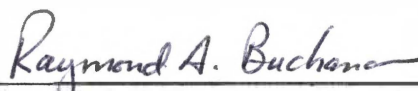


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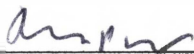


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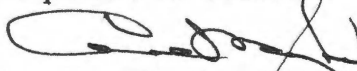
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Thesis

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**Nitridation Reactions in Two-Phase Cr(Pt) + Cr₃Pt Alloys as a Basis for
a New Synthesis Route to Form Near-Surface Composite Structures**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Sarah Kate Wrobel
August, 2002

Dedication

This thesis is dedicated to my parents, Dana and Charlene Baham, and my husband, Mike Wrobel, for inspiring me and believing in me. Your love, support, and encouragement are what have enabled me to achieve my goals and become the person I am today.

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Abstract

Recent research has focused on studying nanoscale materials because of the novel properties and behaviors they exhibit. Nanoscale dispersions of complex ceramics are of interest for functional applications because of their potential to exhibit unique magnetic, optical, chemical, and electrical properties and behaviors, however they are difficult to make. Internal oxidation reactions in multi-phase alloys offer a possible route for the controlled synthesis of these types of functional surfaces. In support of this application, the nitridation behavior of model single-phase Cr(Pt) and Cr₃Pt alloys were studied individually and in combination at 800°C and 1000°C. Results suggest that nitridation of the two-phase Cr(Pt) + Cr₃Pt alloy followed the underlying two-phase microstructure, which effectively acted as a template and led to the formation of a dispersion of the Cr₃PtN perovskite phase, derived from Cr₃Pt metal precipitates. Interestingly, the nitridation behavior of the Cr₃Pt phase differed when present as the matrix phase as opposed to as a second phase precipitate. Details of the modes of nitridation are presented.

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1. Introduction

Oxidation reactions in multi-phase alloys yield an incredibly wide variety of reaction products. Many alloys being designed for high-temperature use contain more than one phase in order to balance difficult to achieve and often conflicting properties, such as low-temperature ductility and high-temperature strength.¹ Oxidation in such alloys is not well understood and can involve oxidation behavior worse, equivalent to, and, occasionally, better than that of the individual component phases. In addition, internal oxidation reactions in multi-phase metal alloys are potentially useful for the controlled synthesis of structures for functional applications (electrical, optical, chemical, magnetic, etc.) due to the formation of novel composite structures under certain reaction conditions. The application of this mode of internal oxidation reactions in multi-phase alloys will be the main focus of the present work.

The objective of this work was to gain further insight into the modes of oxidation in two-phase alloys. Specific emphasis was placed on the examination of the in-place, or “in-situ” mode of internal oxidation. Previous work² has established sufficient evidence to show that this mode of internal oxidation in two-phase metal alloys could be used to controllably form complex ceramic islands. In order to gain a better understanding of how to manipulate this phenomenon, the oxidation behavior of the components of a model two-phase system were studied individually and in combination.

2. Significance of Multi-Phase Alloy Oxidation Research

In recent years, a large amount of research has been conducted in the area of nanoscale science. It is well known that nanoscale materials and structures have the potential to exhibit novel properties and functionalities that are not exhibited in materials and structures of a larger scale. In general, when a sample size, grain size, or domain size becomes comparable with a specific physical length scale, such as the mean free path, the domain size in ferromagnets or ferroelectrics, or the correlation length of a collective ground state like superconductivity, then the corresponding physical phenomenon will be strongly affected.³ For example, fine magnetic particles, such as SiO₂ thin films containing nanoscale Fe particles have been shown to possess intrinsic magnetic behavior as a function of particle size.⁴ Particles of a single domain structure exhibit enhanced coercivity, and are therefore of great interest for applications in magnetic or magneto-optic recording.⁴

Nanocomposites of complex ceramic phase islands are of interest for functional applications because of their potential to exhibit unique magnetic, optical, chemical, and electrical properties and behaviors.³⁻⁷ The key to successful utilization of these nanoscale complex ceramic phase islands lies in the development of synthesis techniques that allow for their production in a controllable, rapid, and inexpensive method. Currently, complex ceramic phase islands are difficult to make, and many complex ceramic phases are not accessible in nanoisland architectures.

Internal oxidation (also applicable to nitridation, carburization, etc.) reactions are a rapid, inexpensive, and controllable method to fabricate ceramic dispersions. For example, internal oxidation is often used in the oxide dispersion-strengthening of certain alloys. J. Troxell et al. has used internal oxidation of dilute silver/aluminum alloy powder to preferentially oxidize aluminum within the silver matrix.⁸ Internal oxidation renders a distribution of fine, uniformly spaced nanoscale aluminum oxide particles that strengthen the pure silver matrix.⁸ When used as a synthesis route to produce ceramic island dispersions, internal oxidation reactions, however are usually limited to the direct, controllable formation of only simple (binary) ceramic phases.⁹⁻¹⁵ We are concerned with developing synthesis routes to form complex ceramic phases because of the more unique properties they exhibit.

Generally, the oxidation of a two-phase alloy occurs according to one or a combination of both of the following limiting cases.¹⁶ Figures 1a and 1b are graphical representations of each of these different modes of oxidation in two-phase alloys. In the first case (Figure 1 a) the phases react cooperatively yielding a single-phase reaction product.¹⁶ In the second case (Figure 1 b) each of the two-phases oxidizes independently yielding a composite reaction product.¹⁶ These two fundamental cases can apply to an oxidant partial pressure which is either below the stability of the least-stable oxide or above it. Cases in which the oxidant partial pressure is below the stability of the least-stable oxide could yield a metal-ceramic composite structure. Cases where the oxidant partial pressure is above the stability of the least-stable oxide could, on the other hand, yield a

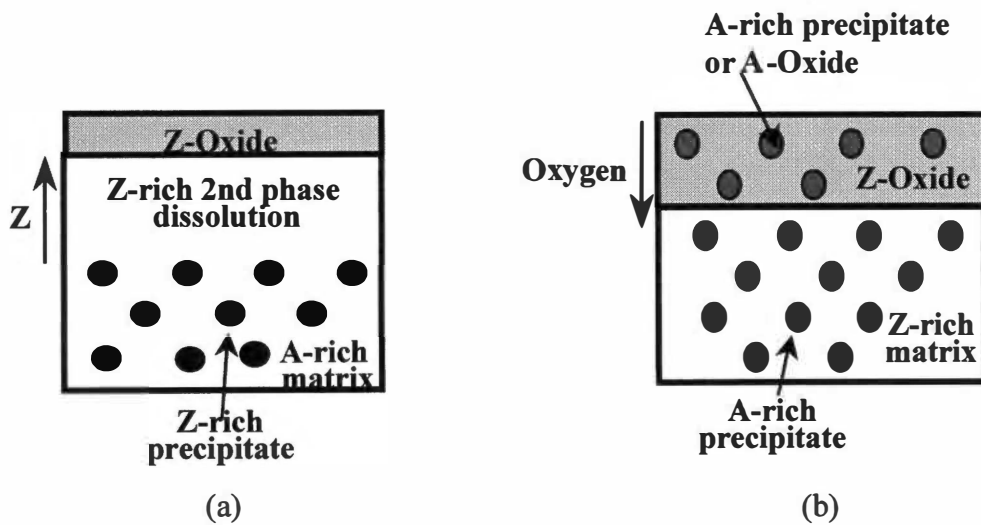


Figure 1. Schematic of the limiting cases for the oxidation reactions in a two-phase alloy (shown here for oxygen).² Figure 1 a represents the cooperative mode where the phases react cooperatively yielding a single-phase reaction product. Figure 1 b shows the independent mode where each phase oxidizes independently yielding a composite reaction product.

ceramic-ceramic composite structure.

Studies of the oxidation of two-phase alloys have primarily been focused on understanding as a design basis for improved high-temperature structural alloys and coatings. The cooperative mode of multi-phase oxidation is of interest in technological applications because it can be used as a design strategy to protect alloys in high-temperature, aggressive environments.^{1,17} Studies of the independent mode of the internal oxidation of multi-phase alloys have been somewhat neglected because this mode of oxidation is not useful for alloy protection. This mode of internal oxidation is dominated by the inward transport of the oxidant with negligible outward diffusion of the alloy components of the individual phases (Fig 1 b). Therefore, the microstructure of the oxidized region closely follows that of the original alloy in size, morphology, spatial distribution, and chemistry of each phase.¹⁶ This independent mode of internal oxidation is often termed “in-situ” or “diffusionless” because it occurs without any appreciable outward diffusion of the alloy components.¹⁶ The key characteristic of in-situ oxidation is that the initial alloy microstructure effectively acts as a template for the reaction product that will form. This in-situ mode of internal oxidation, therefore, holds great potential for use as a synthesis route to controllably produce functional complex ceramic island dispersions.

To develop a proof of principle, previous work² was done using a two-phase alloy with a multi-component compound second phase dispersion, of similar metal component stoichiometry to the desired complex ceramic phase dispersion, as the initial template. Upon exposing the alloy to reactive gaseous species at conditions that promoted in-situ internal oxidation, a complex ceramic phase dispersion of the desired metal component stoichiometry was formed. It is, however, necessary to develop a fundamental understanding of how to better control and manipulate this process. The focus of the present work was, therefore, to gain a mechanistic understanding of the factors that control this phenomenon.

3. Review of Related Literature

3.1 Oxidation

“Under most conditions of use, metals are thermodynamically unstable with respect to ambient gases, and depending on their composition and the reaction conditions, will react to form oxides, sulphides, carbides, nitrides, etc. or mixtures of reaction products.”¹⁸

Oxidation reactions are encountered in many areas, and are most commonly considered in high-temperature environments containing reactive gaseous species. Oxidation reactions can have detrimental effects on materials by causing a loss of material, which often leads to the loss of load-bearing capabilities.^{2,18} However, when managed properly, the rate of degradation can be greatly slowed, and oxidation reactions are used to form protective scales. Essentially all high-temperature alloys and metallic coatings rely on continuous, slow growing oxide scales for protection against the environment.^{1,17-24}

Oxidation reactions in multi-phase alloys differ greatly with respect to the behavior of corresponding single-phase alloys in both oxidation kinetics and the microstructure of the reaction products. These differences are due to the segregation of alloy components between the phases and the different physiochemical characteristics of the phases themselves (e.g. oxidant solubility, component diffusivity) as well as the possibility for preferred transport paths along the interface between the phases.^{16,25-33} Oxidation reactions in multi-phase alloys can form an incredibly wide variety of surface reaction products. The focus of the present work is on internal oxidation reactions in multi-phase alloys. The oxidation behavior of the individual component phases of these multi-phase alloys will also be examined. It is therefore necessary to review the fundamentals of internal oxidation in both single- and multi-phase alloys.

3.1.1 Internal Oxidation in Single-Phase Alloys

Internal oxidation is the process by which an oxidant (oxygen, sulfur, carbon, nitrogen, etc.) diffuses into an alloy and causes sub-surface precipitation of the oxides (or sulfides, carbides, and nitrides, respectively) of one or more alloying elements.³⁵ Internal oxidation reactions in both single- and multi-phase alloys has been extensively researched over the last fifty years. Through a significant amount of work done by C. Wagner and reviewed by others,^{18,34-38} a theoretical understanding of the processes and mechanisms that occur during the internal oxidation of single-phase alloys has been well established.

Birks and Meier³⁵ define four conditions essential for internal oxidation to occur:

- 1) The Gibbs free energy of formation per mole O_2 , ΔG^0 , of the solute metal oxide, BO_v , must be more negative than that of the base metal oxide.
- 2) ΔG for the reaction $B + vO = BO_v$ must be negative. Therefore, the base metal must have a solubility and diffusivity for oxygen, which is sufficient to establish the required activity of dissolved oxygen, O , at the reaction front.
- 3) The solute concentration of the alloy must be lower than that required for the transition from internal to external oxidation.

- 4) No surface layer must prevent the dissolution of oxygen into the alloy at the start of oxidation.

Internal Oxidation Kinetics

Derivations of internal oxidation kinetics are presented or reviewed in several references.^{18,34-38} A simplified treatment done by Birks and Meier³⁵ will be presented here for a planar specimen of binary alloy A-B, where B is a dilute solute that forms a stable oxide (Figure 2). The assumption is made that the oxidation occurs under an ambient $P(O_2)$ that will allow for the oxidation of B but will be too low to oxidize A.

This approximation assumes that the dissolved oxygen concentration varies linearly across the internal oxidation zone. Fick's first law is therefore used to determine the oxygen flux through the internal oxidation zone:

$$J = \frac{dm}{dt} = D_o \frac{N_o^{(s)}}{XV_m}, \quad (\text{Eq. 1})$$

where $N_o^{(s)}$ is the oxygen solubility in A (atom fraction), V_m is the molar volume of the solvent metal or alloy, and D_o is the diffusivity of oxygen in A. Counter-diffusion of the solute B is assumed to be negligible, so the amount of oxygen accumulated in the internal oxidation zone per unit area of reaction front is:

$$m = \frac{N_B^{(o)}vX}{V_m}, \quad (\text{Eq. 2})$$

where $N_B^{(o)}$ is the initial solute concentration. An alternate expression for the flux is obtained through differentiating Equation 2 with respect to time:

$$\frac{dm}{dt} = \frac{N_B^{(o)}vX}{V_m} \frac{dX}{dt}, \quad (\text{Eq. 3})$$

Equation 1 can be set equal to Equation 3 and rearranged to yield:

$$XdX = \frac{N_o^{(s)}D_o}{vN_B^{(o)}} dt. \quad (\text{Eq. 4})$$

Integrating Equation 4, assuming $X = 0$ at $t = 0$, gives the following expression:

$$X = \sqrt{\frac{2N_o^{(s)}D_o}{vN_B^{(o)}}t}, \quad (\text{Eq. 5})$$

which defines the penetration depth of the internal oxidation zone as a function of oxidation time. According to this equation, the penetration depth of the internal oxidation zone has a parabolic time dependence: $X \propto \sqrt{t}$. It can also be seen that at a fixed time, the penetration depth is inversely proportional to the square root of the atom fraction of solute in the bulk alloy. Also, if the solute concentration of an alloy is known, the solubility-diffusivity product, $N_o^{(s)}D_o$ (permeability) of oxygen in the matrix metal can be determined by carefully measuring the front penetration as a function of time.

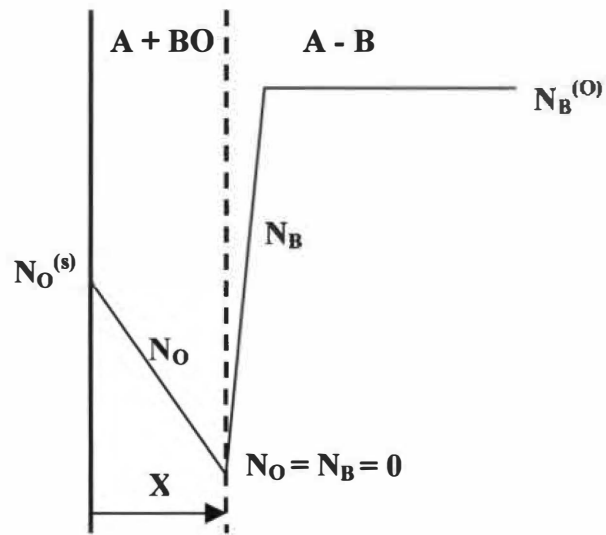


Figure 2. Schematic drawing showing simplified concentration profiles for the internal oxidation of binary alloy A-B.³⁵

Precipitate morphology

The morphology of the oxide precipitates formed during internal oxidation very often define or have an effect on the overall corrosion process or the alloy properties.^{35,39} During oxidation, there is competition between the nucleation rate as the internal oxidation front advances and the subsequent growth and coarsening rates of the particles. This “competition” typically determines the size of the oxide particles. “The longer the time a nucleated particle has to grow between the arrival of oxygen and solute at its surface and the next nucleation event which depletes the supply of solute, the larger will be the particle”.³⁵ Factors that favor high growth rates will tend to increase particle size, while factors that favor high nucleation rates will decrease the size of the particles.

Birks and Meier³⁵ presented a list of general factors that determine the size of internal oxides. Larger oxide particles tend to form with:

- a) deeper front penetrations, X ,
- b) higher solute concentrations, $N_B^{(O)}$,
- c) lower oxygen solubilities and lower p_{O_2} ,
- d) higher temperature,
- e) higher particle-matrix interfacial free energies, and
- f) less stable oxides.

Wagner studied the internal oxidation of Cu-Pd and Cu-Pt alloys.⁴¹ Oxidation of these two alloys formed Cu_2O in the alloy matrix beneath an external scale of Cu_2O . While studying the theory involved in this experiment, Wagner was able to determine that alloys containing high concentrations of the base metal can form both a surface scale and internal precipitates of the same phase.

J. Megusar and G.H. Meier studied the internal oxidation of Co-Ti alloys of varying compositions at different temperatures.⁴² Internal oxidation of these alloys yielded three oxide structures, δ -TiO, TiO_2 , and $CoTiO_3$, which were formed through successive solid-state reactions according to the following process. δ -TiO was the first oxide to form, which further oxidized to form TiO_2 because there is very little difference in stability between the two oxides. As the oxygen activity continued to increase the TiO_2 reacted with Co and O to form the complex phase, $CoTiO_3$.

3.1.2 Internal Oxidation of Two-Phase Alloys

When compared to single-phase alloys, the internal oxidation of two-phase alloys presents a number of differences, which are primarily a result of limitations on the diffusion of the alloy components created by the presence of two phases. The added complexity of multi-phase systems makes it difficult to predict the oxidation behavior. Gleeson and Gesmundo¹⁶, among others,²⁵⁻²⁸ have reviewed this subject and provided a fundamental explanation of the general processes that occur during the oxidation (both internal and external) of multi-phase alloys, which was described in previous sections of this paper. Several internal oxidation studies on multi-phase alloys have been conducted

over the last several years.^{9-15,42-47} The different alloys and oxidation conditions used in each of these studies produced a wide variety of internal oxidation structures.

A number of experimental studies have been conducted using two-phase alloys containing a solid-solution phase and a compound phase. While in-situ internal oxidation was observed in many of these cases, most reactions formed a simple, binary oxide in a metal matrix. W.T. Wu et al. studied the internal oxidation of two-phase Co + Co₁₇Y₂.⁹ The microstructure of the internal oxidation zone closely followed that of the original alloy, thereby exhibiting in-situ internal oxidation. The islands of Co metal remained unchanged in composition, shape, and spatial distribution, while the large Co₁₇Y₂ phase particles were transformed into a fine two-phase mixture of Co metal and Y oxide.

In another study that produced similar results, G.Y. Fu et al. examined the internal oxidation of two-phase Co + Co₁₇Ce₂.¹⁰ At all temperatures studied, the microstructure of the internal oxidation region followed closely that of the original alloy. The oxidized samples showed only an outer two-phase region that appeared darker, but had the same microstructure as the alloy. In this oxidation zone, the dark Co phase islands remained in the same metal state as those in the original alloy, while the Co₁₇Ce₂ phase particles were converted into a two-phase mixture of Co metal and Ce oxide.

Y. Niu et al. studied the oxidation of Ag(Y) + Ag₅₁Y₁₄ under 1 atm and 10⁻²⁰ atm O₂ at 700°C.¹³ Oxidation under 1 atm O₂ produced internal oxidation of Y in the pure Ag matrix beneath a thin layer of Ag. The microstructure in the internal oxidation zone closely followed that of the original alloy. The Ag(Y) phase remained in the same metallic state with the same number, size, and spatial distribution as the original alloy, while the Ag(Y) + Ag₅₁Y₁₄ eutectic islands were converted into a mixture of Ag and Y₂O₃. The morphology of the internal oxide particles, however, changed with depth in the alloy, where they were small and globular near the surface, and became more elongated and perpendicular to the surface deeper into the alloy. Oxidation under low P(O₂) produced different results than those found under 1 atm O₂. Complex scales formed, but in-situ internal oxidation was not observed. The authors attributed the changes in oxidation behavior with the oxygen pressure in the gas to the reduced concentration and penetration of oxygen in the alloy under low P(O₂).

Castello et al. studied the internal sulfidation of two-phase Co(Ce) + Co₅Ce alloys, which produced duplex scales, but still consisted of only simple ceramic phases.¹¹ These duplex scales contained an outermost layer of pure Co sulfide followed by an inner region of complex composition: the outer zone was a mixture of Co sulfide and Ce sulfide, and the inner zone of this same layer consisted of a mixture of Co metal and Ce sulfide.

Several studies were also found in the literature where the internal oxidation of two-phase alloys produced complex ceramic phases, but had different stoichiometry than the unoxidized phases from which they were formed. In one example, Brady et al. observed in-situ oxidation in two-phase Cr(Nb) + Cr₂Nb alloys that were oxidized at 1100°C in air.

The compound matrix phase, Cr_2Nb , reacted to form a fine mixture of a complex nitride phase CrNbN , and at least one additional phase, thought to be Cr_2N or Cr .⁴⁴

M. Castro Rebelo et al. studied the internal oxidation of two Fe-Nb alloys containing 15 and 30 wt.% Nb (two-phase $\text{Fe}(\text{Nb}) + \text{Fe}_2\text{Nb}$) under low oxygen pressures at 600 to 800°C.⁴⁵ At 700°C and 800°C, Fe-15Nb wt.% internally oxidized to form a mixture of Fe metal with Nb oxide identified as NbO_2 close to the alloy and Nb_2O_5 close to the outer alloy surface. Also, darker islands corresponding to the Fe_2Nb phase in the outermost scale region were identified as FeNb_2O_6 . The reaction in Fe-30Nb wt.% produced similar results. Fe_2Nb islands that were larger than the ones found in Fe-15Nb wt.% internally oxidized to form a mixture of Fe metal and Nb oxide. In a thin, outermost region, the Fe_2Nb islands became a mixture of Fe metal with FeNb_2O_6 . In all cases, the distribution of the internal oxides formed followed closely that of the Nb-rich phase of the original two-phase alloy.

The aforementioned studies all involved reaction products that differed in metal component stoichiometry from the metal precursor phase. To use internal oxidation in two-phase alloys as a synthesis approach, it would be desirable from a microstructural control standpoint to have the resultant ceramic phase dispersion mirror the metal component stoichiometry of the initial metal compound phase. Brady et al.² and Kosec et al.⁴⁶ recently demonstrated such a situation. Brady et al. examined the nitridation behavior of two-phase $\text{Cr}(\text{Pt}) + \text{Cr}_3\text{Pt}$ alloys.² The alloy, consisting of Cr_3Pt dispersions in a $\text{Cr}(\text{Pt})$ matrix, was held in nitrogen at 1000°C for 24 hours. Cross-section SEM micrographs of the nitrated alloy are given in Figures 3 a and b. Nitridation resulted in the formation of an external Cr_2N scale followed by two sub-scale nitridation zones. The first, near-surface sub-scale nitridation region contained nitrated- Cr_3Pt particles in a nitrated- $\text{Cr}(\text{Pt})$ matrix, and the sub-scale nitridation region below contained nitrated- Cr_3Pt particles in a $\text{Cr}(\text{Pt})$ -metal matrix. Characterization of the nitrated sample indicated that the alloy exhibited in-place internal nitridation of Cr_3Pt dispersions to form Cr_3PtN .

In another study, L. Kosec et al. examined the internal oxidation of two-phase $\text{Ag}(\text{Te}) + \text{Ag}_2\text{Te}$ (Ag -1.3Te at.%).⁴⁶ The samples that were oxidized at 750, 800, and 830°C at 1 atm produced a region of two different types of oxide particles, differing in size and shape, in an essentially pure Ag matrix formed through two different modes of internal oxidation. Similar to the reaction that occurred during the nitridation of the Cr-Pt alloy previously described in the work done by Brady et al., coarser particles, identified as Ag_2TeO_3 , were of similar size, shape, and spatial distribution as Ag_2Te particles in the original alloy. These particles were formed through primary in-situ internal oxidation of Te in the form of an intermetallic compound. However, very small (~1 nm to ~1 μm) oxide precipitates homogeneously distributed in the matrix, also formed through secondary diffusive internal oxidation of Te dissolved in the Ag matrix. Therefore, both in-situ and classical modes of internal oxidation were present (simultaneously) in the oxidation of the Ag-Te alloys.

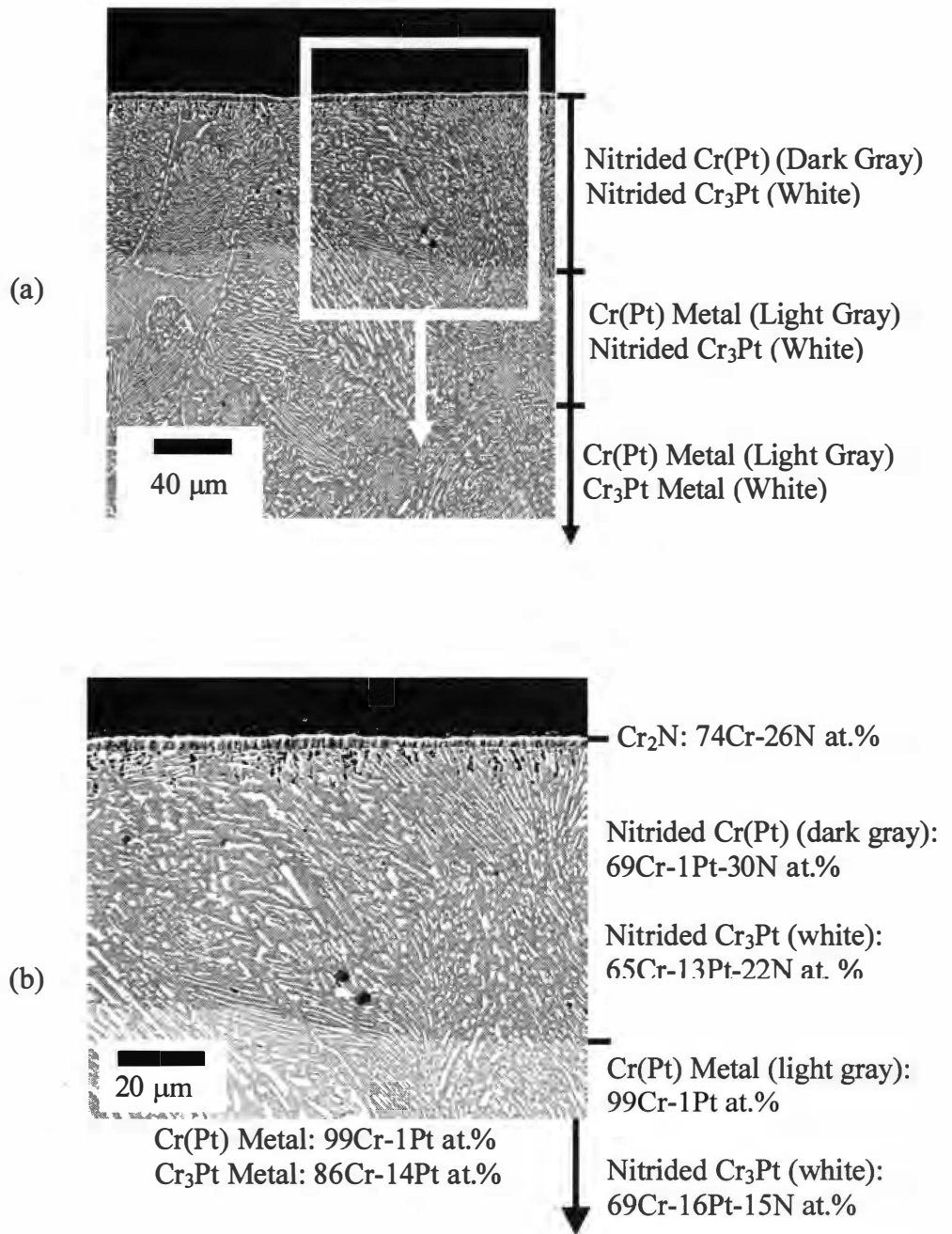


Figure 3. SEM cross-section micrographs of Cr-5Pt at.% heat-treated at 1350°C for 8 hours, 1050°C for 12 hours, then held in high-purity nitrogen at 1000°C for 24 hours. Nitridation of the original Cr + Cr_3Pt structure produced Cr-nitride + Cr_3PtN , followed by Cr-metal + Cr_3PtN . Figure (a) is a low-magnification overview and (b) is a high magnification view of the boxed region.²

3.2 Nitridation Properties of Unalloyed Chromium

The model system that was utilized in this study consisted of chromium-based alloys containing a mostly chromium matrix. Nitrogen was the oxidant selected for this study because it exhibits a high solubility in chromium⁴⁸⁻⁵⁵, which favors internal nitridation reactions. A brief description of the nitridation properties of unalloyed chromium will follow.

Cr₂N and CrN are the two intermediate phases that exist in the solid state (see Cr-N phase diagram in Figure 4).⁴⁷ A.U. Seybolt and D.H. Haman⁴⁹ were able to show that nitridation of chromium occurs by the inward diffusion of nitrogen through Cr₂N, and that it follows a parabolic law:

$$k_p(N_2) = 2.15 \times 10^{-5} \exp \frac{-33,000 \pm 1600}{RT} (g - cm^{-2})^2 \text{ sec}^{-1}. \quad (\text{Eq. 6})$$

The nitride layer that forms on pure chromium is very adherent, and may also enter deeper along grain boundaries in addition to forming a surface layer.

As mentioned earlier, for in-place internal reactions to occur, the metallic matrix phase must exhibit a high permeability to the oxidant under conditions for which the diffusion of the metallic components is relatively low.^{2,18,27-29} Nitrogen exhibits a high solubility in chromium (Figure 4). M. Venkatraman and J.P. Neumann⁴⁷ reported that the solubility of nitrogen in chromium in equilibrium with Cr₂N above 900°C is given by:

$$\log(at.\%N) = 4.36 - \frac{7100}{T}. \quad (\text{Eq. 7})$$

Using this expression, the solubility of nitrogen in chromium at 1000°C is 0.0607 at.% N. As reported by A. H. Scully⁴⁹, D. Caplan et al. determined that the solubility of nitrogen in chromium between the temperatures 700°C and 1320°C could be expressed in terms of weight percent nitrogen by the equation:

$$\log_{10} W = \frac{-7250}{T} + 3.86 \quad (\text{Eq. 8})$$

where W is weight percent nitrogen and T is absolute temperature. Using this equation, the solubility of nitrogen in chromium at 1100°C is 0.0146 wt.% N. When compared to another oxidant such as oxygen, which exhibits a low solubility in chromium at this same temperature, nitrogen is more likely to favor internal reaction modes.

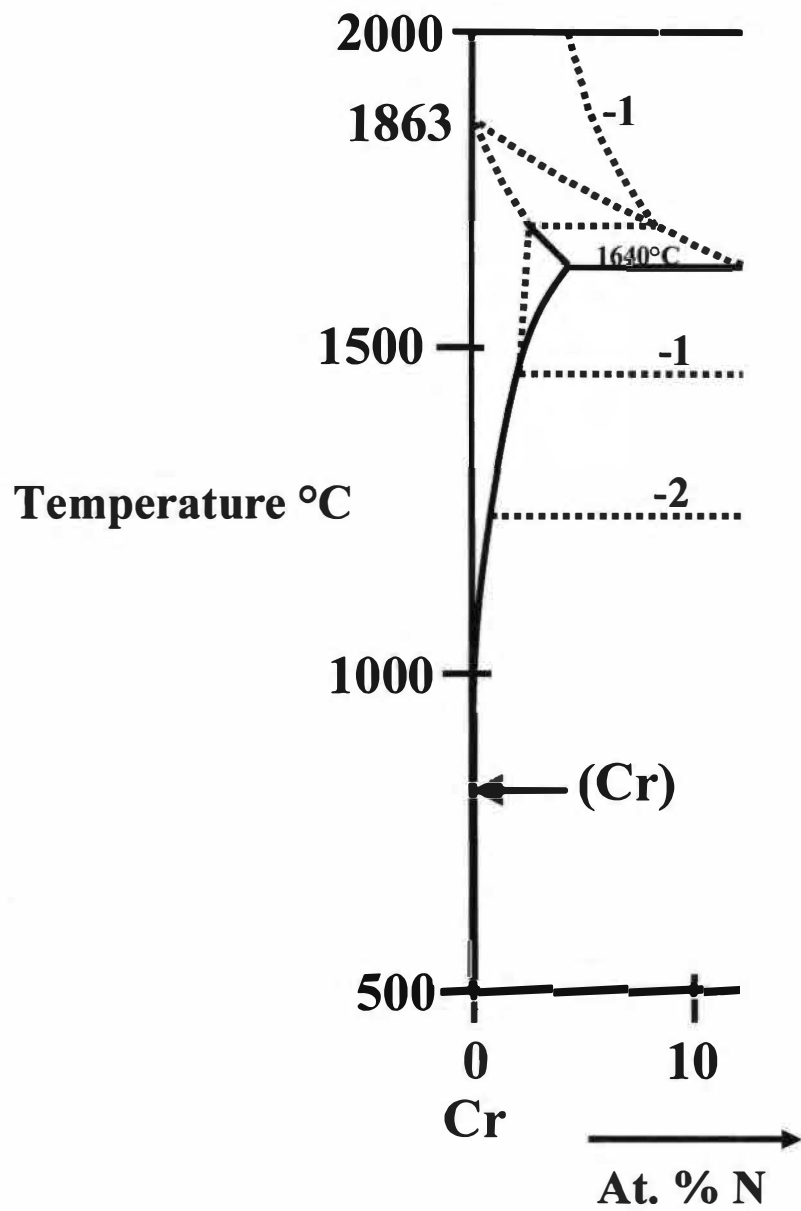


Figure 4. Schematic of the Cr-N phase diagram.⁴⁷

4. Critical Issues

Oxidation reactions in multi-component, multi-phase alloys yield a wide variety of reaction products. In-place internal reactions in multi-phase alloys are driven by the inward transport of the oxidant with negligible outward diffusion of the metal components. Therefore, the initial alloy microstructure acts as a template, and the reaction product exactly mimics the size, morphology, spatial distribution, and chemistry of each phase in the underlying alloy. The purpose of this research is to study the fundamentals of oxidation reactions in multi-phase alloys and to determine if the in-place mode of internal oxidation in two-phase alloys can be used to controllably yield a complex ceramic dispersion.

The selection of model alloys in the Cr-Pt system was based on several criteria. The alloy selected for this study was chromium-based with a chromium matrix. For in-place internal reactions to occur, it is critical that the matrix phase of the alloy exhibits a high permeability to the oxidant species. Pure chromium exhibits high permeability to nitrogen and therefore favors internal nitridation, which is the reaction mode desired for this study. Platinum, on the other hand, does not react with nitrogen.

One aspect that must exist for in-place internal reactions to be used as a synthesis route to form complex ceramic dispersions is that in the selected system, an appropriate precipitation reaction must exist, which yields a precursor metallic precipitate phase that has similar metal component stoichiometry to the desired complex phase.² As can be seen in Figure 5, the Cr-Pt phase diagram shows decreasing platinum solubility with decreasing temperature. Therefore, a Cr₃Pt second phase can be precipitated. The Cr₃PtN perovskite phase, which is a complex nitride phase with similar metal component stoichiometry to Cr₃Pt, has been reported by M. Nardin, et. al. to exist.⁵⁰

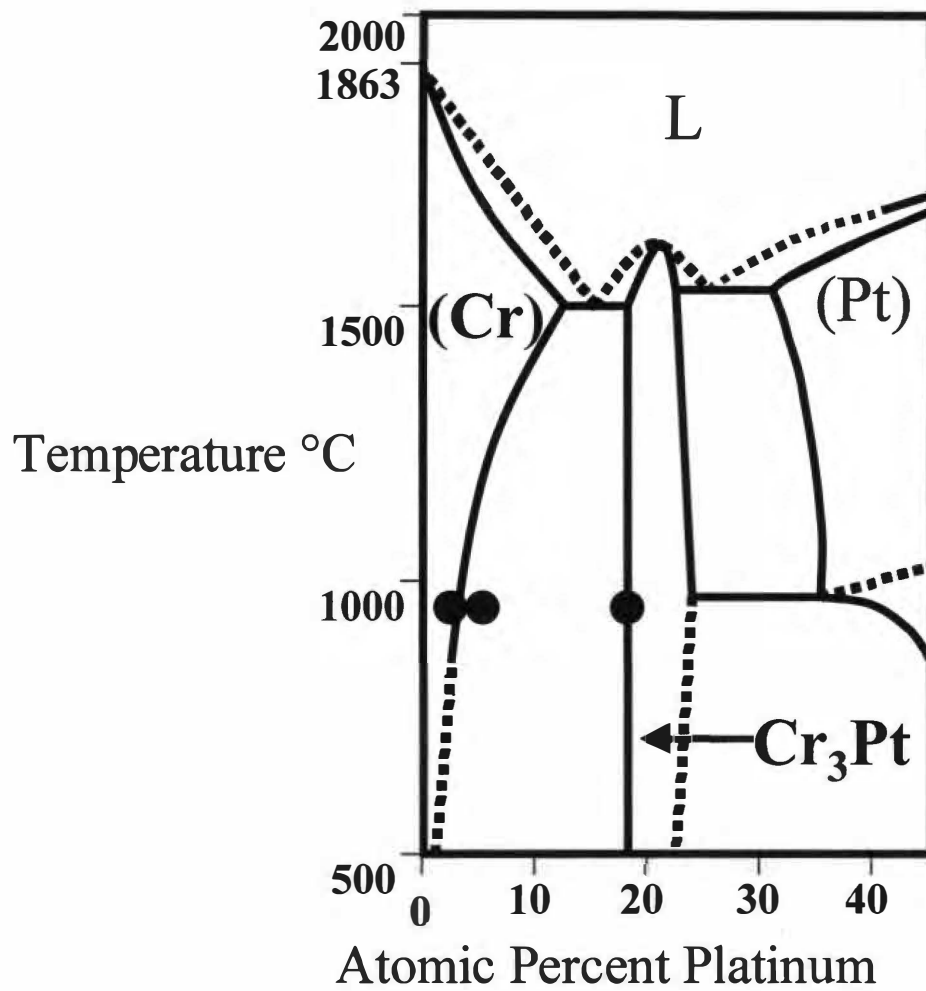


Figure 5. Schematic of the Cr-Pt phase diagram.⁴⁷ The large circles on the phase diagram indicate the compositions of each alloy studied during nitridation treatments: Cr-2.25Pt at.%, Cr-5Pt at.%, and Cr-17Pt at.%.

5. Experimental Methods

Chromium-platinum based alloys were selected as the model system for this study. The following sections will contain descriptions of the processes used to fabricate and prepare the alloy samples for nitridation experiments. A brief summary of the methods used to nitride and characterize the alloy samples is also provided.

5.1 Sample Fabrication

The chromium-platinum alloys of varying Pt content were fabricated by repeated arc-melting a mixture of appropriate amounts of chromium and platinum chips under an argon atmosphere. The alloys were then drop-cast into ingots approximately 7.62 cm in length and 1.27 cm in diameter. Each sample was weighed after fabrication to determine whether any material was lost due to vaporization.

Under a Process Science Initiative (PSI) effort in collaboration with T.A. Lograsso and D.L. Schlagel from Ames Laboratory, Cr(Pt) + Cr₃Pt microstructures derived from (100) and (111) orientated Cr-5Pt at.% single-crystals and directionally solidified structures of the Cr-13Pt at.% eutectic were grown. These single-crystal and directionally solidified alloy precursors were used to control and/or modify the precipitated Cr(Pt) + Cr₃Pt structure. Alloys of the specified compositions were fabricated by arc-melting the pure metal components in an argon atmosphere. The alloys were prepared as either fingers, approximately 1 cm in diameter and 7.62–10.16 cm long, for arc-zone melting investigations, or as chill-cast rods for directional solidification. Arc-zone melting⁵¹ was conducted using growth rates of 6 mm/hr and 12.5 mm/hr at 14 V and 240 amps. Directional solidification was conducted in a Bridgman crystal growth configuration using alumina crucibles. Operating temperatures were approximately 150°C above the melting point and solidification rates of 10 mm/hr were used for single-crystal growths and 100 mm/hr for directional growths. Following fabrication, individual single-crystals were oriented to the principal crystallographic axis using back reflection Laue method and were harvested from the as-grown ingots by an electrical discharge machine (EDM). Compositional profiles of the single-crystal portions of the samples were measured both longitudinally along the ingot as well as radially across the diameter for each alloy. Significant chemical segregation in both directions was apparent. This was likely due to liquid convective flows driven by the large density differences between Cr and Pt. Figure 6 a is a longitudinal compositional profile of the Cr(Pt) + Cr₃Pt (111) orientated single-crystal alloy. Similar compositional profiles were made of each of the single-crystal samples. As shown in Figure 6 b, these compositional changes were taken into account when extracting crystals from the ingots.

5.2 Heat Treatments

All alloys were heat-treated in vacuum (4×10^{-8} atm) at varying temperatures for different lengths of time before exposure to nitrogen in order to form the desired Cr-Pt or two-phase Cr(Pt) + Cr₃Pt structures. During heat-treatments, the alloys were enclosed in an alumina (Al₂O₃) crucible and covered with tantalum foil inside the furnace. The first

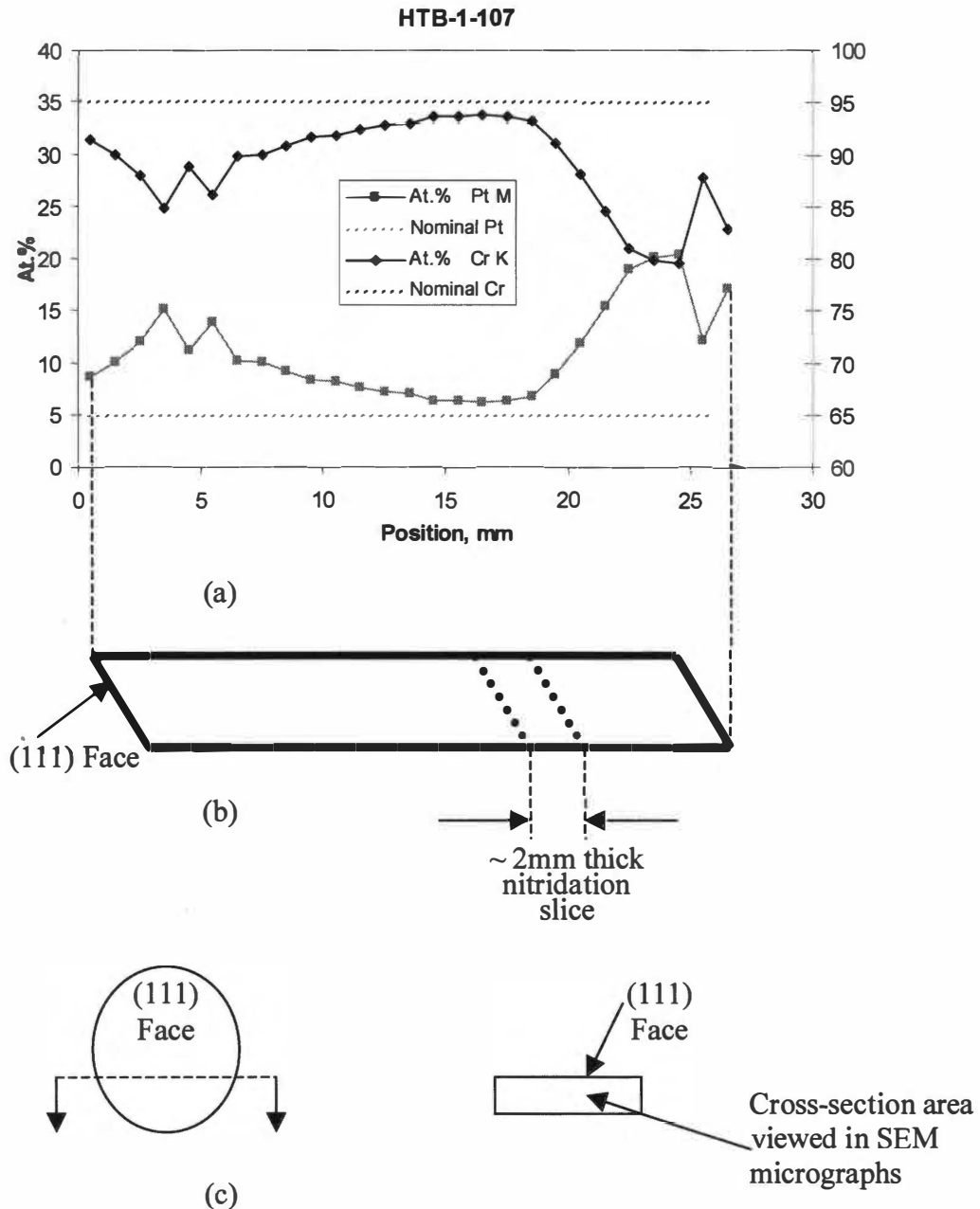


Figure 6. Compositional profile and schematic drawings of Cr(Pt) + Cr₃Pt (111) oriented single-crystal alloy. Figure 6 a shows a longitudinal segregation pattern of the (111) oriented Cr-5Pt at.% single-crystal ingot. Figure 6 b is a schematic of the single-crystal section showing the area with a nearly Cr-5Pt at.% composition from which a nitridation slice was cut. Figure 6 c is a schematic of the nitridation slice showing the cross-sectional area viewed in SEM micrographs, which is perpendicular to the (111) oriented face.

three ingots (Cr-2.25Pt at.%, Cr-5Pt at.%, and Cr-17Pt at.%) were heat-treated in vacuum using a two-step process to precipitate a metallic dispersion. The furnace temperature was raised to 1350°C and held for 8 hours, then the temperature was lowered to 1050°C and held for 12 hours. The initial heat treatment at 1350°C brought the Cr-5Pt at.% alloy into a dilute Cr(Pt) solid solution. When the furnace temperature was lowered and held at 1050°C for 8 hours, a Cr₃Pt second phase was precipitated into the dilute Cr(Pt) matrix (see the Cr-Pt phase diagram in Figure 5). Similar heat-treatment methods were used on the alloys with different compositions in order to obtain the desired precursor metallic phase(s).

5.3 Sample Preparation

The heat-treated alloys were cut with an electrical discharge machine (EDM) to make several disk-shaped coupon slices with a surface area of approximately 2.5 cm². As explained earlier, the single-crystal samples contained significant chemical segregation along the longitudinal direction. A composition of Cr-5Pt at.% was desired for this study for comparative purposes. So, according to compositional profiles, ~2mm thick slices were cut from the single-crystal sections where the composition was closest to the desired Cr-5Pt at.%. The longitudinal composition profile with graphical representations of the (111) oriented Cr(Pt) + Cr₃Pt single-crystal alloy are given in Figures 6 a, b, and c. Similar procedures were followed to extract coupons from the other single-crystal alloys. Careful measures were taken to cut slices from the single-crystals along the principal crystallographic axis.

Prior to nitriding, each coupon was polished with silicon carbide paper to a 600-grit finish and the dimensions were measured. The coupons were then rinsed in acetone using an ultrasonic cleaner, dried with lint-free tissue, and weighed. Coupons were then re-weighed after exposure to nitrogen.

5.4 Nitrogen Furnace Treatments

Each of the coupons was exposed to nitrogen at varying temperatures and lengths of time. The coupons were hung in a molybdenum wire cage in a vertical tube furnace at a pressure of 10⁻⁷atm. High-purity nitrogen at 1 atm flowed through the furnace for 2 hours at room temperature. The flow was then shut off and the furnace temperature was raised to the desired temperature, which was held for the specified length of time. Each nitrided coupon was weighed following treatment. Information about the appearance of each coupon (scale appearance, color, spallation, etc.) was also recorded.

5.5 Characterization

Nitrided samples were characterized by x-ray diffraction (XRD) using Cu K-alpha radiation (1.5406 Å) and scanning electron microscopy (SEM). It should be noted that in analyzing the raw XRD data, no Joint Committee on Powder Diffraction Standards (JCPDS) file exists to identify Cr₃PtN. Fe₃PtN has a structure very similar to Cr₃PtN, and it was therefore used to identify this phase in the alloys. Some select samples were also characterized by electron probe microanalysis (EPMA) using pure element standards for Cr, Pt, and a BN standard for nitrogen.

6. Experimental Results

6.1 **Microstructure and Composition of the Original Heat-Treated Alloys**

The three alloys used in this study, with compositions of Cr-2.25Pt at.%, Cr-5Pt at.%, and Cr-17Pt at.%, were subjected to a two-step vacuum heat-treatment prior to nitridation. Referring to the Cr-Pt phase diagram in Figure 5, the furnace temperature was raised to 1350°C and held at this temperature for 8 hours, which brought the Cr-5Pt at.% alloy into a dilute Cr(Pt) solid solution. The temperature was then lowered and held at 1050°C for 8 hours to precipitate out a Cr₃Pt second phase into the dilute Cr(Pt) matrix. Figures 7, 8, and 9 show cross-section SEM micrographs of each heat-treated alloy microstructure. X-ray diffraction was also performed on each sample to determine the phases present after heat-treatment (Figures 10, 11, and 12). The microstructure seen in the cross-section SEM micrograph of the Cr-2.25Pt at.% alloy (Figure 7) appears to be single-phase solid-solution Cr(Pt), which is consistent with XRD data (Figure 10) that indicates the presence of only Cr. The microstructure of the heat-treated Cr-5Pt at.% alloy, as seen in Figure 8, indicates the presence of two phases. X-ray diffraction data (given in Figure 11) for the heat-treated Cr-5Pt at.% alloy shows that the alloy contains both Cr and Cr₃Pt phases. As desired, Cr-17Pt at.% alloy is made up of mainly a Cr₃Pt matrix with some evidence of a second phase identified as Cr by XRD (as can be seen in the SEM cross-section micrograph in Figure 9 and XRD data in Figure 12).

6.2 **Microstructure and Composition of the Nitrided Alloys**

Following vacuum heat-treatment, each alloy was exposed to nitrogen at varying temperatures and times. The microstructures of the products that formed during these nitridation treatments will be described in the following sections.

6.2.1 Nitridation of Alloys Containing Cr(Pt) + Cr₃Pt Phases in Combination and Individually

Cr-5Pt at.%

Two-phase Cr(Pt) + Cr₃Pt (Cr-5Pt at.%) alloys were held in nitrogen at 1000°C and 800°C for 1 hour, 24 hours, and 100 hours. SEM cross-section micrographs of the alloys nitrided at 1000°C are given in Figures 13 a, b, c, and d. In all cases (including those nitrided at 800°C), nitridation yielded an external surface layer followed by two sub-scale nitridation zones. X-ray diffraction was performed to identify the phases present (XRD data for the Cr(Pt) + Cr₃Pt (Cr-5Pt at.%) alloy held in nitrogen at 1000°C for 1 hour is given in Figure 14). Electron probe microanalysis was also performed on the Cr(Pt) + Cr₃Pt (Cr-5Pt at.%) alloy held in nitrogen at 1000°C for 24 hours to determine the composition of each phase. Referring to Figure 13 c, the microstructure consisted of a 3 µm thick external surface layer of Cr₂N (74Cr-26N at.%) followed by the first sub-scale nitridation zone, which was approximately 75 µm thick and contained light dispersions of composition 65Cr-13Pt-22N at.%, corresponding to nitrided Cr₃Pt, in a nitrided Cr(Pt) matrix (dark gray) of composition 69Cr-1Pt-30N at.%. The second sub-scale nitridation

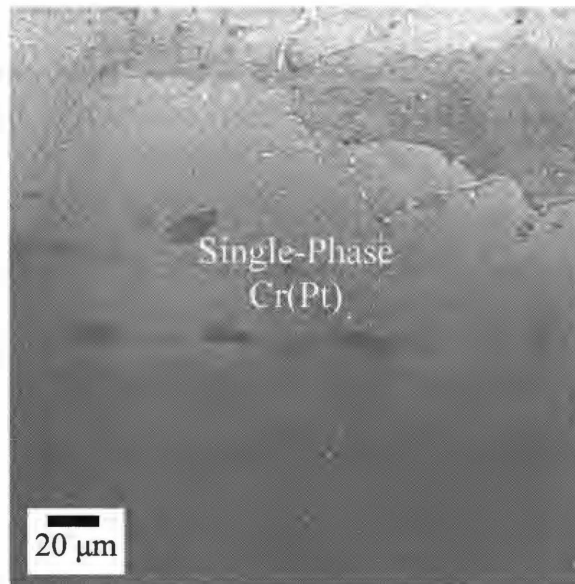


Figure 7. SEM cross-section micrograph of Cr-2.25Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours.

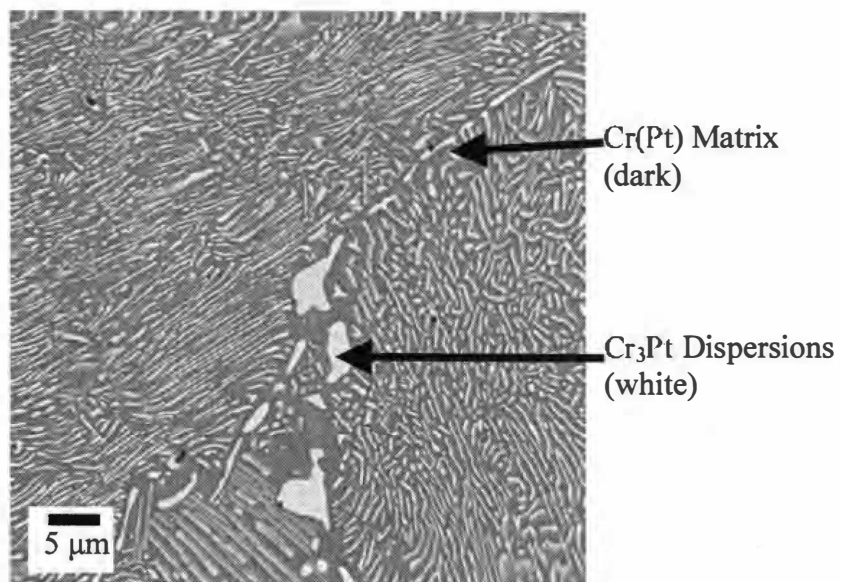


Figure 8. SEM cross-section micrograph of Cr-5Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours.

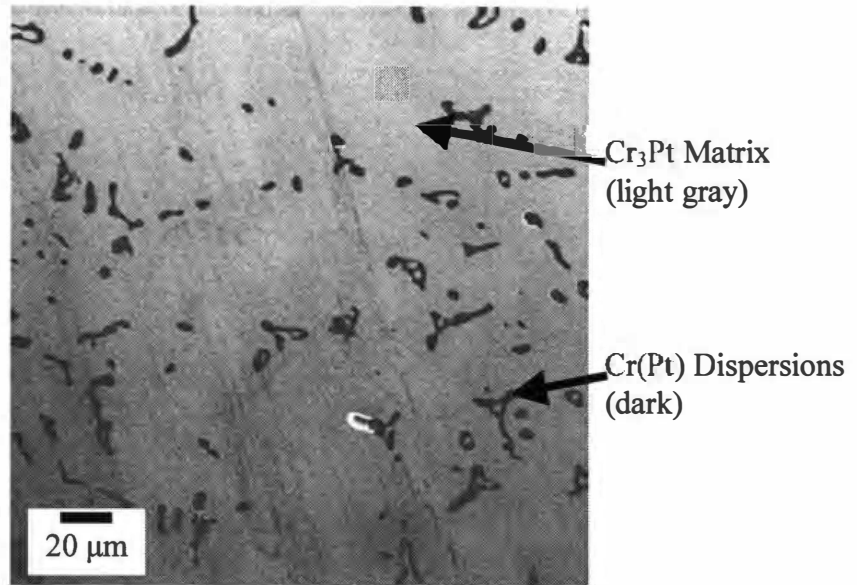


Figure 9. SEM cross-section micrograph of Cr-17Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours.

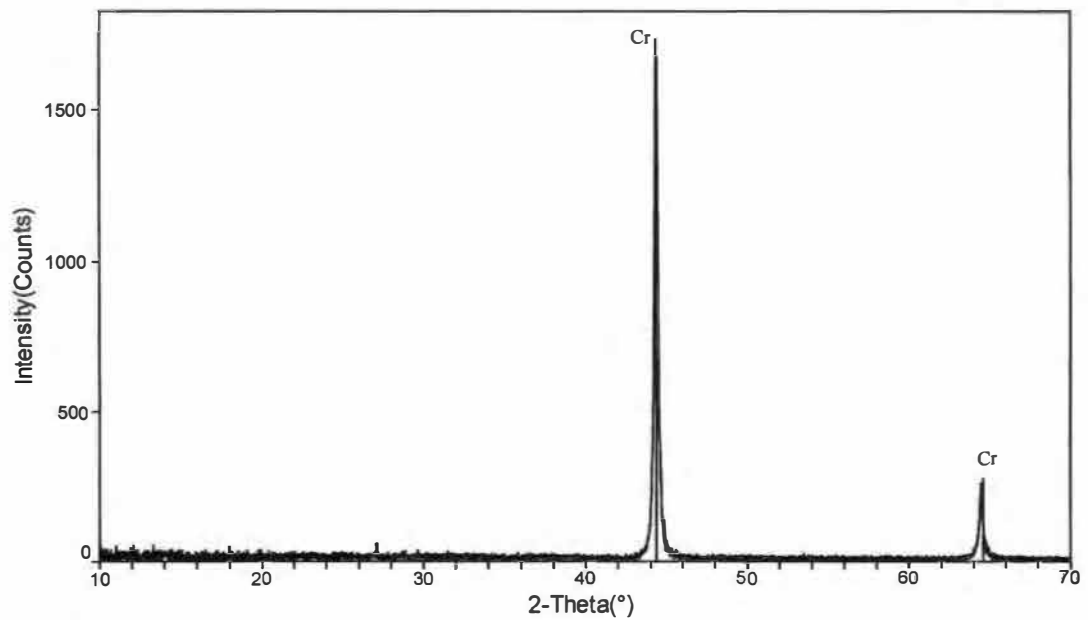


Figure 10. XRD data for Cr-2.25Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours with peak positions indicating the phases present: Cr.

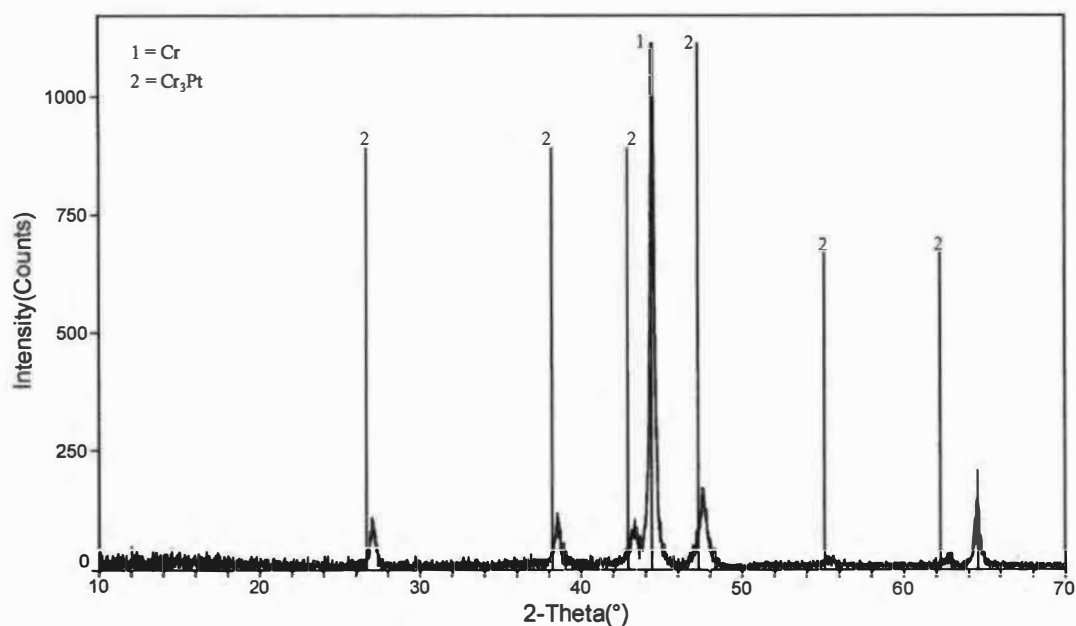


Figure 11. XRD data for Cr-5Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours with peak positions indicating the phase present: Cr and Cr₃Pt.

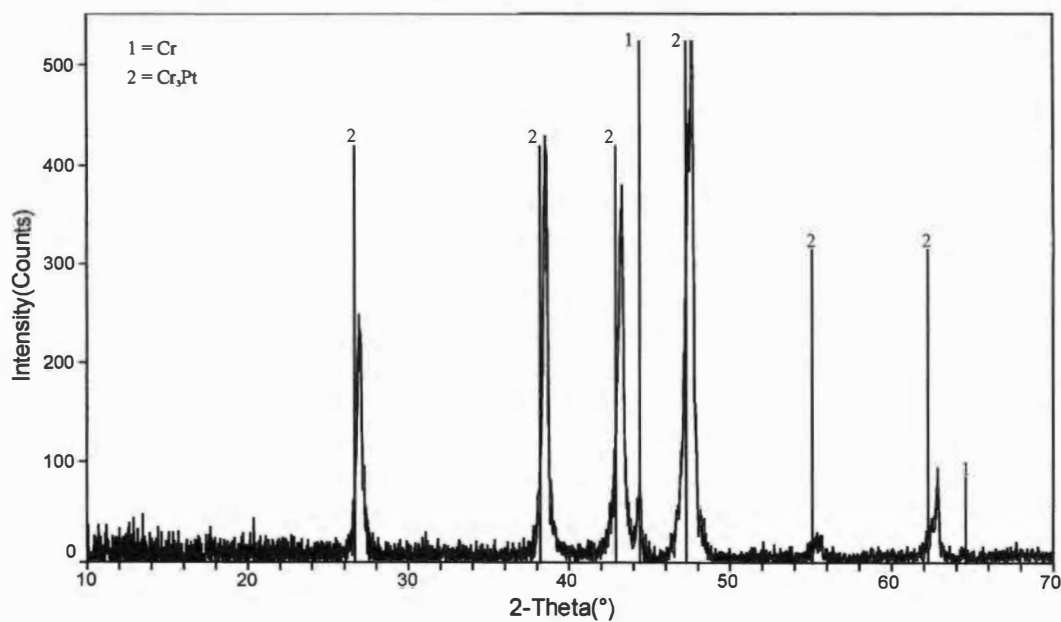


Figure 12. XRD data for Cr-17Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours with peak positions indicating the phases present: Cr₃Pt and Cr.

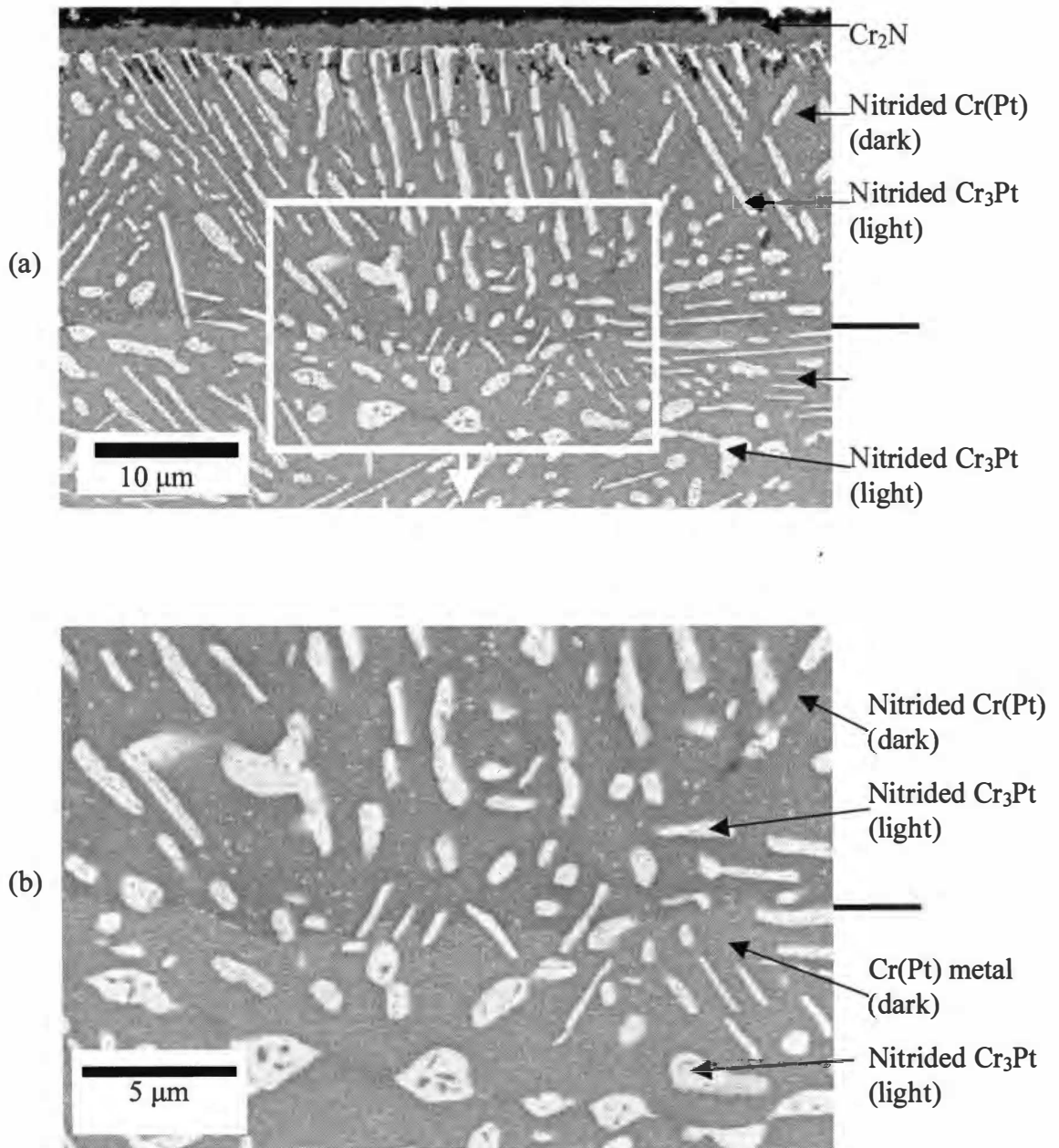


Figure 13. SEM cross-section micrographs of Cr-5Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours, then held in high-purity nitrogen at 1000°C for (a) 1 hour, (b) high-magnification view of the boxed region in 1 hour micrograph, (c) 24 hours, and (d) 100 hours.

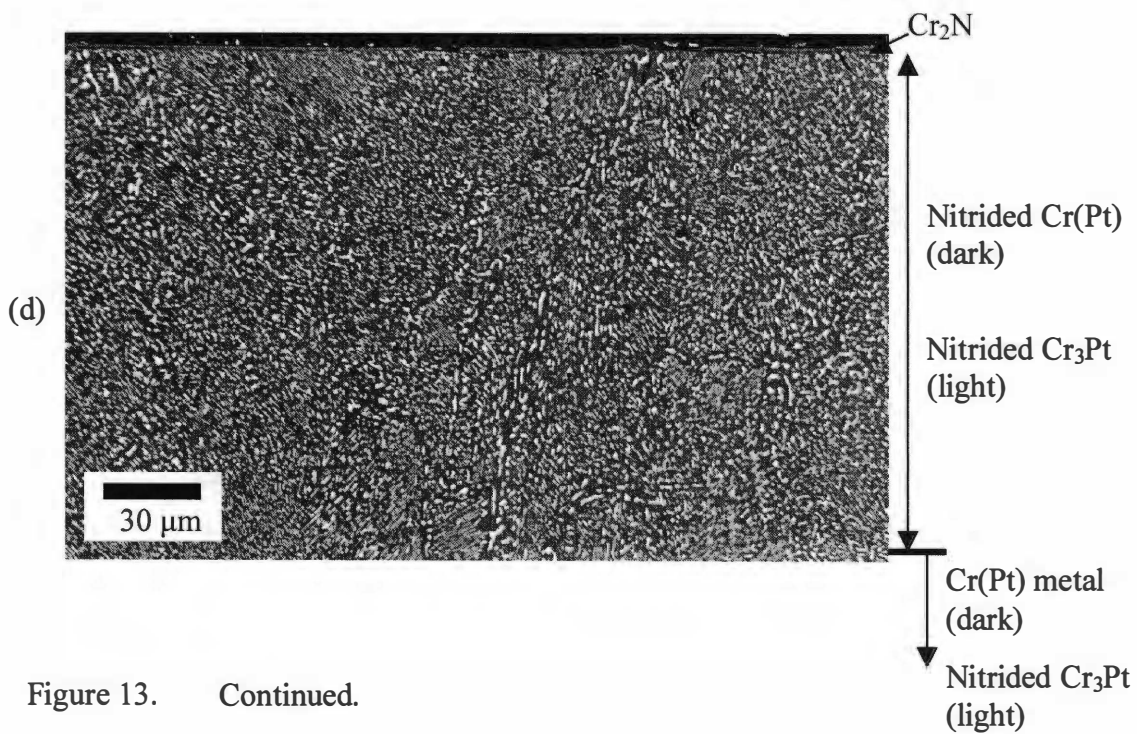
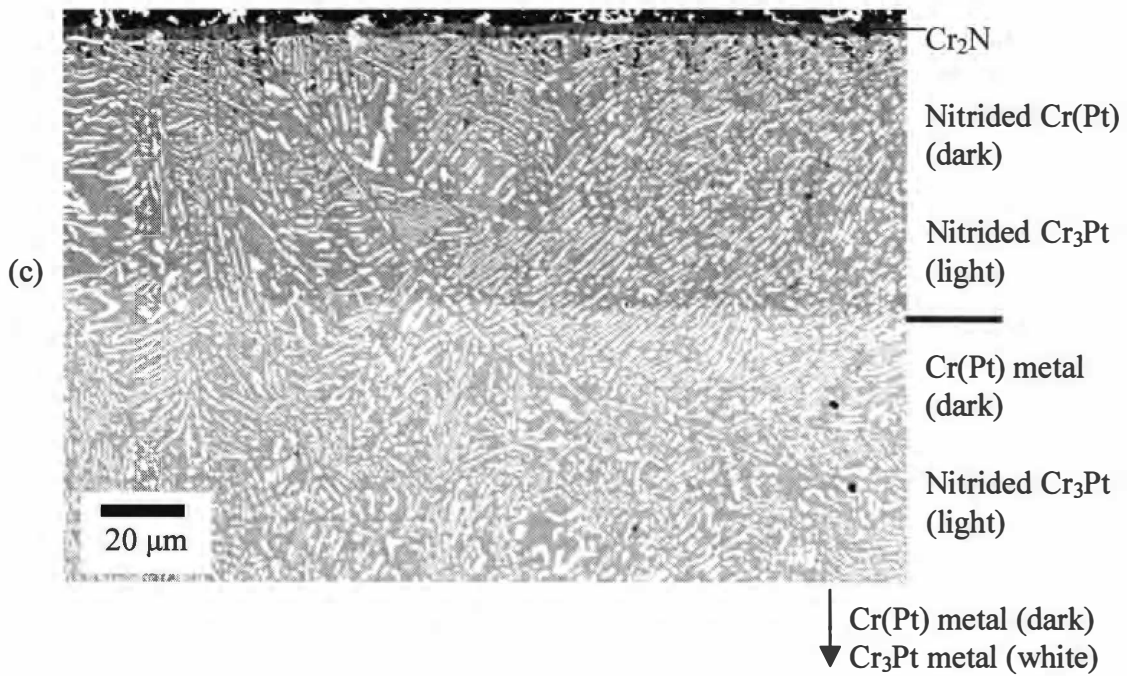


Figure 13. Continued.

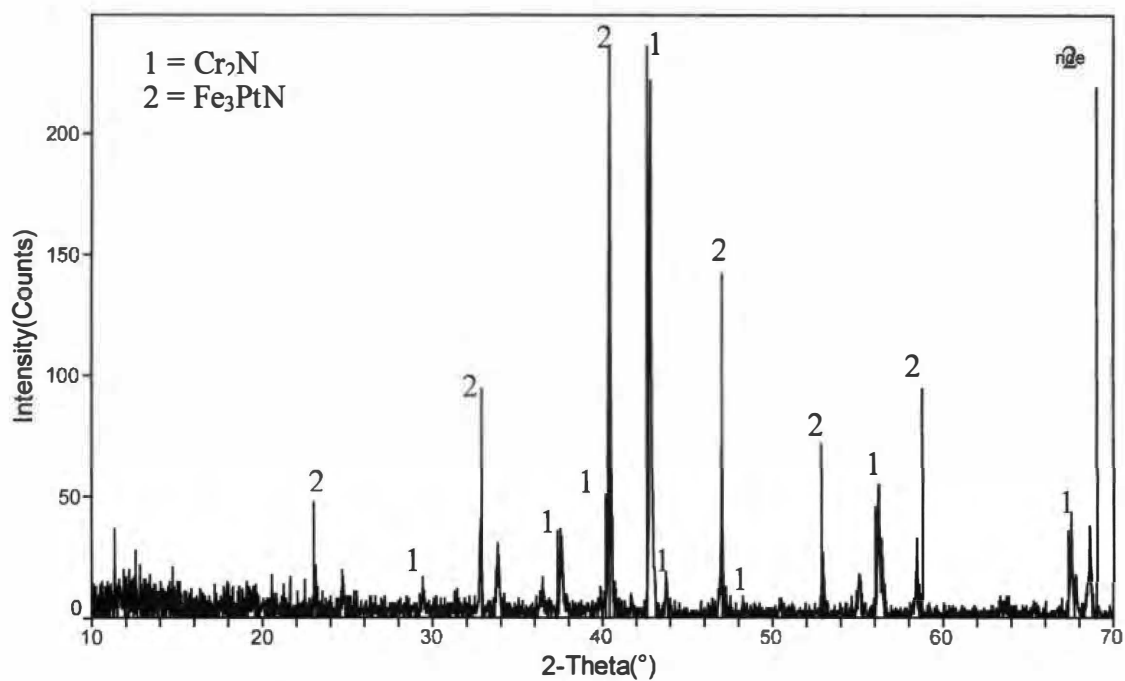


Figure 14. XRD data for Cr-5Pt at.% nitrided at 1000°C for 1 hour with peak positions indicating the phases present: Cr_2N and Cr_3PtN . (Note that no JCPDS file exists to identify Cr_3PtN . Fe_3PtN has a structure very similar to Cr_3PtN and was used to identify this phase.)

zone (near the non-nitrided alloy) was approximately 100 μm thick and contained light dispersions of nitrided Cr_3Pt with a composition of 65Cr-16Pt-15N at.% in a matrix of 99Cr-1Pt at.%, metallic Cr(Pt). (Note that the compositions of the Cr_3Pt and nitrided Cr_3Pt regions should be considered semiquantitative due to the likelihood of beam overlap with the surrounding Cr-rich regions as a result of the fine, generally micron range size alloy structure.) Nitridation of the original Cr-5Pt at.% alloy, consisting of Cr_3Pt dispersions in a Cr(Pt) matrix, yielded Cr_3PtN in a nitrided Cr(Pt) matrix near the surface, and Cr_3PtN in a metallic Cr(Pt) matrix near the alloy. The microstructure of the sub-scale nitridation zones replicated the initial alloy structure. In some nitrided Cr_3Pt regions, darker second-phase particles were evident, particularly in the 1 hour sample.

This nitridation behavior was consistent in all cases examined for Cr-5Pt at.% alloys nitrided at varying temperatures and times. The depth of nitrogen penetration into the alloy increased with increasing exposure temperature and time. It was also evident in all cases that the Cr_3Pt -phase particles nitrided to a greater depth in the alloys than the Cr-matrix.

To gain insight into the reaction mechanisms, the nitridation behavior of alloys representing the compositions of the Cr(Pt) matrix phase (Cr-2.25Pt at.%) and the Cr_3Pt precipitate phase (Cr-17Pt at.%) of the two-phase Cr-5Pt at.% alloy were also studied. Each of these alloy compositions was selected to extend slightly into the two-phase field in order to fix the Cr and Pt activities. The nearly single-phase alloys were arc-cast and vacuum heat-treated following the same methods as those for the two-phase Cr-5Pt at.% alloys.

Cr-2.25Pt at. %

Cross-section SEM micrographs of the Cr(Pt) (Cr-2.25Pt at.%) alloys that were held in nitrogen at 1000°C for 1 hour, 24 hours, and 100 hours are given in Figures 15 a, b, c, and d. Referring to Figure 15 a, the microstructure consisted of an outer surface scale of Cr_2N followed by a sub-scale nitridation zone. Alloys were also nitrided at 800°C, and in all cases studied for this alloy, nitridation reactions yielded microstructures indicating similar nitridation behavior. Also in all cases, the sub-scale nitridation zone contained second-phase dispersions that were not necessarily present in the initial alloy microstructure. In addition to the Cr_2N phase, x-ray diffraction also indicated the presence of a Cr_3PtN phase (XRD data for the Cr-2.25Pt at.% alloy held in nitrogen at 1000°C for 100 hours is given in Figure 16.). Again, as in the case of the Cr-5Pt at.% alloy, the depth of nitrogen penetration into the alloy increased with increasing temperature and time of nitrogen exposure.

Cr-17Pt at. %

The Cr_3Pt (Cr-17Pt at.%) alloy exhibited nitridation behavior different from the alloys with compositions of Cr-2.25Pt at.% and Cr-5Pt at.%. Cross-section SEM micrographs of the Cr_3Pt (Cr-17Pt at.%) alloys held in nitrogen at 1000°C for 1, hour, 24 hours, and 100 hours are given in Figure 17 a, b, and c. EPMA analysis on the Cr-17Pt at.% alloy

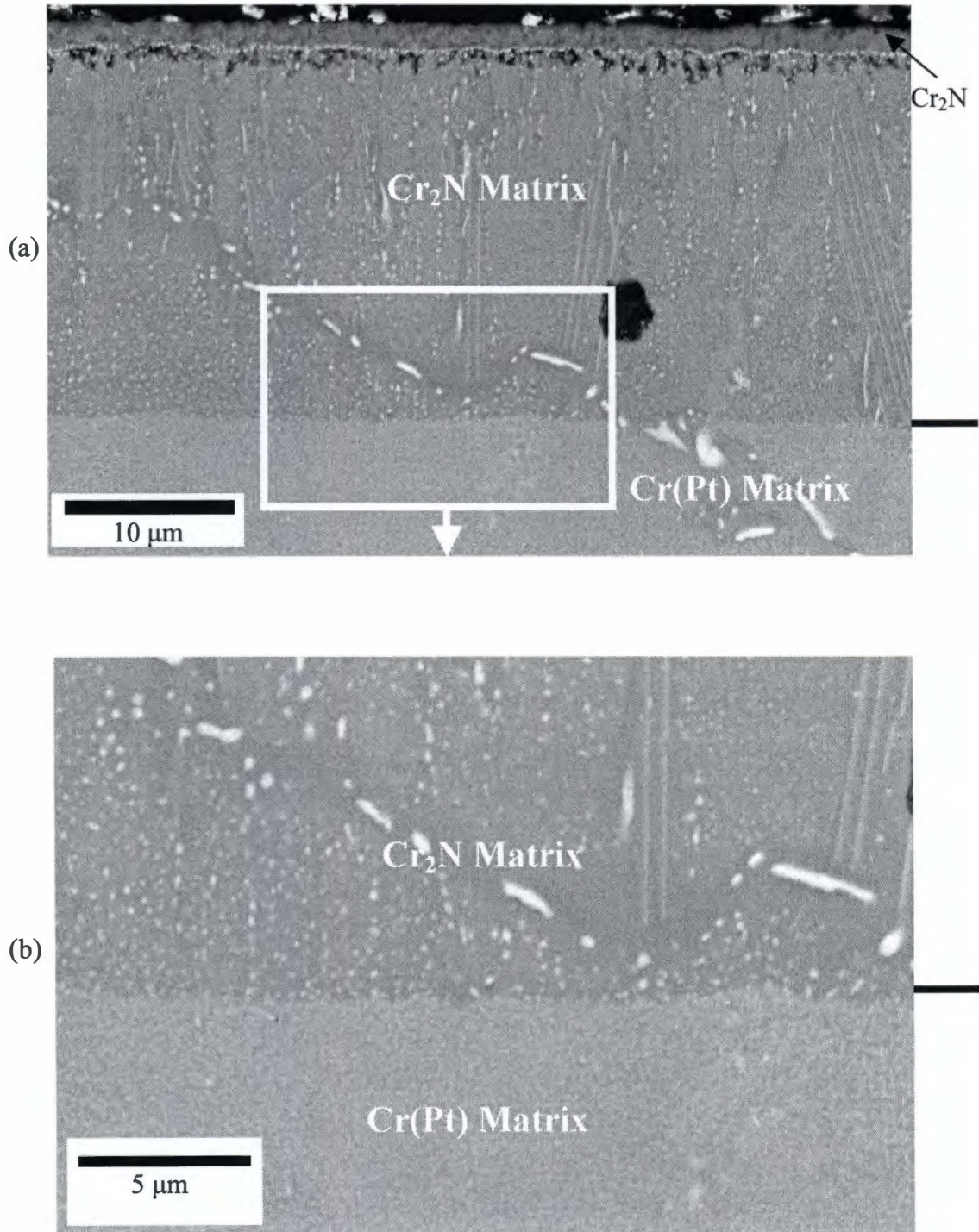


Figure 15. SEM cross-section micrographs of Cr-2.25Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours, the held in high-purity nitrogen at 1000°C for (a) 1 hour, (b) high-magnification view of the boxed region in 1 hour micrograph, (c) 24 hours, and (d) 100 hours.

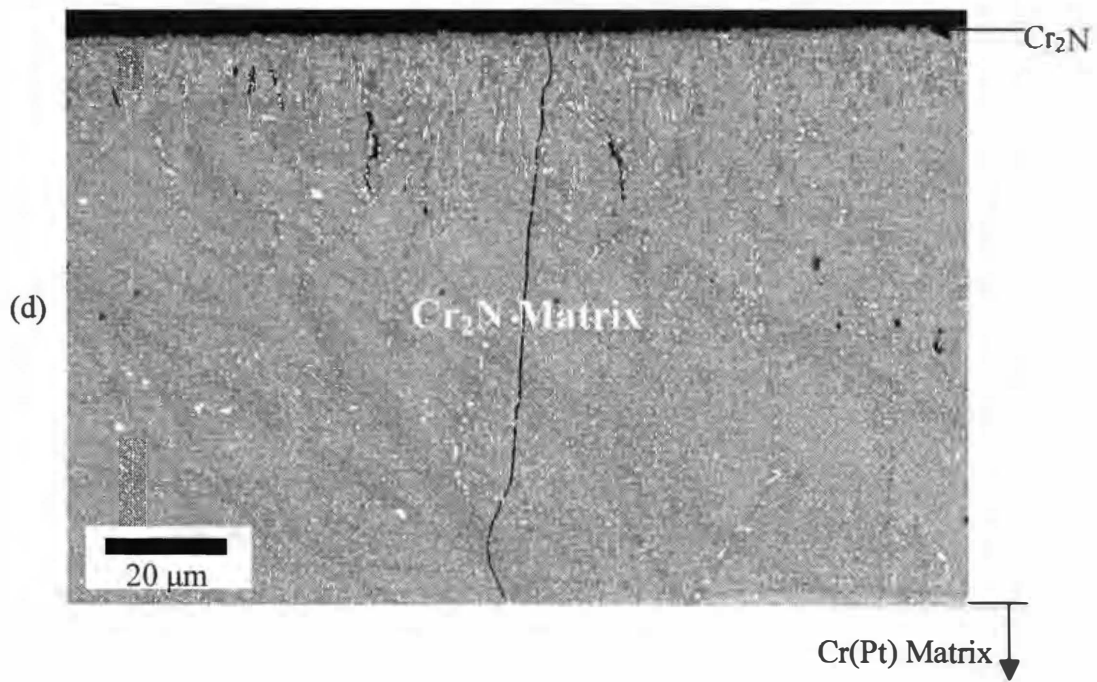
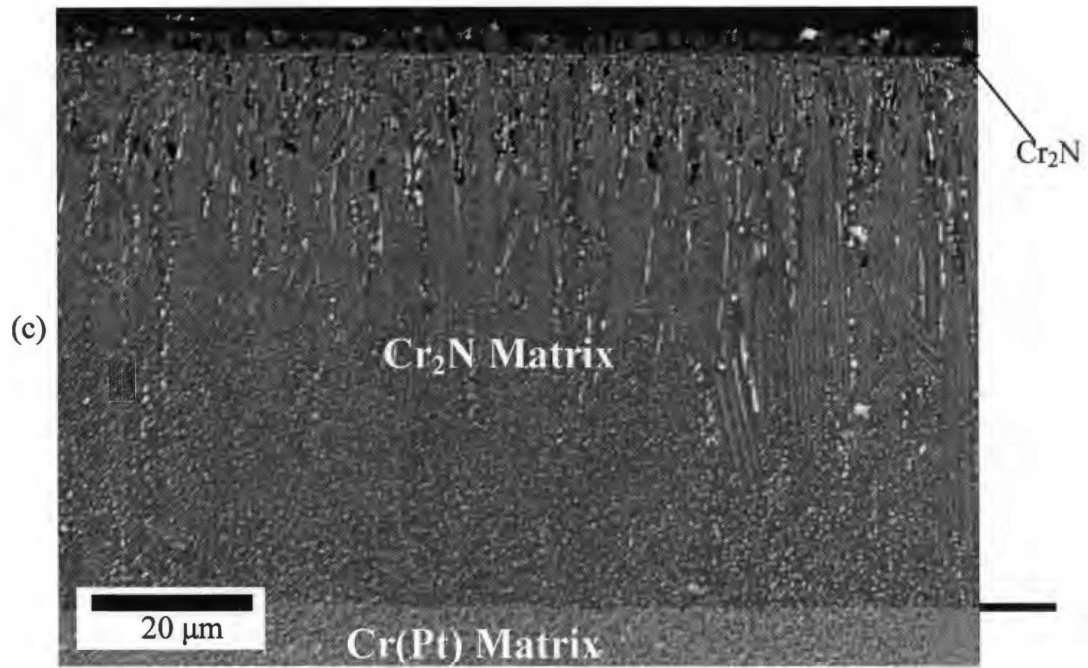


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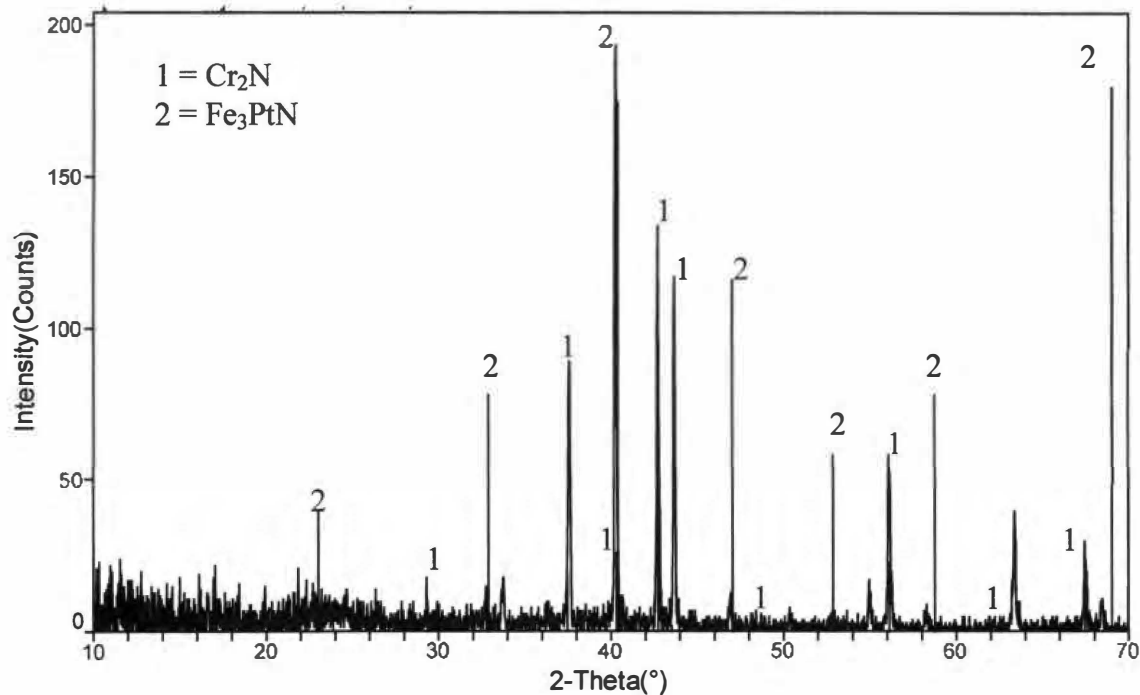


Figure 16. XRD data for Cr-2.25Pt at.% nitrided at 1000°C for 100 hours with peak positions indicating the phases present: Cr₂N and Cr₃PtN. (Note that no JCPDS file exists to identify Cr₃PtN. Fe₃PtN has a structure very similar to Cr₃PtN and was used to identify this phase.)

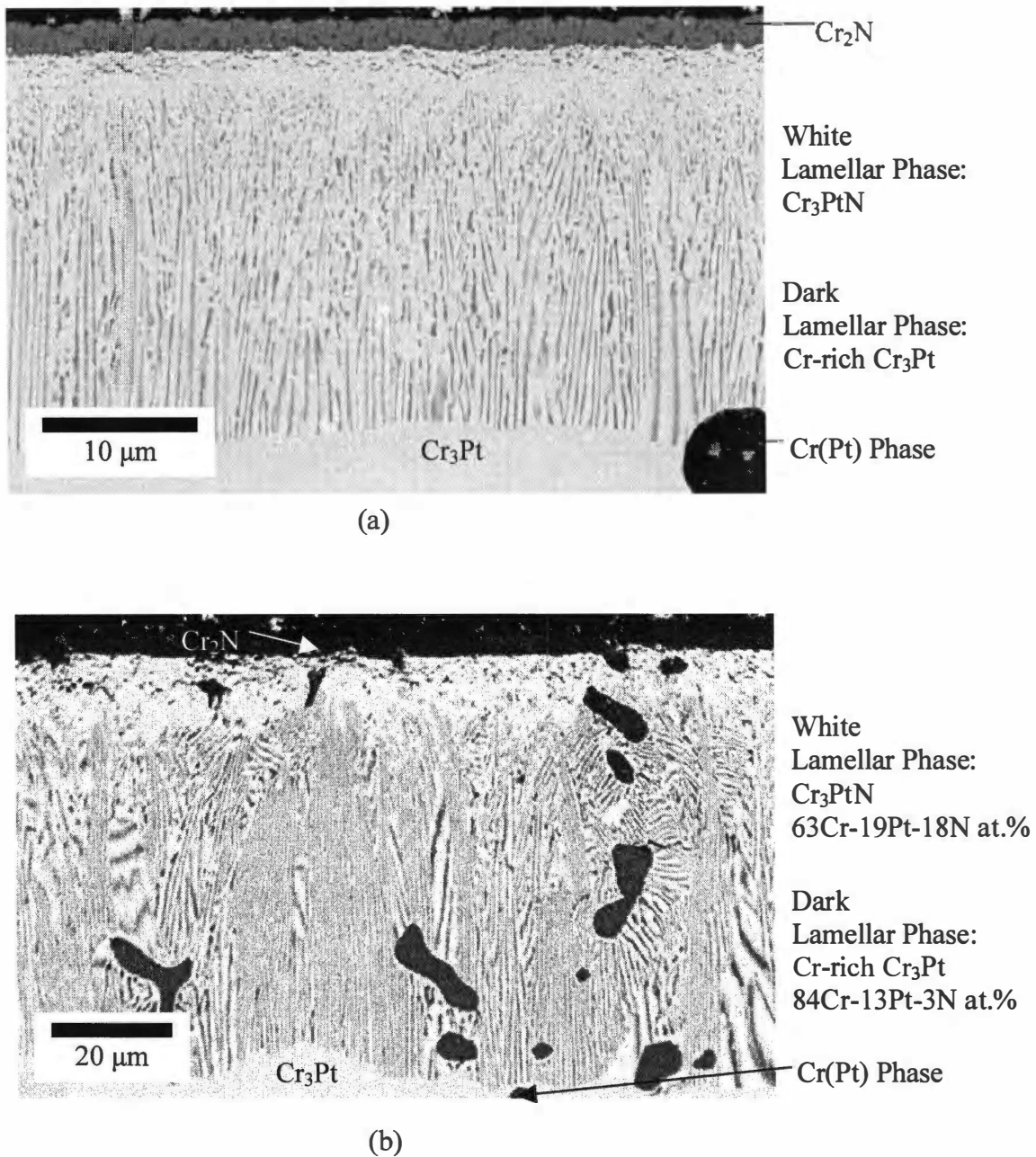


Figure 17. SEM cross-section micrographs of Cr-17Pt at.% vacuum heat-treated at 1350°C for 8 hours, 1050°C for 12 hours, then held in high-purity nitrogen at 1000°C for (a) 1 hour, (b) 24 hours, and (c) 100 hours.

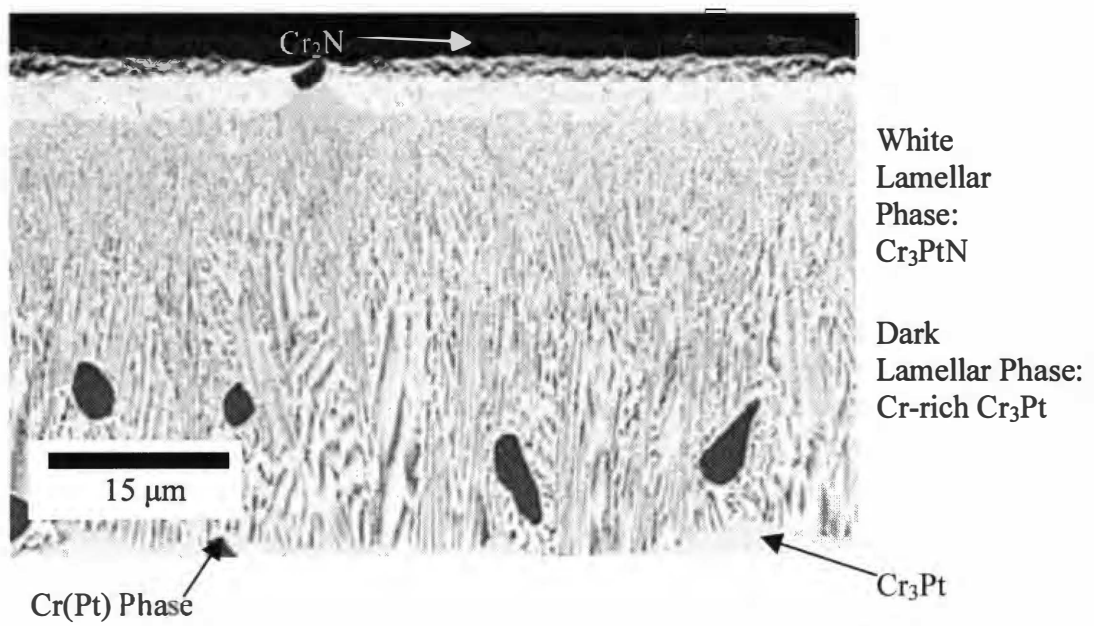


Figure 17. Continued.

nitrided at 1000°C for 24 hours showed that the microstructure contained an external layer of Cr₂N, followed by a layer of Cr₃PtN with a composition 63Cr-19Pt-18N at.%. The region below had a complex lamellar structure consisting of at least two-phases. Referring to Figure 17 b, the white lamellar phase had a composition 63Cr-19Pt-18N at.%, which was consistent with the Cr₃PtN phase, and the dark lamellar phase had a composition of 83Cr-13Pt-3N at.%, consistent with a Cr-rich Cr₃Pt phase possibly with some nitrogen in solution. The scale of the microstructure in these regions was so fine that the EPMA analysis should be considered semiquantitative due to the possibility of beam overlap with adjacent phase(s). The nitridation behavior of the alloys of this same composition studied at 1000°C and 800°C for varying exposure times resulted in microstructures indicating similar nitridation behavior.

Kinetics

The kinetics curves for the two-phase Cr(Pt) + Cr₃Pt (Cr-5Pt at.%) alloy and the nearly single-phase Cr(Pt) (Cr-2.25Pt at.%) and Cr₃Pt (Cr-17Pt at.%) alloys held in nitrogen at 1000°C and 800°C are presented in Figures 18 and 19. Also included on this plot are normalized weight gain values for the directionally solidified (DS) Cr-13Pt at.% eutectic, and the Cr(Pt) + Cr₃Pt (100) and (111) oriented single-crystal (SC) alloys, which will be discussed later.

Internal nitridation kinetics were also determined in terms of depth of nitridation in the Cr matrix phase. The Cr(Pt) + Cr₃Pt (Cr-5Pt at.%), Cr-2.25Pt at.%, the directionally solidified Cr-13Pt at.% eutectic (DS), and the Cr(Pt) + Cr₃Pt (100) and (111) oriented single-crystal (SC) alloys all contained a primarily Cr matrix. Depth of nitridation in these alloys was measured as the distance from the alloy surface beneath the external scale to the transition area from the nitrided matrix-phase region to the non-nitrided matrix phase region. As mentioned earlier, in the two-phase Cr(Pt) + Cr₃Pt alloys, the Cr₃Pt precipitate phase nitrided to a greater depth than the Cr matrix phase. The depth of nitridation in the Cr₃Pt precipitate phase was most easily determined in the nitrided Cr(Pt) + Cr₃Pt (100) oriented single-crystal and directionally solidified Cr-13Pt at.% eutectic alloys (which will be discussed later). These values were also included in the plot. The Cr-17Pt at.% alloy, which contains a mostly Cr₃Pt matrix rather than Cr, was also included for comparison. Plots of the subscale nitridation depth values, as a function of nitridation time^{1/2} are given for each of these alloys nitrided at 1000°C and 800°C in Figures 20 and 21.

6.2.2 Nitridation Behavior of Other Alloys Examined

Cr-25Pt at.%

The nitridation behavior of a Cr₃Pt alloy with a composition of Cr-25Pt at.%, and therefore a 3Cr:1Pt stoichiometry as is present in Cr₃PtN, was also examined. This alloy was arc-cast, vacuum heat treated at 950°C for 24 hours, then held in nitrogen at 950°C for 24 hours to get as close as possible to single phase Cr₃PtN. The cross-section SEM micrograph of the nitrided alloy is shown in Figure 22. The identification of the phases present after nitridation was determined via x-ray diffraction, which is given in Figure 23.

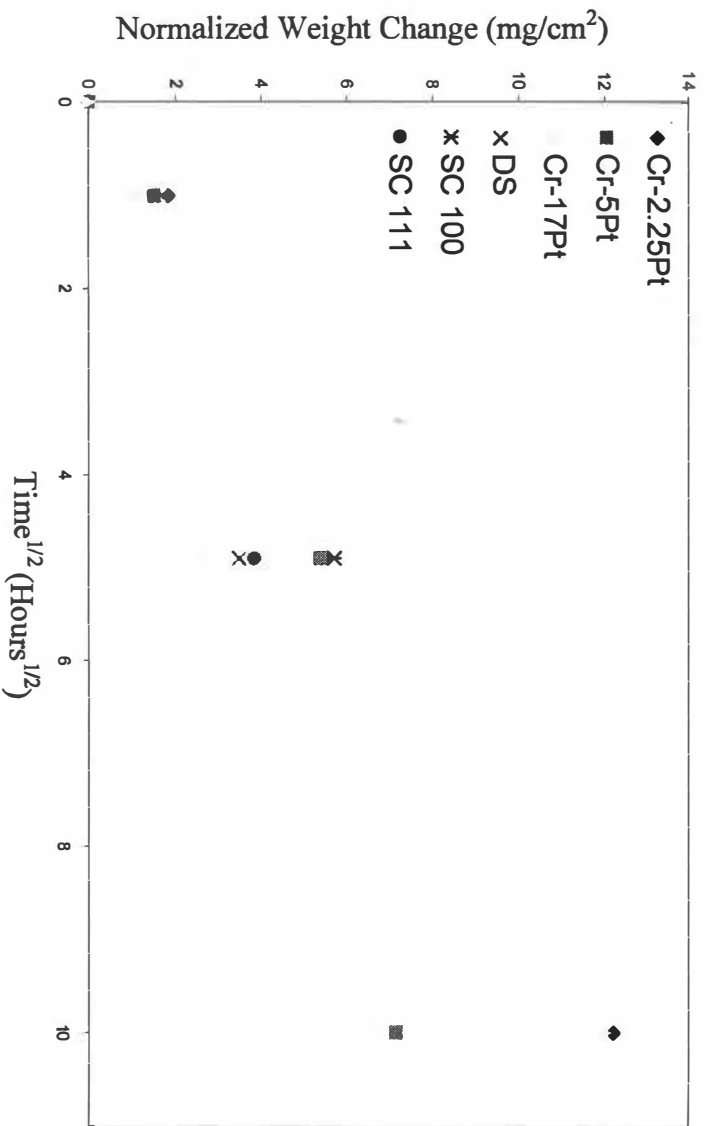


Figure 18. Nitridation kinetics plots for the alloys held in nitrogen at 1000°C.

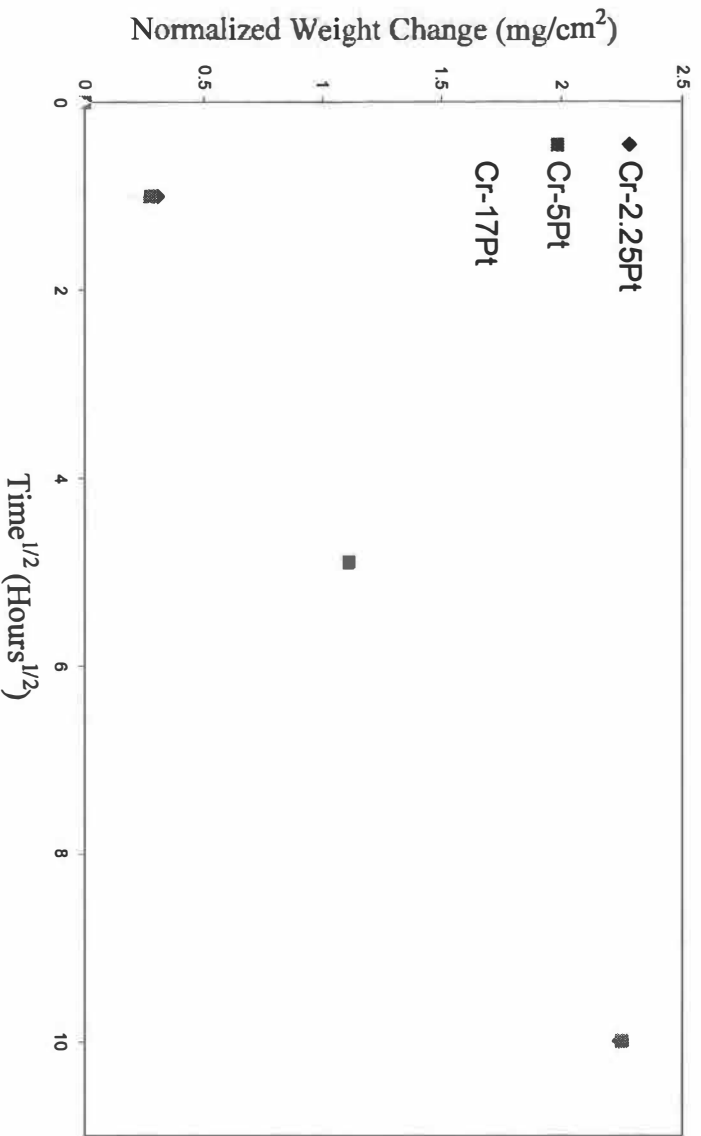


Figure 19. Nitridation kinetics plots for the alloys held in nitrogen at 800°C.

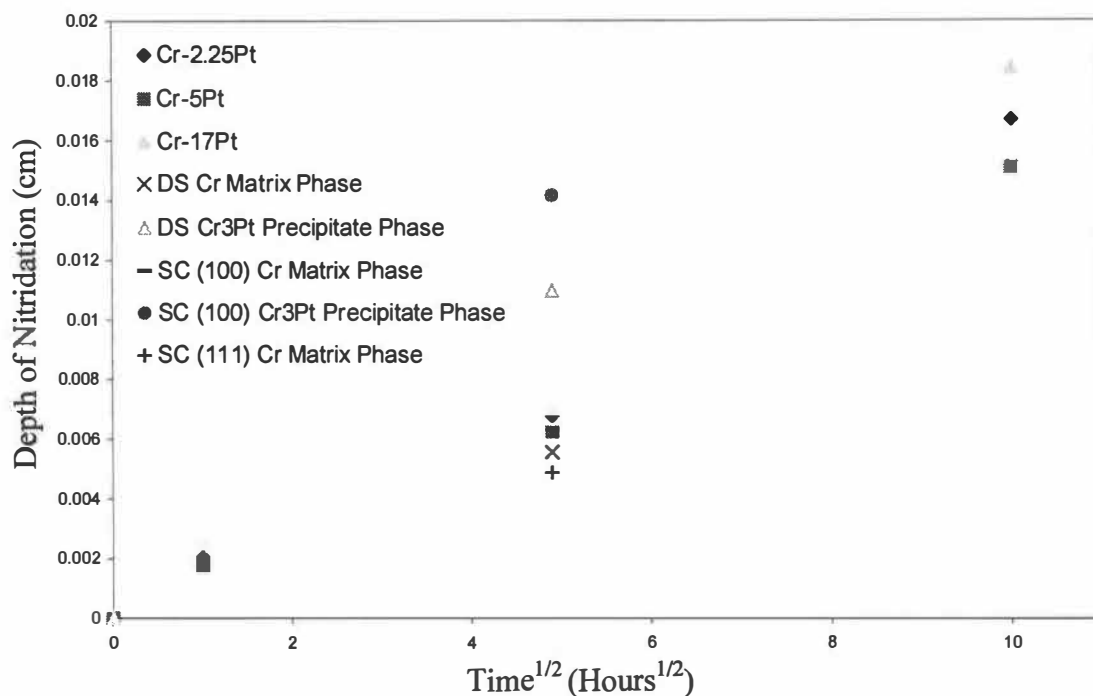


Figure 20. Plot of depth of nitridation (cm) in the Cr matrix phase over time^{1/2} for each alloy held in nitrogen at 1000°C.

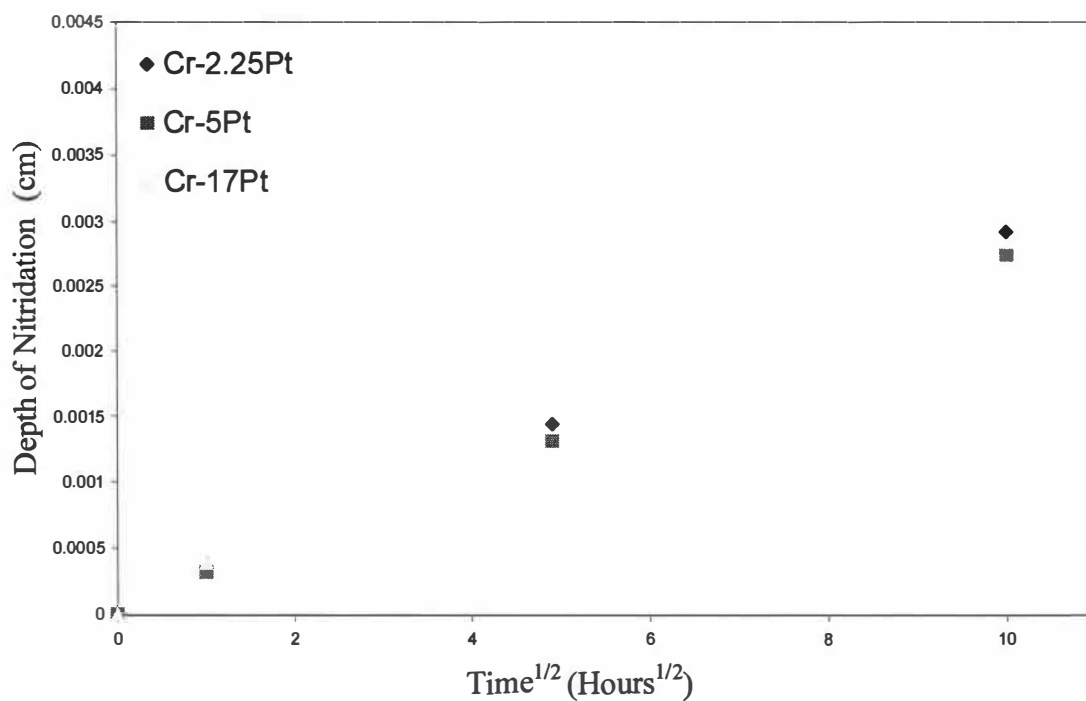


Figure 21. Plot of depth of nitridation (cm) in the Cr matrix phase over time^{1/2} for each alloy held in nitrogen at 800°C.

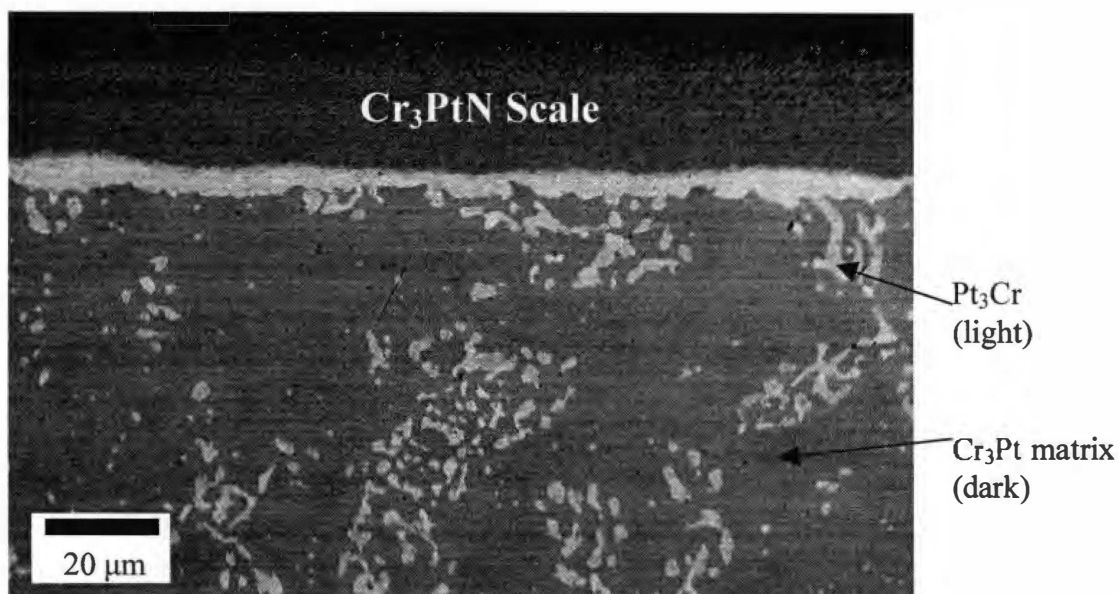


Figure 22. SEM cross-section micrograph of Cr-25Pt at.% vacuum heat-treated at 950°C for 24 hours, then held in high-purity nitrogen at 950°C for 24 hours.

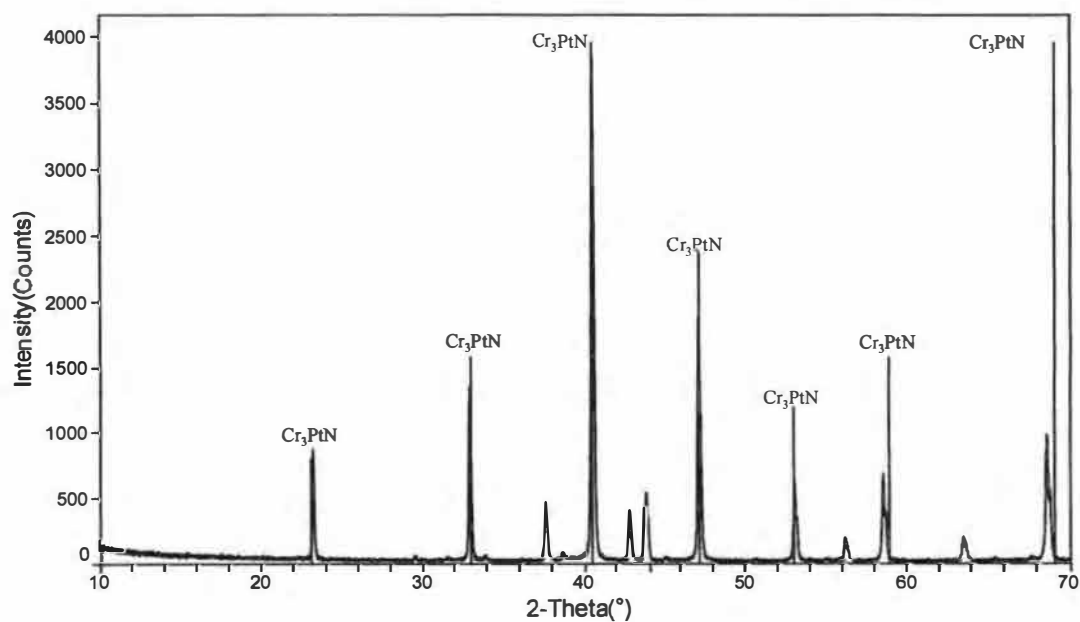


Figure 23. XRD data for Cr-25Pt at.% nitrided at 950°C for 24 hours with peak positions indicating the presence of the Cr_3PtN phase. (Note that no JCPDS file exists to identify Cr_3PtN . Fe_3PtN has a structure very similar to Cr_3PtN and was used to identify this phase.)

The microstructure consisted of Pt₃Cr (light) particles in a Cr₃Pt (dark) matrix beneath a surface scale of Cr₃PtN.

Directionally-Solidified Cr-13Pt at.% Eutectic

Alloys consisting of directionally-solidified (D.S) Cr-13Pt at.% eutectic structures and Cr(Pt) + Cr₃Pt microstructures derived from (100) and (111) orientated Cr-5Pt at.% single-crystals and were also studied to examine the effect of different Cr(Pt) + Cr₃Pt microstructures on the nitridation mechanism. The directionally-solidified Cr-13Pt at.% eutectic alloy was vacuum heat-treated at 1450°C for 8 hours, then cooled to 1050°C, and held at this temperature for 12 hours. The cross-section SEM micrograph of this directionally-solidified Cr-13Pt at.% eutectic alloy after being held in nitrogen at 1000°C for 24 hours is given in Figure 24. The microstructure of this nitrided alloy indicated similar behavior to the original Cr-5Pt at.%. Referring to Figure 24, the microstructure consisted of an external Cr-nitride scale followed by a sub-scale nitridation zone that consisted of Cr₃Pt-nitride precipitates in a Cr-nitride matrix. The second sub-scale nitridation zone (near the un-nitrided alloy) consisted of Cr₃Pt-nitride precipitates in a metallic Cr matrix. While the microstructure in both sub-scale nitridation zones mimicked that of the original underlying alloy microstructure, all of the Cr₃Pt-nitride phase dispersions, contained darker, second-phase particles.

Cr-5Pt at.% Single-Crystal at (100) Orientation

Figure 25 is a cross-section SEM micrograph of the nitrided Cr(Pt) + Cr₃Pt microstructure derived from a (100) orientated Cr-5Pt at.% single-crystal. As explained earlier, the chemical composition of the Cr(Pt) + Cr₃Pt single-crystal alloys varied along the length of the ingots. A ~2 mm thick slice was cut from the area of this ingot closest to a having composition of Cr-5Pt at.% according to the measured compositional profile. The alloy was subjected to the same vacuum heat-treatment as described in the previous paragraph, then was nitrided at 1000°C for 24 hours. Referring to the cross-section SEM micrograph in Figure 25, the microstructure contained an external Cr-nitride scale followed by two sub-scale nitridation zones. Immediately below the external scale, in the first sub-scale nitridation zone, were nitrided Cr₃Pt precipitates in a Cr-nitride matrix. The second sub-scale nitridation zone (near the un-nitrided alloy) contained Cr₃Pt-nitride precipitates in a metallic Cr matrix. Again, the nitrided regions replicated the underlying alloy structure and exhibited similar nitridation behavior to the original Cr-5Pt at.% and directionally solidified Cr-13Pt at.% eutectic alloys. Also, as was the case of directionally solidified Cr-13Pt at.% eutectic alloy, all of the Cr₃Pt-nitride phase dispersions contained darker, second-phase particles.

Cr-5Pt at.% Single-Crystal at (111) Orientation

The nitridation behavior of Cr(Pt) + Cr₃Pt alloy derived from a (111) orientated Cr-5Pt at.% single-crystal was again similar to the original Cr-5Pt at.% alloy. Figures 26 a and b are cross-section SEM micrographs of this alloy that was subjected to the same vacuum heat-treatment and nitridation processes as previously described. Referring to Figure 26 a, the cross-section SEM micrograph showed a multi-scale structure consisting of two

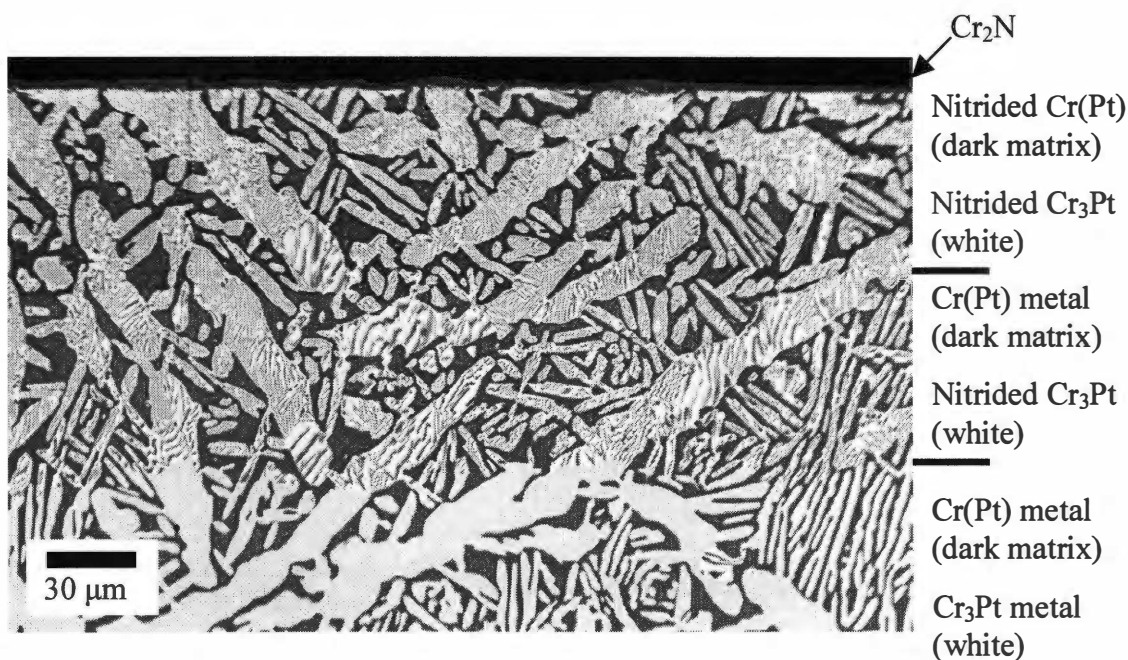


Figure 24. SEM cross-section micrograph of directionally-solidified Cr-13Pt at.% eutectic (as received) held in high-purity nitrogen at 1000°C for 24 hours. Note that all nitrided Cr₃Pt dispersions contain a darker second phase.

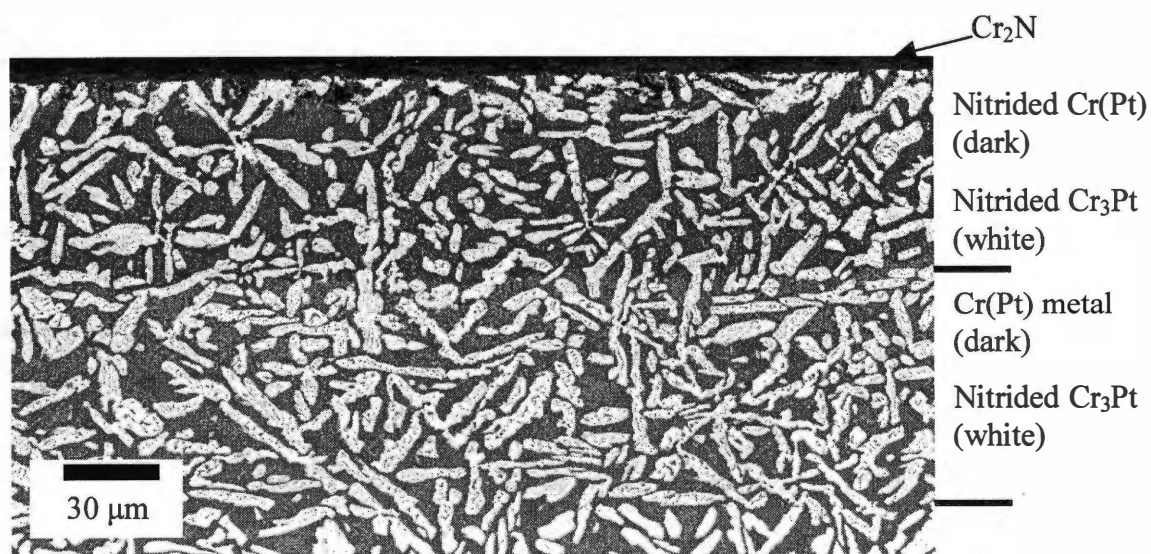


Figure 25. Cross-section SEM micrograph of Cr-5Pt at.% single-crystal (100) orientation vacuum heat-treated at 1450°C for 8 hours, 1050°C for 12 hours, then held in high-purity nitrogen at 1000°C for 24 hours. Note that all nitrided Cr₃Pt dispersions contain a darker second phase.

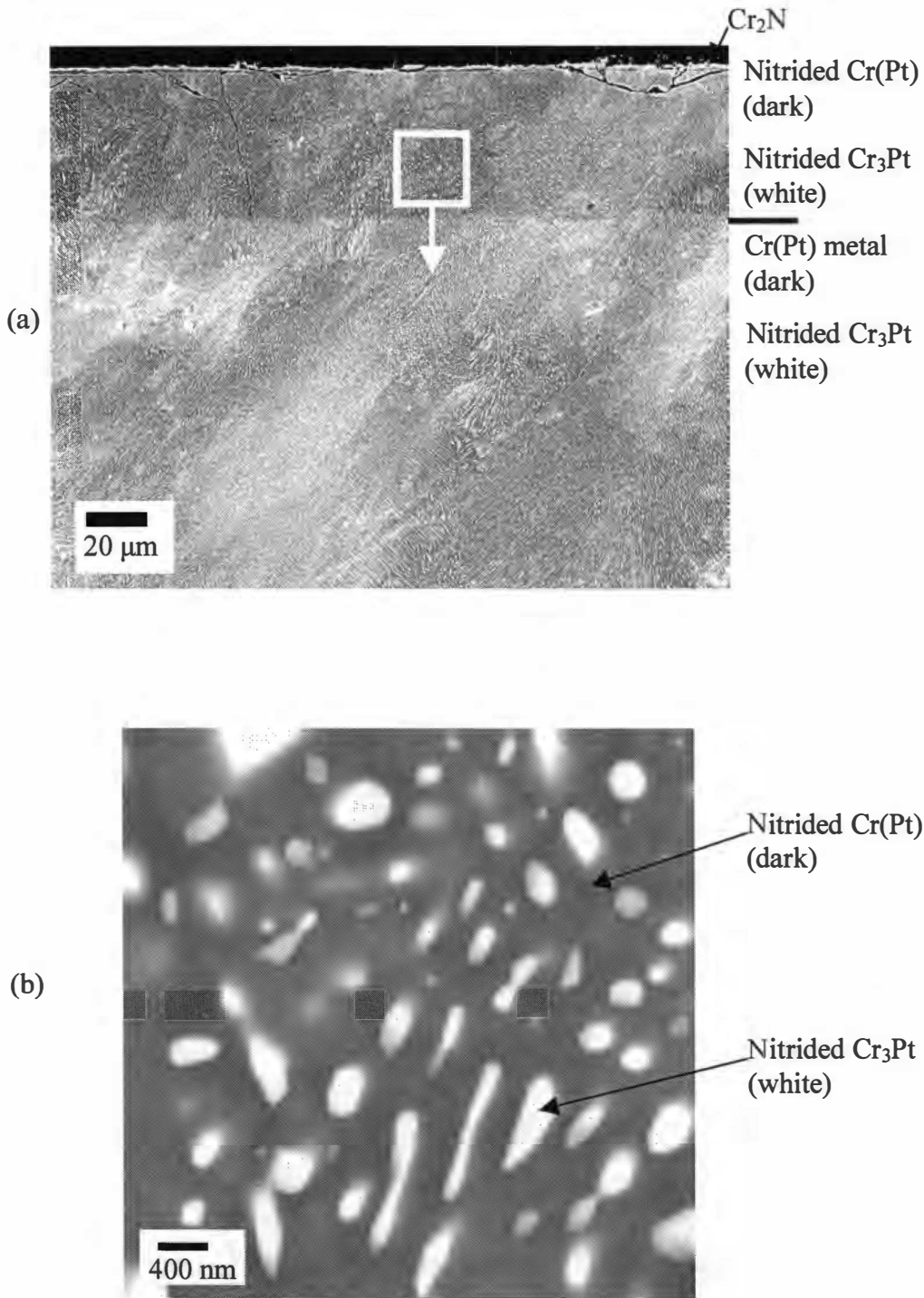


Figure 26. Cross-section SEM micrographs of Cr-5Pt at.% single-crystal (111) orientation vacuum heat-treated at 1450°C for 8 hours, 1050°C for 12 hours, then held in high-purity nitrogen at 1000°C for 24 hours. (a) is a low magnification overview, and (b) is a high-magnification view of the boxed region.

sub-scale nitridation zones. Immediately below the $\sim 2\text{ }\mu\text{m}$ thick external Cr-nitride scale was the first sub-scale nitridation region ($\sim 44\text{ }\mu\text{m}$ thick) that contained nitrided Cr_3Pt precipitates in a Cr-nitride matrix. The region below (near the un-nitrided alloy) consisted of Cr_3Pt -nitride precipitates in a metallic Cr matrix. Some Cr_3Pt and Cr_3PtN particles appeared long and thin, while others were short and circular. Many particles appeared to be on a nano-scale (Figure 26 b). The darker second-phase regions within the Cr_3Pt -nitride dispersion cores seen in alloys containing larger Cr_3Pt phase dispersions were evident in this alloy.

7. Discussion

The nitrided microstructure of the two-phase Cr-5Pt at.% alloy contains an external layer of Cr-nitride followed by two sub-scale nitridation zones, which replicated the original underlying alloy microstructure in size, shape, number, and spatial distribution. The same type of behavior was observed in each of the Cr-5Pt at.% alloys studied at varying nitridation time-temperature exposure conditions, and the Cr-nitride external layer was present in all cases. These results suggest an initial period of cooperative nitridation to form the single-phase external Cr-nitride surface layer followed by a transition to sub-scale in-place internal nitridation that replicated the underlying alloy structure. To further discern the mechanisms involved in this reaction, the nitridation behavior of single-phase Cr(Pt) and Cr₃Pt alloys of varying Cr:Pt stoichiometry and two-phase Cr(Pt) + Cr₃Pt alloys with varying volume fractions of the Cr₃Pt phase were also studied.

The nitridation of the Cr(Pt) (Cr-2.25Pt at.%) alloy resulted in an external Cr-nitride surface layer followed by a sub-scale nitridation region, and the reaction was dominated by the high permeability of nitrogen into Cr(Pt). The microstructure also contained a fine second-phase dispersion of particles in both the sub-scale nitridation zone and the un-nitrided alloy. It is speculated that this second phase dispersion could be Cr₃PtN in the sub-scale nitridation zone as was indicated by x-ray diffraction and Cr₃Pt in the metal. However, the sub-scale nitridation region may not be a result of in-place internal nitridation because the alloy was likely single-phase at the nitridation temperature. While it is unclear exactly what type of reaction mechanism resulted in the formation of this second phase dispersion, several possibilities are suggested. Referring to the Cr-Pt phase diagram in Figure 5, Pt solubility decreases with decreasing temperature. So it is possible that this fine second phase could have formed during cooling and after the primary nitridation reaction took place. It is also possible that the second phase dispersion could have formed from either internal nitridation or a solid solution precipitation reaction.

The complex microstructure of the nitrided single-phase Cr₃Pt with a composition of Cr-17Pt at.%, suggests that a discontinuous-type phase transformation occurred rather than in-place internal nitridation. As described earlier, the microstructure of this nitrided alloy consisted of an external Cr₂N layer followed by a layer of Cr₃PtN with a composition of 63Cr-19Pt-18N at.%. A complex, lamellar-type region consisting of at least two-phases followed this layer. The composition of the light-colored lamellar phase was identified as 63Cr-19Pt-18N at.%, which is consistent with Cr₃PtN. The darker lamellar phase had a composition of 83Cr-13Pt-3N at.%, which is consistent with a Cr-rich Cr₃Pt phase. The Cr₃PtN structure requires a 3Cr:1Pt ratio. This alloy, however, contains an almost 5Cr:1Pt ratio, which is more Cr-rich. It is therefore speculated that during nitridation, this reaction is driven by the need reject the excess Cr from the Cr₃Pt phase to stabilize the Cr₃PtN structure.

To test this theory, the nitridation behavior of a Cr-lean Cr₃Pt alloy (with a composition of Cr-25Pt at.%) was studied. Referring to Figure 22, upon nitridation the alloy formed a

single-phase Cr_3PtN scale rather than the complex lamellar structure formed in the Cr_3Pt , Cr-17Pt at.% alloy, which is consistent with the mechanism proposed above.

The discontinuous-type phase transformation that occurred during the nitridation of the Cr-17Pt at.% alloy, where the Cr_3Pt phase was the initial alloy matrix phase, was not observed in any of the nitrided Cr-2.25Pt at.% or Cr-5Pt at.% alloys, where the Cr(Pt) phase was the initial alloy matrix phase and the Cr_3Pt phase was present as a dispersed phase. This is likely due to the fact that when the Cr(Pt) phase is present as the matrix phase, it may accommodate the Cr that is rejected when the Cr_3Pt phase dispersions are nitrided to form Cr_3PtN .

However, in some of the $\text{Cr(Pt)} + \text{Cr}_3\text{Pt}$ alloys, the nitrided Cr_3Pt phase dispersions contained second-phase regions at the particle core. These second-phase regions at the core of the nitrided Cr_3Pt dispersions seemed to be more prevalent in larger Cr_3Pt particles, as evidenced in the nitrided Cr-5Pt at.% single-crystal (100) orientation and directionally solidified Cr-13Pt at.% alloys that contained large Cr_3Pt phase particles (refer to Figures 24, and 25), which suggests a particle-size effect. Evidence of second-phase regions at the core of the nitrided Cr_3Pt dispersions was also found in some Cr-5Pt at.% alloys (refer to Figures 13 a and b). While it was not apparent, it is possible that these second-phase regions could have been present in the alloys containing finer particles. However, due to their small particle size, it was very difficult to determine for certain. It is speculated that these second-phase regions could correspond to the $\text{Cr-rich Cr}_3\text{Pt(N)}$ lamellae observed in the Cr-17Pt at.% alloy, which can be explained as follows. Large particles create a greater distance over which the excess Cr must diffuse out of the Cr_3Pt particle and into the Cr(Pt) matrix during nitridation in order to stabilize the Cr_3PtN structure. As a result, during nitridation some of the excess Cr is unable to diffuse out, and therefore remains in the particle core forming Cr-rich second-phase regions. These second-phase regions were not observed in fine Cr_3Pt phase particles because the smaller diffusion distance allows for more complete Cr-rejection during nitridation. A schematic representation of this process is presented in Figure 27.

Kinetics data was examined in order to detect any apparent trends and to determine whether any differences existed between the nitridation of single- and two-phase alloys. Weight gain and depth of nitridation in all alloys increased with increasing time and temperature, and the nitridation rates in all alloys appeared to be comparable. Significant differences between the nitridation rates of the single-phase and two-phase alloys were not evident. The nitridation of the Cr-2.25Pt at.% alloy at 800°C and 1000°C appeared to follow the parabolic rate law. However, the small number of data points and scatter in data rendered it difficult to come to any other significant conclusions.

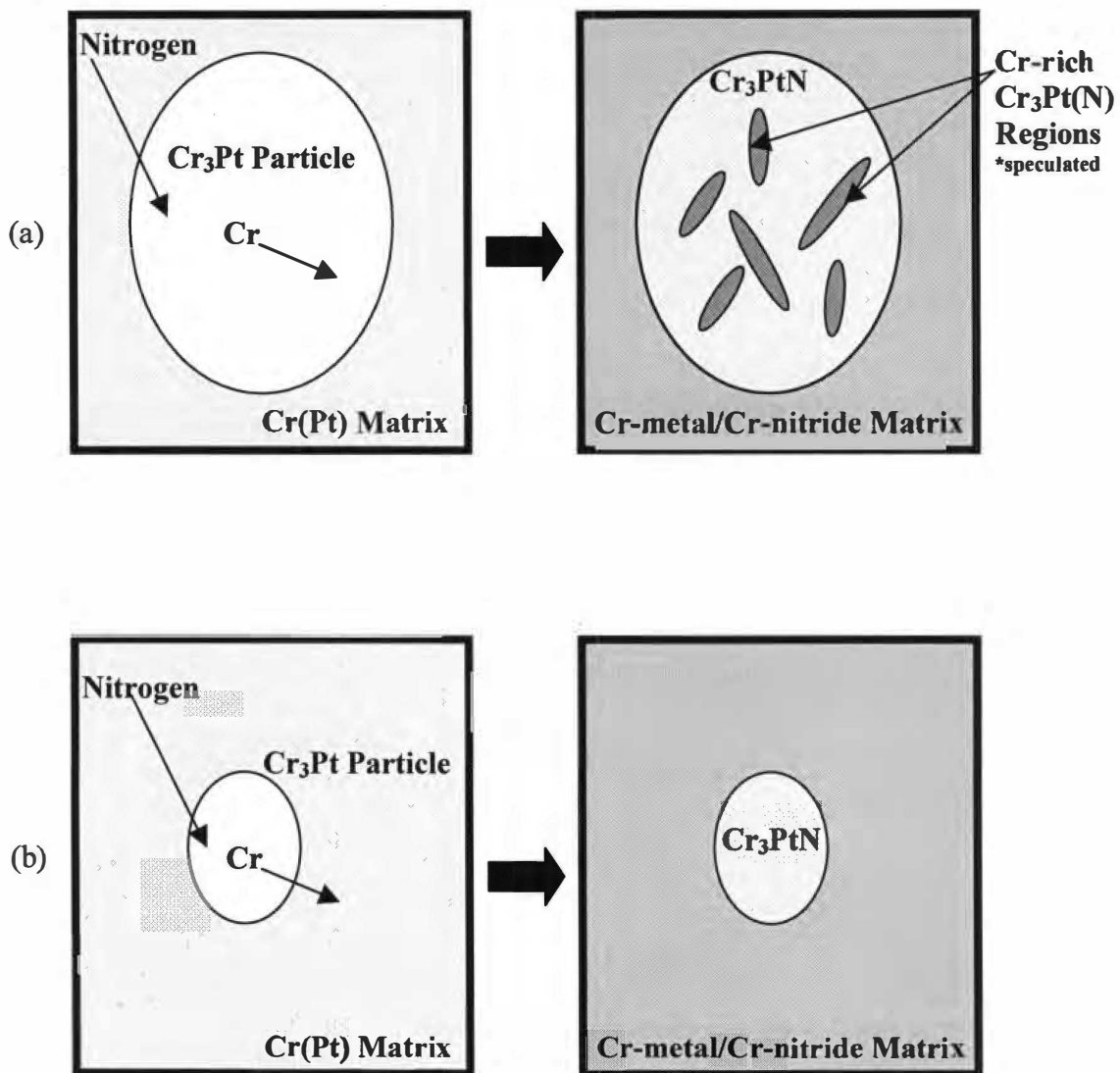


Figure 27. Schematics showing the effect of particle size on nitride products that form for (a) coarse particles and (b) fine particles.

In the nitrided Cr-5Pt at.% alloys, the Cr₃Pt particles nitrided to a greater depth in the alloys than the Cr(Pt) matrix in all cases. Although it is not clear exactly why this occurred, it is speculated that the Cr₃Pt particles may exhibit a higher nitrogen solubility than the Cr(Pt) matrix phase over the 800–1000°C temperature range of nitridation. Referring to the Cr-N phase diagram in Figure 4, the solubility of N in un-alloyed Cr is actually fairly small at the temperatures studied (1000°C and 800°C). Brady et al.⁴⁴ observed similar trends in the air oxidation of two-phase Cr(Nb) + Cr₂Nb alloys. Oxidation in air resulted in extensive sub-scale nitridation beneath a layer of Cr₂O₃ and a region of mixed Cr + Nb oxides. In this sub-scale nitridation region, the depth of nitridation was greater in the Cr₂Nb Laves phase than in the Cr solid-solution phase

All microstructural characterization, including scanning electron microscopy, x-ray diffraction, and electron probe microanalysis, of the nitrided Cr-5Pt at.% alloy structures were consistent in showing that the nitridation of the Cr₃Pt precipitate phase formed nearly single-phase Cr₃PtN perovskite. Similar behavior was observed by Kosec et al., who formed Ag₂TeO₃ from Ag₂Te particles. Interestingly, they also observed classical internal oxidation in the Ag(Te) solid solution matrix to form Ag₂TeO₃ as well. Possibly similar to what was seen by Kosec et al.,⁴⁶ some nitrided Cr(Pt) + Cr₃Pt alloys contain evidence to suggest the presence of fine second phase dispersions in the matrix that may have formed from a similar classical internal nitridation reaction.

Therefore, these results indicate that the Cr(Pt) + Cr₃Pt system does not completely follow ideal in-place internal nitridation. They do, however, support the concept that a template process can be used to form Cr₃PtN dispersions from Cr₃Pt precipitates. The microstructure in the nitrided Cr-5Pt at.% (111) oriented single-crystal contained many particles on a nano-scale (~ 200 nm). This observation provides evidence to support the possibility of using the proposed template process as a synthesis technique to form nano-scale complex ceramic dispersions.

8. Conclusions

1. Nitridation of the Cr(Pt) + Cr₃Pt (Cr-5Pt at.%) alloy was consistent with the formation of Cr₃PtN from Cr₃Pt dispersions. No evidence was found to suggest that Cr₃Pt internally nitrified to form Cr₂N + Pt.
2. The nitridation behavior of the component phases of the two-phase alloy (Cr(Pt) and Cr₃Pt) were examined separately to better understand the mechanistic details. The reaction that occurred during the nitridation of the Cr(Pt) (Cr-2.25Pt at.%) alloy was dominated by the inward penetration of nitrogen. The Cr₃Pt (Cr-17Pt at.%) alloy, however, followed a discontinuous-type phase transformation, which was speculated to be driven by the need to eliminate excess Cr to stabilize the Cr₃PtN structure (which requires 3Cr:1Pt).
3. To verify the proposed nitridation mechanism in the single-phase Cr₃Pt (Cr-17Pt at.%) alloy, the nitridation behavior of an alloy with a 3Cr:1Pt ratio (Cr-25Pt at.%) alloy was examined. Nitridation of this Cr-lean Cr₃Pt alloy nearly directly formed a Cr₃PtN scale, which suggests nitridation behavior consistent with the proposed mechanism.
4. Discontinuous-type phase transformations were not observed in the two-phase alloys where the Cr₃Pt phase was present as a dispersions in a Cr(Pt) matrix because the matrix is speculated to accommodate the rejected Cr during nitridation. There were some examples of inner cores of a Cr-Pt rich phase within the nitrified Cr₃Pt particles, which is suspected to correspond to the Cr-rich Cr₃Pt(N) lamellae observed in the Cr-17Pt at.% alloys. These second phase regions within the nitrified Cr₃Pt particles appeared to be more prevalent in large particles, and are therefore speculated to be a result of a particle-size effect.
5. While the Cr-Pt system did not appear to exhibit ideal in-place internal nitridation, results did provide evidence to support the use of a template process to produce Cr₃PtN from Cr₃Pt.

9. Future Work

Nanocomposites of complex ceramic phase islands are of interest for functional applications because of their potential to possess novel magnetic, optical, chemical, and electrical properties and behaviors. The key to using in-place internal oxidation as a synthesis route to produce nanoscale complex ceramic islands is to set the initial alloy template prior to oxidation so that it contains a precipitate compound phase dispersion on the nanoscale. This is likely possible only for thin films due to possibility of coarsening. If the precursor metallic compound phase is precipitated on the nanoscale, then the complex ceramic dispersion can potentially be formed on the nanoscale. Several methods of making nanoscale dispersions include rapid solidification, quenching, or using amorphous or metastable precursors. It would therefore be beneficial to explore several of these possibilities in the future. It would also be useful to try the proposed synthesis technique on systems of known technological interest in order to explore the potentially unique properties and behaviors they may exhibit. Finally, it is recommended that more work be done to verify the proposed particle-size effect on the nitridation of Cr_3Pt dispersions in the Cr(Pt) matrix. One proposed method of further investigating the particle-size effect would be to study the nitridation behavior of several $\text{Cr(Pt)} + \text{Cr}_3\text{Pt}$ alloys with varying microstructures.

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Vita

Sarah Kate Baham was born in Lake Charles, Louisiana on October 2, 1977. She grew up in Lake Charles where she attended grade school at Our Lady Queen of Heaven School and high school at A.M. Barbe High School. During the summer of 1994, Sarah and her family moved to Memphis, Tennessee, and she graduated from Collierville High School in 1995. After high school, Sarah stayed in Memphis and attended Christian Brothers University. While at CBU, Sarah met her future husband, Mike Wrobel, and earned a Bachelor of Science degree in Mechanical Engineering. After graduating from CBU, Sarah moved to Knoxville to pursue a Master of Science degree in Materials Science and Engineering. She and Mike were married in June of 2001.

Sarah plans to graduate from the University of Tennessee with a Master of Science degree in Materials Science and Engineering in August of 2002. She was recently hired by Citgo Petroleum Corporation where she will begin working as an engineer in the summer of 2002.