr through the oxide layer, other techniques such as depth-resolved auger electron spectroscopy must be used, as in [81].

A comment is also required concerning the issues encountered during the \textit{in-situ} monitoring of sample #7, exposed for four hours at 550°C. Through the course of this measurement, the combination of oxide layer transparency and a rough oxide/metal interface drastically reduced the signal intensity that we were able to recover. This challenge was not expected prior to experimentation and in principle is difficult to design against. Depending on the particular composition and thickness of the oxide layer grown, scattering of this type has the potential to destroy the ability to monitor samples using TGS. The type of detection that is employed using the transient grating technique inherently relies on specular reflection from a sample under investigation. If this property is lost, then the technique is no longer appropriate. Normally, some degree of surface roughness may be accommodated. However, this issue is exacerbated in the context of these experiments as chromium-rich oxides are almost entirely transparent at 785 nm, the wavelength used for our probing lasers [73].

The issue noted above requires further comment about the appropriateness of the theory we propose to apply to determine oxide film thicknesses. We state in Section 3.4 that multi-layer thermal and acoustic properties may be modeled in this system by considering energy deposition at the surface of a film-substrate system. Most system that have been considered in this context are comprised of thin metallic films atop less conductive substrates. In this case, the approximation of laser energy deposition near the surface is a good one, as the optical skin depth for metallic conductors is on the order of nanometers. However, this assumption fails in the case of our thin oxide films. We see this particularly in sample #7, whose oxide layer is largely transparent to the probe laser wavelength. If grown oxide layers are transparent or semi-transparent to the incident pump laser (at 532 nm in this case), then the model for the excitation process, as it has been constructed in the literature so far, is no longer appropriate. This is a serious complication, as the development of the concept of effective thermal diffusivity is predicated on the multi-layer response of systems with highly localized energy deposition at the surface. The physics model for this process still holds, of course, but for the case of a semi-transparent film on a metallic substrate, the problem must be re-solved with appropriate boundary conditions for energy deposition. This procedure would be complicated by the fact that the optical properties of the oxide layer are sensitive to its chemical composition, which we have seen is variant in both space and time. A more detailed analysis of this problem is necessary before quantitative information about grown oxide film thicknesses may be determined using these methods.
5.5 Future Work

Following the methodological development and experiments carried out for this thesis, a number of questions must still be addressed. The obvious first step in the continuation of this project will be to procure and test a new set of avalanche photodiodes with parameters more suited to the study of thermal grating decay. The detectors we use here are well-suited to the study of acoustic propagation in materials in the hundreds of megahertz range, as they were in the development of the DH-TGS technique as described in Section 3.3. However, for the study of thermal transport properties, this hardware is unsuitable. Without suitable hardware for this purpose, we cannot accurately measure both the thermal and elastic transport properties, despite the appropriate optical configuration in DH-TGS to do so. This restriction has also not allowed us to sufficiently test the informed fitting method that has been developed to determine thermal transport properties from phase grating TGS responses. Specifically, the ability to make a phase-insensitive determination of the thermal diffusivity needs to be rigorously tested using an appropriate experimental configuration. In practice, if the method we described here is truly phase-insensitive within a certain range of absolute heterodyne phases, the DH-TGS technique becomes a much more powerful tool in its implementation.

One final note on experimental parameters that need further testing. In all of our discussion and analysis, we assume that the incident power from both the pump and probe lasers is not enough to damage the material surface in question. For metallic materials, with the laser powers used in this implementation of the experiment, this is almost always true. However, post-exposure optical imaging of some samples revealed areas that appeared as though they may have been slightly damaged by the incident pump laser. Spots observed were not conclusive due to other small non-uniformities in the oxide layer surface. As a quick future test, already oxidized samples should undergo continuous DH-TGS monitoring for a significant length of time at different incident laser powers to ensure that the surface is not being damaged.

In addition to the experimental upgrades and methodological validation, the final step in the determination of the surface film thickness must be completed as well. Namely, a solution and minimization scheme must be constructed around the multi-layered thermal response problem such that the inverse problem can be efficiently solved. By the inverse problem, we again refer to the ability to measure a film layer thickness through a measured effective thermal diffusivity and prior knowledge of the thermal transport properties of both the film and substrate material. Finding a solution to this problem becomes even more complicated due to possible non-localized deposition of laser heating throughout the surface oxide film. It remains to be seen if the construction of the parameter ‘effective thermal diffusivity’ is still meaningful in the distributed excitation case. This point also begs a higher level question. Is this technique actually an effective method for studying very short timescale oxidation processes? At this time, the answer is not evident. If a solution can
be found for the inverse problem, taking into account the optical properties of the oxide films that are grown, then the answer to that question will become more clear.

5.5.1 Future materials

Another complication that is observed in these experiments is that of non-uniform oxidation as a function of surface grain orientation and, more generally, the possible formation of many different oxide layers. Moving forward, future tests seeking to validate this methodology further should pick material systems to study which primarily form oxide layers of a uniform composition and/or use materials with known crystal orientations. The orientation-dependent transport complication can be solved by either selected single crystals of materials to test with known surface orientations, or by constructing grain orientation maps of large-grained polycrystalline samples and selecting areas to test with similar surface orientations. The post-exposure surface finish of the samples tested in this study should still be of sufficient quality that grain orientation mapping with electron backscatter diffraction (EBSD) can be conducted to confirm that grains with similar orientations grew oxides of similar character.

Doing these types of tests on Fe-Cr alloys, however, would not remove the issue of multiple oxide layers of different compositions. Although the model alloy that we chose to study here gets close to an engineering application appropriate alloy, it was perhaps too challenging a first test case. Immediate future studies should focus on single component materials which form passive oxide layers with known properties. Based on the relative abundance of available data in terms of thermal, mechanical, vibrational, and optical properties compared to more complex engineering alloys, single crystals of pure chromium are the obvious choice for continuing testing. Having oxide layers that grow of a single composition will also make solving the inverse, distributed energy deposition problem much easier.

5.5.2 Additional analysis for Fe-12Cr-2Si measurements

Throughout the study conducted here, we have restricted our interest to the measured effective thermal diffusivity measured using DH-TGS. As described in Chapter 3, TGS measurements are also sensitive to the elastic mechanical properties of materials under investigation. In particular, the effects of thin films layered onto substrates have been well-studied in the literature [23]. Developing the ability to measure thermal transport from phase grating measurements is indeed only of interest because the phase grating response contains information about the acoustic properties of systems under investigation as well. However, we have not yet conducted any analysis on the variation in the acoustic response of Fe-12Cr-2Si samples during in-situ characterization. As the elastic modulus of oxide layers grown on these samples is greater than that of the substrate, we expect the measured surface acoustic wave (SAW) frequency to vary as a function of exposure time [82–84].
Figure 5-12: Measured SAW speed as a function of exposure time for oxidation at 550°C. The speed is given as the product of the measured dominant frequency and the known imposed grating wavelength, \( c = f_{\text{max}} \lambda \). The methods used to find the dominant frequency in each measurement have not yet been optimized.

For sample #6, we have conducted a preliminary analysis of the change in measured SAW speed as a function of exposure time. This data is shown in Fig. 5-12. Each point represents the location of the peak acoustic oscillation found in a filtered power spectrum of the experimentally recorded trace. Similarly to the response observed for the effective thermal diffusivity for this sample, there is an initial linear change in the response before it levels at longer exposure times. This effect scales as we would expect for the growth of a stiff surface layer onto a compliant substrate. There is no doubt more information contained in this elastic component of the TGS response for these materials which still needs to be analyzed for both the in-situ and ex-situ data collected as part of this study. As the field of measuring film thicknesses through measured acoustic properties is well-established, this component of the data may eventually prove more useful for the real-time determination of grown oxide layer thickness.

5.6 Implications

Before considering the implications of the work presented here, we must first re-state the motivating goals of the project. At the outset, we sought not only to investigate the short timescale oxidation behavior of a model Fe-Cr-Si alloy, but in doing so create systems and methods with which a wide variety of material systems might be tested. This second goal has largely been met. By modifying the experimental implementation of traditional transient grating spectroscopy, we are able to create an all-optical, non-contact, non-destructive methodology to continuously monitor the
thermal and elastic transport properties of dynamically changing material systems, and we dub this technique dual heterodyne phase collection TGS (DH-TGS). In doing so, we realize that to monitor the performance of both thermal and elastic properties with short measurement times, we must use the ‘phase grating’ response of the heterodyne amplified TGS measurement. As previous experiments have largely relied on the alternative ‘amplitude grating’ response to measure thermal transport properties, we develop an informed fitting method to recover thermal transport properties from the phase grating response. Indeed in this work we focus primarily on thermal performance determination from DH-TGS measurements as this area is less well-explored than the elastic acoustic response of layered systems. The formalism for solving the multi-layer thermal transport problem is presented, but the details of solving the inverse problem to determine a grown film layer thickness is left as future work.

The realization of the first goal stated above is, as of yet, incomplete. Due to experimental complications, which have been described at length, the quality of the data collected for this work is not sufficient to unambiguously determine the thickness of a thin oxide layer grown on a metallic substrate continuously as a function of time. Several steps have been presented which must be completed before data of the type collected in this work can be used to monitor film thickness as we intended at the outset. Most importantly, as the thin oxide films are completely or partially transparent to the incident pump and probing lasers, a more detailed model of the energy deposition, excitation, and detection process must be constructed. Only after a validation of the ‘effective thermal diffusivity’ argument for this more complicated model has been provided should additional experiments be conducted on simpler material systems.

Despite the lack of clarity in the experimental results presented here, the overall implications of this work are positive. Even if the processes and methods developed herein are proven to be inappropriate for the study of short timescale oxidation, they are nevertheless a powerful set of materials investigation tools. We have the ability to optically monitor both the thermal and elastic characteristics of materials undergoing dynamic forcing with second-scale resolution. In addition we now have an experimental test stand capable of reaching reasonably high temperatures with a controlled vacuum/cover gas environment. This stand can be swapped from the DH-TGS experimental apparatus without making changes to the optical alignment of the system, allowing for extremely flexible testing should other stand configurations be preferred. With this capability in hand, a wide variety of interesting materials systems may be studied. The future application space for methods such as the ones developed here used with dynamic systems is extremely broad as these methods may be used to short-circuit traditional destructive analysis in the materials development and optimization process.
Bibliography


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