Development of a Nitrogen-Modified Stainless-Steel Hardfacing Alloy

DISSERTATION

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Abstract

A 2nd generation hardfacing alloy, Nitromaxx, has been designed through an integrated approach of chemical modification, characterization, and testing. Nitromaxx is a stainless-steel alloy modified with 0.5wt% nitrogen which has improved elevated temperature properties and wear performance. This is achieved by changing both the microstructure phase balance and inherent deformation characteristics of the metal. The alloy is fabricated by a powder metallurgy-hot isostatic pressing (PM-HIP) method, rather than traditional cladding methods. This allows for alloy property modification by equilibrium heat treatment while eliminating significant fabrication defects, so that component life is extended wear and galling performance is improved.

The design approach involved extensive characterization of severely worn and galled surfaces of the 1st generation of hard-facing alloys. Observation of samples after galling testing showed highly inhomogeneous deformation in regions of the gall scar, leading to the design hypothesis that strain-localization is a controlling mechanism in severe wear of stainless-steels. Additionally, the presence and subsequent loss was investigated and correlated microstructurally to the transition to poor galling behavior in the existing stainless steel hardfacing NOREM02. This provided new insight and identification of
key microstructural and mechanical properties that improve galling performance: 1) increased strain-hardening rate in the metal matrix at elevated temperature, 2) increased yield strength in the matrix leading to higher hardness, and 3) increased volume fraction of hard, non-deforming phases. All of these alloy design goals can be realized by the addition of nitrogen, which 1) at high concentration is shown to lower the stacking fault energy in the stainless steel matrix, 2) increases interstitial matrix strengthening, and 3) increases the volume fraction of nitride phases. These observations have been confirmed qualitatively and quantitatively based on metallographic techniques, SEM and TEM studies, and X-ray diffraction measurements. The Nitromaxx alloy is demonstrated to achieve comparable wear and galling characteristics to Stellite 6 at elevated temperatures, while eliminating cobalt.

Keywords

Hardfacing; Wear; Galling; Alloy design; Nuclear materials; Valve Seats;
Dedication

To Laura, without whom this would not have been possible.
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Chapter 1: Motivation and Approach

Hardfacing alloys are wear and galling resistant materials that are applied as thick coatings on metal parts. These coatings are often greater than 1mm thick and are used where alloy parts encounter high surface loads associated with metal-to-metal contact, such as gear teeth, screw threads, and valve seats. In the nuclear industry, valve seat hardfacing alloys are also subjected to high surface temperatures that can reach 350°C in PWR reactor operation. Component lifetimes must exceed 20 years, as dictated by power plant lifetimes and the difficulty in valve part maintenance. These rigorous material requirements have been met in the past by cobalt-based Stellite alloys, which have excellent wear and galling properties and can be welded as a cladding onto a part[1].

Stellite-clad valve seats can become a significant source of cobalt contamination in reactor coolant systems, leading to high levels of residual radiation from cobalt activation. Two surfaces in unlubricated sliding contact will result in wear debris formation even at nominal contact loads.[2] This wear debris (typically 1-100 µm sized particles for metals[3]) can then circulate in the coolant environment. The tiny size of such wear debris results in great difficulty in removing all such particulates practically. Irradiation with neutron sources, such as nuclear fuel, can then transmute the cobalt alloy to the radioactive Co-60 isotope, which has decay half-life of over 5 years. These
circulating particles can then spread residual radiation around the primary coolant system, causing residual exposures that limit worktimes and increase personnel rotation turnover.

A “cobalt-free” stainless-steel based hardfacing alloy is therefore attractive to the nuclear industry to eliminate a source of residual radiation and to ensure long-term metallurgical compatibility. NOREM02 is one such alloy that was developed by EPRI during the late 1980s[4]. The microstructure and wear and galling properties of this alloy at room temperature are similar to Stellite 6. The weld-cladding properties are also acceptable within controlled process windows. However, the wear and galling resistant properties in particular degrade significantly above 200°C. This has been attributed to the loss of a strain-induced martensite transformation above 200°C from ex-situ X-ray diffraction characterization[5]. In other can lead to an abrupt decrease in several mechanical properties, including strain-hardening rate and elongation to failure[6]. However, no mechanistic studies of the process have been done in the literature, and the mechanism by which the transformation effects wear properties remains un-elucidated.
Figure 1
Wear Loss as a function of temperature in NOREM02 and Stellite 6 under 100 MPa Load for 100 Cycles [5]

A primary problem causing this is that galling is not a clearly understood phenomenon, and materials that can resist this form of severe adhesive wear are poorly understood. The galling resistance of many Iron-based and Nickel-based alloys has been studied previously in order to find a suitable substitute for the Co-based Stellite alloys [2, 6-8]. The results of these surveys, however, found little correlation in the material properties and microstructure responsible for good galling properties. From a review of the literature, good galling properties have shown no correlation with any one, or combination of basic material properties in all alloy systems. From the investigations presented in the present work, one primary reason for this confusion may be that severe adhesive wear occurs by different mechanisms in different alloy systems and microstructures. In such a case, to explain good galling properties, correlations must be restricted to a single alloy system and/or microstructure, as suggested by Rigney.
Welding and weld cladding are particularly difficult to achieve in hardfacing alloys because a compromise in material properties is necessary to achieve both weldability and wear resistance. These alloys generally exhibit composite microstructures comprised of a matrix metal phase with interspersed hard ceramic or carbide phases for increased wear resistance[7]. This composite microstructure has an inherently lower coefficient of thermal expansion, so that thermal cycling during the cladding process can generate large internal stress and cracking. Welded microstructures may also be prone to forming fast crack pathways along boundary networks of hard phases[8]. In principle, the wear resistance can be improved by increasing the yield strength and strain-hardening behavior of the metal matrix, both of which increase the hardness of the composite microstructure[9]. Unfortunately, this can result in increased thermal stresses within the cladding layer and subsequent cracking. Therefore, it is generally desirable for weld cladding material to have a low mismatch in the coefficient of thermal expansion (CTE), high weld ductility, and low-strain hardening rate. These attributes, however, are precisely those likely to degrade wear and galling properties[7], due to the low hardness, low resistance to strain-localization, and low amount of secondary phases which resist surface deformation and abrasion. A compromise in properties must therefore be reached if hard-facing alloys are to be fabricated by weld cladding procedures.

PM-HIP manufacturing offers an alternative to address these necessary compromises. Powder processing requires a lower temperature and therefore generates less stress during part manufacturing. The melt material is initially solidified into a micron-sized powder, and packed into forms of near-net-shape. The powder is then densified >1000°C in an
inert atmosphere at high pressure (>100 MPa). The temperature is sufficient for diffusion and densification to readily occur in most alloys, yet no melting is allowed to occur during the process. The material is then cooled in a slow and controlled manner. Local thermal stresses, transients, and cycles are therefore minimized during PM-HIP processing compared to weld cladding. PM-HIP techniques therefore allow material properties such as hardness, strain-hardening, carbide volume fraction, and microstructure to be optimized for wear and galling, without compromises for weldability.

The present work, therefore, is composed of two primary parts: one, an investigation into alternative alloy systems fabricated by PM-HIP to investigate severe adhesive wear mechanisms; and two, a modification of an austenitic stainless steel alloy using nitrogen, again to investigate the improved high temperature galling properties found via modification. Using combined wear testing, metallography, electron microscopy, and X-ray diffraction techniques, the microstructural, mechanical, and chemical changes to the galled surfaces are investigated to help explain the macroscopic wear behavior. In the austenitic stainless steels, in particular, a hypothesis is proposed that a strain-localization process controls the initiation of galling behavior. Using this hypothesis, alloy modification strategies are proposed to help prevent strain-localization from occurring using nitrogen additions to the alloy and equilibrium heat treatments. These modifications are then studied for wear morphology, microstructural changes, and deformation mechanism to help explain the origin of good galling resistance in austenitic stainless steel alloys.
Chapter 2: Introduction and Background

Introduction

Hardfacing materials for valve applications operate in severe conditions, with a high-oxygen steam environment under large compressive loads. Consequently, these materials must be resistant to corrosion and wear under the full range of operating temperatures. Both corrosion and wear, however, are not single monolithic phenomena, and comprise a whole family of different processes that are highly dependent on local environment, loading conditions, materials, and geometry. In the controlled environment of a nuclear coolant system (free of sulfur and chloride ions) the primary mode of corrosion is aqueous oxidation. In all commercial hardfacing alloys, the problem of aqueous corrosion is mitigated by the formation of an adherent passivation layer, often of Cr$_2$O$_3$ that forms from chromium alloying of stainless steels, cobalt, and nickel alloys. Maintenance of passivity in hardfacing alloys is thus the first design constraint, as corrosion can cause material loss, abrasive particle formation, surface roughening, enhanced surface adhesion, and interaction with the wear process that can dramatically reduce part lifetimes.

The primary consideration for hardfacing alloys is the rate of wear. In an unlubricated material pair, free from impinging particles or liquids, the active wear mechanism is adhesive wear in the plastic regime. In steady-state adhesive wear (the Archard wear
regime), wear is controlled by the hardness of the material, which determines the asperity bond area and wear particle size, therefore determining the wear rate.

Stellite cobalt alloys and austenitic stainless steels are good choices for hardfacing materials under high temperature valve seat conditions, as they both form a protective adherent oxide that prevents corrosion, and have relatively low wear rates at operational loads when hard carbides are added to the microstructure. The temperature stability of mechanical properties is also acceptable for both alloy grades. Austenitic stainless steels are limited for replacement of Stellite alloys, however, by their tendency to gall under high loads and especially at high temperatures, which causes seizure of valve parts. The goal of this alloy design project is therefore to understand what gives Stellite such good wear and galling resistance, and engineer that same galling resistance to austenitic stainless steel hardfacing alloys at high temperatures.

**Adhesive Wear and Galling**

Wear is a general term for degradation and removal of material that occurs between at two surfaces in contact under load[10]. Wear itself is a subset of the field of tribology, the study of solid surface interactions, and is confined to when material removal occurs by damage to a materials surface. As a consequence of this broad definition, wear is further classified by the source of the damage process, which can involve mechanical deformation bonding, hard particle gouging, surface stress fatigue, electrochemical corrosion and environmental interactions, oxidation in metal alloys, and other more specialized forms (fretting wear, electric arc wear, etc.). The operative mechanisms that
occur locally are affected by geometry and conditions of the mechanical system, including loading, sliding speed, geometry, surface roughness, and finishing procedure, as well as the material deformation characteristics, including elastic moduli, hardness (related to yield strength), work hardening, thermal properties, toughness, and surface energies. The large number of processes and variables involved has led to efforts to map the parameter spaces for wear conditions, resulting in wear mechanism maps. (also called P-V maps, or Ashby maps), similar to those found for other processes like creep. Because wear, however is highly dependent on geometry and the other properties listed above, these wear maps must be investigated for each particular system and show little cross-compatibility that would be useful for design.
Figure 2
Wear mechanism map for unlubricated mild steel, normalized to part size and yield strength[11]. Note the region of seizure at the top of the map at high loads.
Figure 3
Plastic strain interactions of an asperity with a wear surface [10]

Simple Adhesive Wear

For unlubricated metal sliding surfaces, adhesive wear is the active mechanisms at low to moderate sliding speeds and high loads, assuming flat part geometry and moderate surface roughness, similar to conditions of most coolant valves. Adhesive wear is governed by the bonding and deformation between mating surface asperities under load. Although the exact shape and distribution of these asperities will depend on the surface preparation, material properties, and geometry, the tribological study of these asperities has been modeled as hemispheres with simple continuum Hertzian mechanics in much past literature. Generally, the elastic stress distribution under an asperity will grow until the yield stress is reached at a distance of approximately 0.5 times the asperity radius[10].
For perfect plastic behavior (no strain hardening), the plastically yielded material under the asperity will then grow while supporting a constant load (as perfect plastic behavior has a constant yield stress). As there are many asperities over the wear surfaces, however, increased macroscopic load on the surface will only bring more asperities in contact and yield loading. In the plastic regime then, the real area of the surfaces in contact will grow proportionally to the macroscopic load for ideal plastic behavior, shown graphically in Fig. 6 below. More complex material behavior, like strain hardening, results in a system of coupled equations for each asperity deformation, the solution of which is still an active area of research [3, 10, 12, 13].

Figure 4
Wear junction considered in Archard Wear Equation [3]. Wear particle formation is considered to form by an (unspecified) statistical damage process, classically.

As a result, each asperity contact is considered an independent contact which can support only a load proportional to the hardness of the material, times the average asperity diameter given near the onset of yield. Consideration of an array of such asperities gives
the macroscopic behavior via the Archard wear equation (sometimes called the Archard
Wear Law, or just the Wear Law, as it may also apply to other forms of wear).

\[ V = k \frac{Lx}{H} \]

Which relates the volumetric wear loss, \( v \), to the macroscopic load, \( L \), the sliding distance
\( x \), and the material hardness \( H \), (related to the yield strength), through the wear constant
\( k \). Typical values for \( k \) range from \( 1 \times 10^{-2} \) for self-mated unlubricated low-carbon steel,
to \( 1 \times 10^{-8} \) for well lubricated dissimilar ceramic materials. Values of \( 1 \times 10^{-5} \) are considered
acceptable for wear-resistant materials (20 year lifetime for a 2mm thick part)[2]. The
classical interpretation for this non-dimensional wear coefficient is a probability for wear
particle formation by fracture away from the bonded asperity interface, as shown
schematically in Figure 4.
Figure 5
Asperity contact junctions for statistical surfaces modeled by Finite Element Simulation for elastic-perfectly plastic deformations

While the Archard equation gives a good agreement with average sliding wear values, the measured wear coefficient for any particular test can vary by up to two orders of magnitude in either direction, even under identical conditions. This is partly due to the variability of wear test setups, but also to the statistical nature of rough interacting surfaces, shown schematically in Fig. 5.
Variation of Real Contact Area, Number of Asperities Contacted, Mean Asperity Contact Area, and Mean Pressure on Each Asperity as a Function of Macroscopic Pressure for Random Surface Texture, Analytical and Simulated. The contact area and load remain roughly constant for each single asperity, but the number of asperities and total contact area grow linearly with macroscopic load in the steady state wear regime (Archard wear regime). [10]

While the Archard equation gives a simple explanation for the results of wear phenomena, gives no information about the mechanism of wear particle formation[2].

This wear law formed the basis for attempts and understanding the basic mechanisms of wear for the next 30 years. Two general approaches are taken to understanding the wear process in this framework: the ‘k – factor’ approach, relating underlying material mechanisms to the probability of wear particle formation (represented by the non-dimensional variable k); and the ‘PV factor’ approach, relating wear mechanisms to the
overall mechanical energy input to the system, represented by the product of the applied stress and velocity. [2]

To predict the behavior of wear materials, a large number of quantitative theories have been proposed to explain the mechanism of wear particle formation using [3]. Empirical investigation of wear particle sizes has shown wear particle size to be roughly inversely proportional to the hardness of the material, and thus each wear particle was considered to remove some amount of yielded material under the surface. Higher hard less material and results in a lower overall wear rate. Surface fatigue, statistical spatial variation in material properties, and interfacial temperature rise have all been investigated in specific wear situations, but for large loads and low sliding speeds (as is the case for hardfacing materials) subsurface crack propagation and plastic instability are of primary concern in literature [14].

In hard, brittle materials like ceramics and tool steels, subsurface cracks running parallel to the adhesion bond interface appear to control the rate of wear particle formation, and have been modeled by Evans and Marshall (1980) and Challen and Oxley with good experimental agreement. In this case, wear can be minimized by increasing toughness and resistance to crack propagation. On the other hand, tough but low hardness materials experience high shear strain on adhesively bonded asperities that can lead to a plastic instability, similar to necking. Experiments by Greenwood and Tabor (1957), and theory developed by Greenwood and extended by Rigney (1972), show that this plastic instability can be minimized by increasing the hardness and work hardening of a material. Thus for materials where these mechanisms compete, as in hardfacing materials, a
balance of hardness and toughness is necessary to minimize wear in the steady state regime. Although these theories are relatively well validated for specific cases of material systems, geometries, and environments, their interaction with other wear mechanisms, like fatigue and inhomogeneous local properties, is still an active area of tribology research. A model that predicts all adhesive wear from material properties and mechanical geometry thus has not yet been developed in the literature [3].

Departures from the Wear Law

Attempts to understand wear in within the paradigm of the Archard Wear Law invariably run into constraints due to the complex and extreme nature of surface tribological systems. Clear evidence can be seen from the so-called ‘wear maps’ published 20 years earlier by Tabor, where oxidative wear occurs with higher sliding speed (resulting in higher surface temperatures) and seizure or galling occurs at higher applied loads. Failure to consider material and chemical constitutive behavior, and resulting local conditions at the wear surface, results in limited applicability of mechanical engineering studies of wear to specific regimes and systems.

Problematic for predicting galling properties in the present application, however, is extrapolation of this framework of the Archard wear law to invalid regimes like galling. The derivation of the Archard wear law explicitly assumes independent deforming asperities at the contacting surface. This is the basis for extrapolating property (i.e. hardness) dependence of wear to many different materials systems. However, where
asperities begin to coalesce, their deformations become dependent, and the Archard wear law may lose validity. Such coalescence behavior is one of the present studies observations from empirical studies of galling. Thus, as a matter of scientific nomenclature, the Archard wear law might better be called the Archard Wear Rule, as law implies a much larger range of generalization than may be appropriate. As of yet no computational studies of dependent or coupled asperity deformation, with or without realistic material constitutive relations, has been attempted to the author’s knowledge, primarily due to computational complexity.

One already recognized example which violates the equal load partitioning assumption behind the Archard wear law is Thermoelastic Instability (TEI) wear behavior (also called thermal mounding or ‘hot spots’). Found in ceramics sliding at high speed (for example in brake applications), TEI occurs when the adiabatic heating from surface plastic deformation results in a positive volume change from thermal expansion. At a critical sliding speed this expansion is large enough, and heat conduction away from the surface is small enough, that the growing asperity takes up load and deformation preferentially, which results in more thermal expansion. This becomes a runaway process in which only the unstable asperity is loaded, resulting in the formation of a ‘hot spot’ which can cause seizure and exponential increases in wear rate.

Tribofilm wear is another wear mechanism that violates the assumptions of steady-state wear processes. In this class of behavior, a transfer film of wear debris forms between the two contacting surfaces, in a manner similar to a solid phase lubricant. Significant temperature and/or strain-rate softening occurs which allows shear strain to be taken up
solely by the tribofilm. Additional wear debris is then retained by the tribofilm, which once formed, can dramatically lower the overall wear rate subsequently. This mechanism is commonly found in polymers sliding on metals, but has also been found in metal-metal and metal-ceramic couples. The result of intimate surface contact and debris retention results in a wide skew of data away from the simple predictions based on the Archard wear law.

![Graph showing wear rate as a function of macroscopic stress](image)

**Figure 7**
Wear rate as a function of macroscopic stress (in g/cm²) for high-carbon steel. The transition to galling type behavior is seen at high stresses [15]

Galling can be characterized as a form of severe adhesive wear, characterized by material transfer and large increases in surface roughness caused by formation of surface protrusions [2]. The transition to galling occurs when most of the asperities have been
plastically deformed, where greater load cannot be supported by deformation of more asperities. At high loads with large local plastic deformation, the nanometer-scale oxide layer on the metal surface can also be broken, and direct metal-to-metal bonding takes place. This leads to rapid interface bond growth, further increasing adhesion and the force required to break the interface bond. Although the mechanics of the process are not fully understood [9, 10] the interface area can then transfer enough force to yield large amounts of material behind the interface, with accompanied material transfer. As this yielding will also increase the interface area, it becomes a runaway process; large material deformation increases the interface bonding, which then takes up more macroscopic load and causes more material deformation and transfer. The applied stress at which this ‘avalanche’ process occurs[16] is then called the threshold galling stress.

To limit galling and increase the threshold galling stress, the area of interface bonding should then be reduced. This can be achieved by modifying the deformation properties of the material, namely increasing the hardness and work-hardening rate, and decreasing the ductile elongation of the material [2]. Increasing hardness will increase the yield strength and lower the steady state wear rate for a particular alloy [17], but a hard material alone does not necessarily provide good galling resistance. [18]. The mechanical behavior of the material after the onset of plastic deformation controls the growth of the bonded interface, and therefore determines galling behavior, with higher work hardening requiring more stress to deform and bond the interface [19]. In brittle materials that do not yield, galling does not occur and fracture phenomena take place preferentially, as in ceramic materials [20]. As discussed previously, however, brittle fracture can increase the
overall wear rate of the material, increasing surface roughening, and the wear will become abrasive in nature.

Figure 8
A schematic of the ASTM G98 Pin-on-block galling test where material of interest (usually the pin) is brought in contact with the mating material (the block) and rotated through one full rotation under load. Surfaces are then examined with a 10X loupe to classify the wear surface

A balance of properties is thus necessary to achieve optimal performance of metal hardfacing material. Although increasing hardness independently is beneficial to wear and galling properties of a particular alloy, hardness is not independent of other properties. If fracture toughness is decreased while increasing hardness, delamination cracking can occur that will roughen the surface and cause higher wear. For example, a strain-transformation 304 stainless steel, although much harder than 316 austenitic steel, has a higher adhesive wear rate during self-sliding experiments with larger wear particle formation and surface roughening for the same conditions [21]. Low fracture toughness
also makes forming and welding parts more difficult and may lower the life of hardfaced parts, like valve seats, through interface cracking. Corrosion resistance must also be high, as under severe loading conditions corrosion erosion can significantly increase the wear rate and surface roughening of stainless steels [22].

*The Role of Microstructure and Geometry on Wear*

*The Role of Second Phases in Wear and Galling*

The existence of hard phases in a matrix affects wear properties by changing local deformation mechanics in hardfacing materials. The steady-state wear rate can be reduced by changing the strength of the bonded asperity interface by introducing carbides or [16-18]. Additionally, a harder second will deform less, causing a smaller area of asperity bonding, both of which allow the interface to break with less total force. This results in lower wear rate, as fracture at the interface is more likely, and the probability of wear particle formation through the material bulk is smaller. The harder phase will also partition plastic strain to the matrix phase, increasing the overall rate of work hardening for the composite microstructure, slowing the growth rate of the bonded interface and increasing galling resistance.

Strain localization is also reduced by the introduction of obstacles into the path of slip bands, requiring greater stress for dislocation bypass or cutting. Both the amount and distribution of carbides affects the adhesive wear and galling properties, as wear resistance is increased with the probability of dissimilar interface bonding (carbide-
matrix bonded asperity interfaces are weaker than matrix-matrix interface). Increasing the total amount, up to one half volume fraction, as well as decreasing the distance between carbides to create a homogeneous dispersion, decreases the adhesive wear by maximizing the probability of dissimilar asperity bond interfaces [23]. As a corollary, alloy carbides (carbides not based on iron, or with crystal structures dissimilar to the matrix, such as niobium carbides) decrease the asperity interface bond strength and decrease the adhesive wear rate [24]. Alloys filled with carbides or other hard particles, such as tungsten carbide particles in a nickel alloy matrix, show the best wear and galling resistance (i.e. under ASTM G98 test standards, no galling is observed at the maximum stress of 350 MPa), with properties approaching the galling-immune monolithic ceramics as the volume fraction of particles approaches unity. These cermet materials however also have poor fracture toughness, formability, and mechanical compatibility problems with metals, similar to ceramic materials [20].

Dual phase microstructures, such as those found in duplex (mixed austenite-ferrite) steels, are less well investigated as tribological materials. Generally, plastic strain is partitioned to the softer of the two phases, the austenite phase for duplex steels, although at higher loads both phases will plastically deform. During steady state wear, the softer phase will then form a tribological layer on the wear surface after the run-in period, due to preferential deformation [25]. Thus duplex steels tend to have similar wear rates as steels of similar austenite composition. Galling of dual phase materials is less well investigated, but appears to depend on the maintenance of the softer tribolayer on the surface. When this layer is broken, for example in sheet bending or near machining
defects, delamination of the surface layer over large areas can occur, causing surface roughening and possible part seizure.

*The Role of Grain Size and Defect Content in Wear*

The grain-size dependence of adhesive wear properties is relatively small. Due to the large surface strains and so-called ‘ratchet-strain’ effect of surface deformation, the initial grain size of metals generally has a very small effect on simple adhesive wear (neglecting the case of single crystals). This is one instance where the effective surface hardness important to distinguish from base material hardness in the Archard Wear equation. Although the two hardnesses are generally correlated, due to the inherent plastic strain and effective grain refinement at the wear surface, the surface hardness and bulk hardness are decoupled with respect to grain size. As a result, very little dependence of adhesive wear is found on grain-size processing.

The effect of grain size on severe adhesive wear, or galling, is less well researched. Thus far in the literature, very little controlled experimental effort has gone into researching the effect of grain size on galling properties.

*Processing Effect on Hardfacing Components*

Powder metallurgy fabrication techniques may be superior in some applications to tradition hardfacing fabrication methods. Welding or cladding is the standard method for application of thick alloy films to hardfacing components. However, this non-
equilibrium processing can result in difficulty controlling the composition of the resulting clad, both from segregation effects during solidification, and especially from dilution effects from the base material [7]. Several layers of clad material may then be necessary to get a resulting composition adequate for hardfacing purposes. Welding defects, inclusions, and cracks can also result surface geometry and property inhomogeneities, causing either direct adhesion or increased surface roughening, which can then lead to seizure and galling. Powder metallurgy can offer parts with superior properties that are free of welding defects and dilution effects, which should lead to increased part lifetime, fewer repairs, and lower cost over the life of the hardfaced part. Additionally, the weldability of an alloy can be decoupled from its wear and galling performance, which can compete for optimization of properties, e.g. high hardness and work hardening are desirable for wear resistance, but not for weldability[2].

**Influence of Materials Properties on Wear**

*Deformation Mechanisms and the effect of Stacking Fault Energy (SFE)*

Work-hardening behavior is controlled by the plastic deformation mechanism of a material. In metals, this occurs by the slip of dislocations and their interaction with themselves and microstructural obstacles, like grain boundaries and precipitates. The amount of dislocation-dislocation interaction is controlled primarily by the ease of dislocation cross-slip (where dislocations change slip systems that allows obstacle bypassing) which in FCC metals is controlled by the dissociation of perfect dislocations into partials. [26].
The SFE affects deformation primarily by controlling the width of partial dislocations that are separated by a stacking fault. The two partial dislocations repel each other through their stress fields, and this repulsion is balanced by a force resulting from the creation of more stacking fault area. The lower the stacking fault energy, then, the wider the separation of partials will be (as a typical example 50-100 nm wide stacking faults in 304 SS with a SFE of approximately 50 mJ/m².) Cross-slip of dislocations depends on the ability of the stacking fault to contract to a perfect dislocation to change slip systems. Wider stacking faults, and low SFE, therefore require more energy to bring the two partials together and makes cross-slip more difficult, which increases dislocation interactions. High SFE materials, such as commercially pure aluminum (SFE ~ 200 mJ/m²), thus deform primarily by cross slip, and have low work hardening. Lower values of SFE prevent cross-slip, leading to planar slip of dislocation pairs and greater dislocation interaction with the formation of sessile locks (such as Lomer-Cottrell locks) that increase work hardening, with typical stress-strain slope of 1500 MPa [27].

Table 1
Strain-Hardening Mechanisms in FCC Metals (After Remy et al[28], and Dillamore[29])
*Note maximum strain-hardening rate not

<table>
<thead>
<tr>
<th>Deformation Mechanism</th>
<th>Max. SHR*</th>
<th>SFE Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Strain-Induced Martensite</td>
<td>µ/2 - µ/4</td>
<td>0 - 20</td>
</tr>
<tr>
<td>2 Twinning</td>
<td>µ/10</td>
<td>10 - 50</td>
</tr>
<tr>
<td>3 Extended Defects (e.g. SF )</td>
<td>µ/20</td>
<td>60 - 125</td>
</tr>
<tr>
<td>4 Dislocation 'Forest'</td>
<td>µ/30</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>5 Solid Solution</td>
<td>µ/50</td>
<td>NA</td>
</tr>
</tbody>
</table>
Twining can be thought of as a limit of this behavior, as a sufficiently low SFE (20 -50 mJ/m$^2$ in most FCC materials) will not be able to keep the bounding partial dislocations from interacting with the global stress field and spreading far apart. The passage of several partial dislocations on successive planes (with accompanying stacking faults) can then alter the stacking sequence to and form a twinning fault, a crystal mirrored about the twin plane. The resulting interaction of subsequent dislocations, multiplied twinning dislocations, and new twins with more twin boundaries then causes an increase in the work hardening behavior (maximum stress-strain slope 2500 MPa [30]) [31].

Figure 9
Deformation Mechanism observed at different stacking fault energies in FCC cobalt alloys[26]
Figure 10
Effect of temperature and SFE on deformation structures in Fe-Mn-Cr-C alloys

A further decrease in SFE can change the deformation mechanism to a stress- or strain-induced phase transformation, depending the magnitude of the phase nucleation barrier [26, 32][26, 32][26, 32][21, 25][21, 25]. A stacking fault in an FCC matrix can be modeled as a single stacking sequence of the HCP structure. This allows calculation of the SFE to a first approximation by finding the difference in energy between the FCC and HCP structures:

\[
SFE = 2\rho \Delta G^{\text{FCC} \rightarrow \text{HCP}} + 2\sigma_0
\]

where \( \Delta G^{\text{FCC} \rightarrow \text{HCP}} \) is the free energy difference between the FCC and HCP structures, \( \rho \) is the areal atomic density of the crystal in atoms/m\(^2\), and \( \sigma_0 \) is the interfacial boundary energy, a small positive constant dependent on the alloy system (~10 mJ/m\(^2\) in stainless steels) [33]. If this SFE is very low (below 20 mJ/m\(^2\) or less), the free energy of the two structures is necessarily very close. For these low SFE values, a stress-induced martensitic transformation from FCC to HCP is found in many systems (\( \gamma \rightarrow \epsilon \) transformation in iron alloys), for example high Mn steels and cobalt alloys [34, 35][34, 35][34, 35][27, 28][27, 28]. As a corollary, the trend of lowering wear rate by lowering SFE and increasing work hardening is observed across several FCC metal systems, including austenitic steels [31], nickel alloys [36], and cobalt hardfacing alloys [26].
Although the SFE is affected by the thermodynamic stability of the FCC to HCP transformation directly, it also affects the $\gamma \rightarrow \alpha$ (FCC to BCC or BCT) martensitic transformation kinetics. $\alpha'$ martensite is known to nucleate preferentially on stacking fault intersections[37] or regions of $\varepsilon$ martensite [38, 39][38, 39][38, 39][31, 32][31, 32] thus lowering SFE may increase the kinetics of the $\gamma \rightarrow \alpha$ transformation.

**The Influence of Stress-Induced Transformations on Wear**

The adhesive wear process is affected by mechanically induced transformations primarily by changing the mechanical deformation and fracture processes. These transformations require a metastable crystal structure, which is transformed by the action of mechanical stresses to a new crystal structure. In metastable materials (like a quenched austenitic stainless steel or other low SFE materials), mechanical deformation can induce a phase transformation by providing defect sites necessary to overcome barriers to nucleation. As the deformation induces transformation,
the martensite will interact with the deforming metal matrix and increase the rate of work hardening, the exact mechanism of which is still under dispute [40]. Two primary arguments are found in current literature: dislocation interaction and strain partitioning. Dislocations will interact with transformed martensite in a similar way as other second phases, pinning at phase boundaries and causing a precipitation strengthening effect. This transformation strengthening is particularly effective at preventing strain localization precisely because martensite forms at defect sites formed by the passage of dislocations. Secondly, as the transformation products have a higher moduli and yield stress themselves, strain partitioning effect will also occur at low strains, while at high strains (with a martensite fraction of 30% or greater) direct deformation of the hard martensite phase must occur [41, 42][41, 42][41, 42][34, 35][34, 35]. Both mechanisms may be responsible, and the predominant effect may be dependent on the properties of the martensite composition, strain, and strain rate. The steels that show strain-induced phase transformations thus have the higher work hardening rates than those that do not (up to 4500 vs. 1500 MPa maximum stress-strain slope, respectively, in 304SS based alloys) [6].

From an engineering perspective, the stability of martensitic phase transformations can be measured by characteristic temperatures. Below the Ms temperature, the driving force from thermal undercooling is great enough to spontaneously form martensite. Quenching a metal from high temperature to below its Ms temperature will thus induce a martensitic transformation. Mechanical phase transformations are also characterized by a similar start temperature, the Ms temperature, defined as the temperature at which martensite transformations take place under a characteristic stress, taken as the yield stress for strain-induced transformations. The upper limit of stability for the mechanical transformation is similarly characterized by the Md temperature, defined as the temperature at which a strain of 0.30 causes a phase transformation of 50% volume fraction and always higher than the Ms. Mechanical phase transformations are then possible at
temperatures between $\text{Ms}^\sigma$ and $\text{Md}_{30}$. Above $\text{Md}_{30}$ the austenite phase is stable, and between $\text{Ms}$ and $\text{Ms}^\sigma$ the austenite phase is metastable under all stresses. Alloys that show mechanical phase transformations thus must have an $\text{Ms}$ temperature below the quenching temperature (to prevent thermal martensite formation) and an application temperature between the $\text{Ms}^\sigma$ and the $\text{Md}_{30}$.

[43]

When plastic deformation occurs by strain-induced phase transformations, however, the strain-hardening behavior is then dependent on the kinetics of the martensite transformation. Faster strain-induced martensite nucleation kinetics, therefore, lead to greater the strain-hardening behavior in the plastic regime, as more martensite forms per unit strain. The nucleation barrier for $\alpha$-martensite in iron however is very high [32], and requires defect sites, like stacking fault intersections or $\varepsilon$-martensite. Lowering SFE (i.e. easier formation of defects and $\varepsilon$-martensite) will provide more low energy nucleation sites to allow $\alpha$-martensite formation, thereby increasing strain-induced martensite transformation kinetics, and strain hardening.

Figure 12
Nucleation of $\alpha$-Martensite on Slip Band Intersection [43]
As the $M_d_{30}$ temperature is an engineering measure of a strain-induced phase transformation, the effective $M_d_{30}$ for $\alpha$-martensite will thus be influenced by all of the above processes, namely the nucleation barrier height, the defect nucleation site number and distribution, barriers to transformation fronts, and the driving forces (BCC phase stability for $\alpha$ martensite, resolved shear stress). Larger grain sizes thus increase the $M_d_{30}$ by increasing the average resolved shear stress in each grain, with a decrease of about 20°C with decreasing grain size from 1mm to 50 µm in 304 stainless steel [44]. Nickel tends especially to decrease the Md temperature by stabilizing the FCC structure and decreasing the volume driving force, at about 20 °C per wt% nickel [44]. Conversely, elements that stabilize the BCC phase or lower the SFE then tend to increase the Md temperature, like chromium (at low wt%) and manganese, respectively.

The difference in wear behavior between materials with FCC to HCP and FCC to BCC phase transformations appears to be qualitatively similar, as both increase the work hardening rate and thus reduce the wear rate of materials. The $\gamma \rightarrow \alpha$ transformation however has a greater strain hardening rate in stainless steels, compared to the $\gamma \rightarrow \varepsilon$ transformation for known ferrous alloys (2500 vs >4500 MPa stress-strain slope, respectively) [45], and is therefore be more desirable for better galling resistance. The $\gamma \rightarrow \varepsilon$ transformation in iron alloys also appears to take place preferentially under high strain rate situations (> 50 m/m s), such as during impact or cavitation erosion, providing increased wear resistance in mixed loading regimes [46]. Ferrous alloys that show only the $\gamma \rightarrow \varepsilon$ transformation have higher ductility, however, due to the plasticity of iron $\varepsilon$-martensite [47], and thus may ultimately be detrimental to galling resistance.

**Conclusions**

Severe adhesive wear, known as galling, is the major design issue for alloys for replacing Stellite in hardfacing in valve applications. The galling process is caused by adhesion of
surface asperities deforming against each other to form a bonded interface that can transfer enough load to cause massive slip localization. The formation of this interface is controlled by the deformation characteristics of the metal, with increased hardness, increased work hardening, and decreased ductility leading to better galling resistance. Second, harder phases, such as carbides, delay galling by decreasing interface bond strength and segregating strain to the matrix, which further increases work hardening, and increases the stress for slip localization. Increased work hardening and decreased ductility can be achieved by lowering the stacking fault energy of metal alloys, which results in changes to the deformation mechanism that have larger amounts of dislocation interaction. In ferrous alloys, strain-induced $\alpha$-martensite phase transformations occur most rapidly at the lowest SFE ($<20$ mJ/m$^2$) due to defect site nucleation and have the highest work hardening behavior (3000 - 5000 MPa stress-strain slope), and are observed in commonly used hardfacing alloys. The design of a corrosion resistant austenitic stainless steel alloy with high work hardening, due to a hard carbide secondary phase and a matrix phase that shows strain-induced $\alpha$-martensite transformation at application temperatures should yield acceptable properties for valve hardfacing applications. Optimization of phase transformation in existing alloys should improve the temperature stability of the mechanical deformation modes and give better wear and galling properties at application temperatures.


Chapter 3: Hardfacing Alloys, Overview and Base Microstructures

A review of the state of current hardfacing alloys, structure and properties is presented as a guide for alloy development. This list is not meant to be exhaustive, as the scope of alloys used for wear resistance span nearly the entire range of engineering metals, depending on application requirements. The alloys listed here are restricted to those in use for valve hardfacing applications at room to elevated temperature (below 500°C). Generally theses hardfacing alloys are designed to be applied as thick films (>1 cm) by weld cladding or similar methods. A wide array of further techniques are used for surface property modification for wear, including surface diffusion treatments (such as carburization), ion implantation, thermal spray techniques, and friction stir processing. These techniques are omitted here for brevity, and the relative merits of the approach taken in this work are subsequently discussed.
Table 2

Test Alloy Hardfacing Compositions, in %wt

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Co</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>Fe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOREM 02</td>
<td>24.5</td>
<td>4.1</td>
<td>4.2</td>
<td>1.9</td>
<td>0.06</td>
<td>3.3</td>
<td>1.2</td>
<td>0.17</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>GallTough Plus</td>
<td>18.5</td>
<td>8</td>
<td>4</td>
<td>1.5</td>
<td>3.5</td>
<td>0.25</td>
<td>0.05</td>
<td>Bal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316 L</td>
<td>18</td>
<td>12</td>
<td>2</td>
<td>2</td>
<td>0.75</td>
<td>0.03</td>
<td>0.1</td>
<td>Bal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tristelle 5183</td>
<td>20</td>
<td>10</td>
<td></td>
<td></td>
<td>5.5</td>
<td>1.7</td>
<td>Bal</td>
<td>9 Nb, 0.4 Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evrit50</td>
<td>25</td>
<td>0.9</td>
<td>3.5</td>
<td>0.4</td>
<td>2</td>
<td>Bal</td>
<td>0.5 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H' alloy</td>
<td>21.6</td>
<td>4.4</td>
<td>4.5</td>
<td>1.8</td>
<td>3</td>
<td>0.69</td>
<td>0.13</td>
<td>Bal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stellite 6</td>
<td>30</td>
<td>3</td>
<td>1</td>
<td>1.5</td>
<td>Bal</td>
<td>1.5</td>
<td>1.2</td>
<td>4 W</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Co-base Hardfacing Alloys

Stellite alloys are based on Co-Cr-W-C or Co-Cr-Mo-C systems, and have become the standard hardfacing solution in industry since their invention in the 1930s. All Stellite alloys are inherently resistant to erosion, cavitation, adhesive wear and galling due to their high hardness and work hardening. Chromium additions give good corrosion resistance through formation of an adherent passivating oxide film similar to stainless steels. Solid solution strengthening is achieved by the use of W or Mo, with W being more effective per wt% but imparting less high temperature and pitting corrosion resistance. The carbide content can also be manipulated by changing the carbon content, increasing hardness and work hardening and increasing abrasion resistance, but lowering
ductility and corrosion resistance by removing Cr from the matrix. Increasing chromium and alloy content also raises the stacking fault energy, by 1.8 mJ/m$^2$ per wt% alloy at low (<20wt%) concentrations[1], which can change the deformation mechanism from strain-induced transformation to twinning. The differences in these factors can be seen in the three Stellite alloys listed in Table 2. Stellite 3 has the highest C content and thus the largest carbide volume fraction, and high W for solid solution strengthening, with correspondingly higher abrasion resistance. The high volume fraction of carbides and high hardness results in brittle behavior for Stellite 3 (no yield point occurs in cast samples), and low weldability. The reduction of Cr from the metal matrix however reduces corrosion resistance in reducing acids, and Stellite 3 is susceptible to pitting corrosion in chloride environments. On the other hand, Stellite 21 has very low C and carbide volume fraction, which reduces abrasion resistance, but conserves Cr and Mo in the matrix, resulting in excellent corrosion and chloride pitting resistance. Additionally, the ductility is increased to up to 20% elongation, due to a combination of low carbide volume fraction and low work hardening. Stellite 6 represents a compromise between the two, with moderate C and carbide content and moderate W content, for good corrosion resistance and acceptable abrasion resistance, while retaining good weldability. This balance of properties have led Stellite 6 to be the industry standard hardfacing solution for a wide range of applications, although for particular applications other Stellite alloys
may offer better performance, such as seawater, highly corrosive, or high temperature applications.

The long half-life of the Co-60 isotope upon neutron activation however makes these alloys undesirable for nuclear applications and provides the impetus for this project, as outlined above.

Cobalt and cobalt-based alloys are known to have inherently low friction and wear properties, attributed by most authors to the relative stability of the HCP cobalt crystal structure [2]. The phase stability of the FCC and HCP phases are very close in terms of free energy difference, and small alloying additions like chromium can be made to form cobalt alloys with a fully FCC structure. This imparts better toughness to the material (as the FCC structure has more active slip systems), while the relative stability of the HCP and FCC structures results in a low SFE (<20 mJ/m²), as discussed above. This low SFE results in high work hardening by deforming with a $\gamma \rightarrow \varepsilon$ phase transition, as found in most Stellite alloys, or twinning, as found in some Stellite alloys like Stellite 21 [3]. The cobalt system also allows carbide precipitation hardening similar to stainless steels, with the same metal carbide phases ($M_7C_3$ and $M_{23}C_6$), which impart higher hardness and work hardenability. The combination of low friction, corrosion resistance, and high strain-hardening lead to excellent wear and galling properties (with no galling observed in the ASTM G98 test) [4]. The FCC and HCP crystal structures and carbide phases in cobalt are stable over a wide range of temperatures, potentially responsible for good
galling properties through stress induced phase transformations, up to 650°C for Stellite 6.

Some researchers attribute the good galling resistance of Co-based alloys to the strain-induced metastable FCC to HCP transformation. Such a transformation is believed to absorb the applied energy and increase the work hardening rate by forming HCP $\varepsilon$-martensitic phase that has fewer operating slip systems, thereby reducing the tendency of the material to plastically deform [7,9]. A similar strain-induce metastable FCC to $\alpha'$ martensite transformation in Fe-based alloys like Nitronic60 [10] and Norem02 [11] alloy has also been reported as the underlying cause for their good galling resistance at low testing temperatures.

Nevertheless, attributing the cause of good galling resistance behavior to strain-induced phase transformation is still under debate. Some authors believe that the good galling resistance of Co-based alloys and other Co-free alloys is due to their low stacking fault energy because of which the cross-slip of dislocations is suppressed leading to increased work hardening rate thereby resisting severe plastic deformation at sites of asperity contact [1,6,13]. Furthermore, from experimental results none of the developed Co-free hardfacing alloys have been able to achieve the good galling resistance properties of Stellite alloys at higher operating temperatures (i.e. >300°C).

_Ni-based Hardfacing Alloys_
Nickel-based hardfacing alloys are the alloy of choice for high-temperature wear applications due to the high yield stress at high temperature, above 750°C [5]. They also have better welding compatibility with low-alloy steel base materials than cobalt-based alloys [6]. Hardfacing nickel alloys are based primarily on a Ni-Cr-C base for corrosion resistance, with additional hardening effects from carbide or intermetallic precipitates from Cu (in Monel alloys) and Nb, Ti, and Al (in Inconel alloys). Mo, W, and B are typically added for greater precipitation strengthening, precipitating modified carbides or borides with higher strength in the Hastelloy alloys. Additions of Mo, Nb, Ti, Al, V, and Hf increase also alloy hardening by influencing precipitate formation, while simultaneously decreasing SFE and increasing work hardening rate in Nimonic series alloys [7].

Although the wear rate is low due to the high hot hardness, however, the low SFE of most nickel alloys (pure nickel has a high stacking fault energy ~200 mJ/m²), leads to plastic deformation with a high degree of cross-slip with low work hardening. Perhaps consequentially, these alloys also show subsequently a low galling threshold stress in self-mated material couples[8]. Nickel alloys for wear generally have lower fracture toughness as well, due to the high volume fraction of second phase particles, like carbides, silicides, or borides, needed to increase the wear resistance of the ductile matrix [9]. These ‘self-fluxing’ alloys then require special thermal spray or other advanced forming techniques to overcome the tendency to crack during conventional welding techniques.

**Fe-based Hardfacing Alloys**

Iron-based alloys offer a more attractive alternative to cobalt-free hardfacing alloy design. As the valve design for nuclear hardfacing materials requires long times at elevated temperatures in
aqueous media, well investigated systems with long-term phase stability, good temperature stability of material properties, and acceptable corrosion resistance. Austenitic stainless steels offer the best corrosion resistance of all steel alloy systems in aqueous environments with moderate to high pH (pH 6-10) [10]. Most austenitic alloys are based on the Fe-Ni-Cr ternary system, with chromium added to form an adherent protective oxide and nickel added to stabilize the austenite phase at room temperature [11]. 316 is a standard stainless steel based on the Fe-Ni-Cr ternary system, a modification of the 18Cr-8Ni alloy[11, 12]. Molybdenum is added to improve pitting corrosion resistance and improve the temperature stability of mechanical properties. Manganese is added as a sulfur getter that precipitates out intermetallics to prevent embrittlement, as well as to increase the solubility of nitrogen which increases the stability of the austenite phase and decrease the SFE to raise the work hardening rate[11]. This leads to good corrosion properties and good temperature stability of mechanical properties up to 600°C.

**NOREM02**

The alloy design of NOREM was intended to be a stainless steel microstructural analog of Stellite alloys which could be applied by weld cladding methods [13]. In particular, the goal was to have a carbide impregnated metastable austenitic matrix with good corrosion resistance. High chromium and high carbon were added to allow carbide precipitation, with enough extra chromium to avoid grain boundary sensitization from [14] matrix depletion. Nickel was added as an austenite stabilizer during solidification. Some nickel was replaced with manganese to lower the SFE and increase the nitrogen solubility, staying under 12% to avoid lowering toughness. Molybdenum was added to improve pitting corrosion, and silicon added to improve high
temperature wear, solid solution strengthening, and lower weld metal viscosity. Although the alloy was designed with a metastable FCC structure and low SFE to promote a strain-induced $\gamma \rightarrow \alpha$ transformation. The combination of carbides, solid solution strengthening and strain-induced phase transformation hardening evidently provides enough strain hardening to give good galling properties [15]. However, the galling resistance of NOREM falls appreciably above 200°C, which recent work has linked to the loss of the strain-induced transformation in ex-situ X-ray characterization. The temperature stability of the transformation, its effect on inherent material properties, as well as the wear morphology connected with the transformation remains to be investigated. This is a primary goal of this work.

_Gall Tough Plus_

To investigate the galling in austenitic stainless steels without the complication of a mixed carbide microstructure, a pure austenitic stainless steel was investigated for galling properties and morphology. GallTough Plus is a modification of the base 316 chemistry, where 4 wt% nickel has been replaced by 2 wt% manganese, and the silicon increased to 4 weight percent. This may serve to lower the stacking fault energy, as manganese and silicon enough to induce twinning deformation and increase work hardening [10], as well as promoting the formation of oxide scale that may reduce adhesion while keeping a fully austenitic structure [16]. Although the exact mechanism is not universally agreed upon, empirically this improves the galling characteristics of the alloy compared to 316L, form 0.1 ksi to 1ksi threshold galling stress.
Figure 13
Threshold galling stress as a function of Si and Ni+0.5Mn Content, used for alloy design of the GallTough alloy[17]

*Tristelle 5183*

Tristelle 5183 is a stainless steel hardfacing strengthened by multiple carbides, both chromium carbides and niobium carbides[18]. The alloy has an austenitic matrix phase when fabricated by
PM-HIP, with Tristelle uses carbide strengthening to improve adhesive wear, but uses niobium carbides as a precipitate instead of chromium. This avoids grain boundary sensitization, as chromium is not depleted during precipitation, and decreases wear rate even more than chromium carbides, as the niobium carbide phase is harder. The niobium carbide itself, however is susceptible to corrosion in high oxygen environments, such as in an air incursion incident [19]. Tristelle alloys show relatively good wear and galling performance even at high temperature. The difficulty of fabrication and machining, however, results in tests that are not comparable to other alloys. For example, surface machining down to the specification in the ASTM G98 test is not possible, resulting in tests that may be biased or unrepresentative of long-term galling tendencies.

**Everit 50**

As a comparison, stainless steels with different microstructures were also studied for galling behavior and morphology. Everit 50 was one such alloy, to investigate ultra-hard microstructures and wear behavior in martensitic stainless steel systems. The high chromium and iron concentration in this system stabilizes the BCC phase and leads to precipitation of chromium carbides (usually M₇C₃), resulting in a hard martensite plus carbide microstructure which improve the wear properties of the alloy. The addition of silicon adds oxidation resistance at elevated temperature (‘fire-scale resistance’), as well as decreasing melt viscosity, which increases the weldability of the alloy. The relatively high hardness and yield strength, along with low alloy content (particularly the absence of molybdenum for pitting corrosion resistance) limits the maximum stress and chemical environments for application.
The addition of 0.5% vanadium should form a fine dispersion of secondary carbides that act as grain boundary pinning sites and increase yield strength by requiring dislocation bypass.

\textit{H' Alloy}

In the course of this investigation, a modified stainless steel alloy based on NOREM02 designed around the principle of lowering stacking fault energy and increasing the BCC phase stability using thermodynamic simulation was attempted. During the fabrication process, it was found, however, that solidification effects resulted in a stabilized duplex plus carbide microstructure. Although this alloying attempt did not yield good galling properties, it did provide much insight. Research into the mechanism of duplex stainless steel galling has not yet been shown, the microstructural heterogeneity should cause a preferential yielding phase [20], which may have important effects on the wear mechanisms in these alloys.

\textit{The Role of Nitrogen Alloying in Iron-based Hardfacing Alloys}

An increase in interstitial nitrogen in an FCC matrix has long been known to increase the yield strength and hardness of austenitic stainless steels [21]. Nitrogen sits in the interstitial sites between metal atoms in the FCC metal structure. Octahedral interstitial sites (with 6-fold coordination) are preferred by nitrogen, although it partially occupies both octahedral and tetrahedral sites. The interstitial atoms then act to distort the crystal structure, increasing the effective Peierls Barrier and shear stress required for dislocation movement[22]. Yield strength of interstitially alloyed steels is thus increased through a resistance to dislocation movement.
Nitrogen is also capable of increasing the strain-hardening rate of an FCC stainless steel matrix by lowering the stacking fault energy (SFE) and changing the plastic deformation mechanism. Traditionally, nitrogen additions in small compositional ranges of conventional SS grades are observed to raise the stacking fault energy [23]. However, nitrogen at higher concentrations (> 0.12 wt% N) has been observed more recently to decrease the SFE significantly. This may be due to segregation or clustering of nitrogen to the stacking fault defect. Nitrogen has thus been shown to have a non-monotonic effect in several austenitic stainless steels, such that it increases SFE at lower concentrations and then greatly reduces it at higher concentrations [24-26]. Lower SFE results in larger equilibrium spacing between bounding partial dislocations. This suppresses the ability of dislocations to change slip planes (i.e. cross-slip) and dislocations are restricted to move on a specific crystal plane of the FCC crystal (typically of the (111) type). When barriers to dislocation motion increase, as defect intersections and reactions occur more often (with the formation of sessile defect content such as Lomer-Cottrell locks). The direct result is a higher strain-hardening rate with lower stacking-fault energy for FCC materials in dislocation slip plastic deformation.

Finally, super-saturation of nitrogen will lead to nitride formation in stainless steels during high temperature processing. Nitride formation is associated with better wear properties in a wide array of high-nitrogen stainless steels, such as 304LN and the Nitronic alloy series [14, 27, 28]. Large (>1 µm), hard particles in a metal matrix have also been shown to suppress strain-localization and shear banding in a variety of cermet
materials (Al-SiC[29] and Co-WC composites). The hypothesis for this effect is due to
the increased path length and complexity of the strain-localized surface to move around
the large, hard phases.

Higher volume fractions of secondary hard phases such as nitrides should therefore shift
increase the stress necessary for the onset of any shear localization process, as galling is
hypothesized to be. This has the additional added benefit of improving other wear
properties, such as friction and abrasive wear as well. Design of an alloy with
thermodynamically stable precipitates will ensure that the alloy phase balance remains
unchanged through the service lifetime of the part.

Conclusions

Cobalt-based Stellite alloys are the standard wear solution for metal hardfacing, with a
microstructure that consists of hard carbides in a high yield strength, highly work hardenable
matrix phase that exhibits a strain induced ε-martensite phase transformation, resulting in a
galling threshold stress higher than 350 MPa. Stainless steel alloys are the best alternative for
nuclear applications due to their corrosion resistance, relatively low cost, and advanced alloy
development. Previous alloy development has led to NOREM alloys that mimic Stellite with a
strain-induced transformation hardened matrix reinforced with carbides; however the galling
properties are diminished at high temperature due to the loss of the strain-induced α-martensitic
transformation. Alloying additions that raise the temperature stability of the α-martensitic
transformation should increase temperature stability of galling properties, such as manganese and
nitrogen which decrease the SFE and provide sites for α nucleation. Elimination of nickel to
stabilize the BCC phase should also increase the Md temperature of the $\alpha$-martensite transformation (as long as a fully austenitic structure is maintained by additions of FCC stabilizers like Mn, C, and N). Different and additional carbide phases, such as niobium or vanadium carbides, may increase wear and galling properties by creating a fine secondary dispersion that delays or prevents strain localization by particle bypass. This allows for greater freedom in engineering the strain-induced phase transformation, due to their lack of grain boundary segregation effects.
Chapter 4: Characterization of Hardfacing Alloys and Galled Samples

The measurement of galling is a macroscopic determination by the methods outlined in the ASTM G98 test. Quantification and microscopic investigation are necessary to understand the mechanisms and material properties that result in galling behavior, in order to understand the effects of alloying on hardfacing performance. To that end, samples taken from the G98 galling test were characterized to determine phase balances on galled surfaces using X-ray diffraction, and cross-sections were taken to observe the microstructure of the wear surface using optical and electron microscopy. By correlating the phase evolution, microstructure, and galling evaluations, a better concept of the mechanism of galling is developed that will help to direct alloying strategies for the next generation of hardfacing alloys.

Three hardfacing alloys, Stellite 6, NOREM02, and Tristelle 5183 were tested using the ASTM G98 button-on-block galling test (alloy compositions shown below in Table 1). Tests were performed at room temperature and at 350°C to mimic operating temperatures in a coolant system. A ranking of the wear behavior was performed according to the ASTM specification, and the stress at which galling onset occurred was recorded, in Table 2 below. Note that due to the high hardness of the hard carbides in the Tristelle
5183, the surface roughness did not meet the ASTM specification, and thus the galling behavior at high temperature is not strictly comparable for this alloy.

Table 3
ASTM G98 Threshold Galling Stress, MPa

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Test Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>Stellite 6</td>
<td>&gt; 240</td>
</tr>
<tr>
<td>NOREM 02</td>
<td>&gt; 240</td>
</tr>
<tr>
<td>Tristelle 5183 *</td>
<td>&gt; 240</td>
</tr>
</tbody>
</table>

Subsequently, phase analysis of the tested buttons surface was performed using X-ray diffraction. A Bragg-Brentano geometry using Cu Kα radiation and a down-beam single-crystal monochromator was used as a pseudo-powder pattern, justified by the rotational symmetry of the wear button. Due to absorption at the source wavelength, the tested volume was only 10-15 microns into the depth of each wear surface, which in some cases was larger or smaller than the depth of the deformed region. Nevertheless, the XRD spectra give an important picture of the relative phase evolution during the wear and galling process.
Finally, the same galling buttons were prepared for cross-section microscopy. This entails first coating the button with an electrochemically deposited metal layer, in this case copper, to protect the wear surface and debris and to prevent edge effects during the polishing process. More details on the careful preparation of wear specimens can be found in reference. Following this, each sample was painstakingly polished down to the site of wear or galling scars to understand the local deformation process that occurred. Micrographs using optical and SEM backscatter images were taken to show crystallographic contrast in the deformed surface region.

**Characterization of Galled Samples Showing Strain-induced martensite**

The worn surfaces from the ASTM G98, shown below, show a highly deformed region near the surface, extending down to undeformed base material over a scale of microns. In Stellite 6, Figure 15 below, the deformed region is marked by a highly localized region near the surface (5 µm at RT and 15 µm at 350°C). Even though significant deformation...
is observed in the near surface region at high temperature, the microstructure shows very little plastic flow. Extensive lath formation into the depth of the materials is evident in Stellite even at high temperature.

The wear surfaces of NOREM02 (Figure 16) and Tristelle 5183, however, show a greater difference with temperature. At room temperature, the wear surface of NOREM02 is localized to a very small layer near the surface (<5 µm) with extensive lath formation. Galled surfaces tested at 350°C, however, show extensive plastic flow without lath formation. Carbides appear to be depleted from the mechanical mixing at the surface. A similar microstructure is observed in Tristelle 5183 at 350°C, where plastic flow around carbides is evident. Extensive crack formation in the large NbC carbide phases (nominal tensile strength of 3.1 GPa) shows the extreme conditions of stress and strain at the wear surface, and directly shows the shear near the wear surface. The comparison between NOREM02 and Tristelle 5183 also shows the effect of carbides in the wear surface, as the larger and greater number of hard phases in Tristelle is more effective at resisting plastic flow near the wear surface. However, without strain-induced martensite, defect-mediated plastic deformation of the matrix proceeds even at high carbide volume fraction. This extensive plastic deformation is the cause of large asperity growth, pile-up and adhesion, which then becomes the onset of the galling process.
Figure 15
Stellite 6 G98 galling button cross-sections, tested at 350 MPa a) RT and b) 350°C. The Wear surface is shown at the top of the image. The depth of deformation and transformation increases with temperature, but no plastic flow is observed.

Figure 16
NOREM 02 G98 galling button cross-sections, tested at 350 MPa and a) RT and b) 350°C. The depth of deformation increases with temperature (from 2 to 15 µm), and at 350°C extensive plastic flow is observed around carbide phases.
Figure 17

Tristelle 5183 G98 Galling button cross-section tested at 350°C and 350 MPa. Extensive deformation and plastic flow can be seen up to 10 µm into the wear surface. Cracking of large carbides, (white particles) evidences the high stresses at the wear surface.

The results of X-ray diffraction phase analysis are shown in Figure 18 below. For each material, a clear deformation-induced martensite is evident at room temperature, FCC to HCP in Stellite 6 and FCC to BCC in Tristelle 5183 and NOREM02. The BCC peak is clearly evident in Tristelle 5183, but the martensitic peaks in NOREM02 and Stellite 6 are less pronounced. This smaller effect is most likely due to the penetration depth of the X-rays, which probe 10-15 µm into the surface, based on X-ray absorption. The diffraction spectra therefore include a large amount of undeformed base material, reducing the observed effect of the transformation. Nevertheless, the effect is robust and observable in all alloys at room temperature.
At high temperature, however, a marked difference between Stellite 6 and the stainless steel based compositions. At 350°C, the HCP martensite peak is still present and even increased, due to the increased wear depth and XRD penetration depth. However, both stainless steel compositions show no increase in the BCC martensitic peak in the probed volume. This is consistent with previous investigations and with the results of in-situ diffraction studies (presented below). The degradation in wear and galling properties is thus correlated with the disappearance of deformation induced martensite.

Although this correlation lends evidence to the hypothesis that galling-resistance is dependent on the presence of deformation induced martensite, the wear surface XRD does not offer direct proof of mechanisms under wear, or inherent material potential for phase transformation. Wear surfaces undergo large strains and local adiabatic heating that may alter the microstructure post-testing. For rigorous confirmation that the transition to severe adhesive wear is dependent on the strain-induced martensite deformation mechanism, observation of the alloy phase composition with strain in-situ is needed over a range of temperatures.
X-ray Diffraction profiles of G98 galling test samples that show strain-induced martensitic transformations. At RT all alloys show a SIM transformation; FCC to HCP in Stellite 6, and FCC to BCC in NOREM02 and Tristelle 5183. At 350°C, the HCP martensitic transformation is relatively unaffected Stellite 6, while the transformation in the stainless steels is absent ex-situ.
**In-situ Characterization of SIM in Hardfacing Alloys**

Two of the hardfacing alloys, NOREM02 and Stellite 6, were chosen for in-situ XRD tensile testing. In-situ X-ray diffraction was performed at the XTMS installation of the Brazilian Nanotechnology National Laboratory (LNNano), which is located at XRD-1 beamline of the Brazilian Synchrotron Light Laboratory - LNLS both part of the National Center for Research in Energy and Materials (CNPEM, Campinas, Brazil). The experimental setup consisted of a customized Gleeble® Thermomechanical Simulator integrated with a synchrotron X-ray beam at 12 keV (λ = 1.033 Å), with diffraction intensity collected by two MYTHEN (silicon microstrip) detector banks in fixed incidence angle geometry\(^1\). The samples were deformed in tension at a constant strain rate of \(1 \times 10^{-4} \text{s}^{-1}\). This strain rate is comparable to macroscopic rates for valve wear surfaces but certainly lower than the extremes experienced at wear surface asperities. The experimental data is expected to give a measure of the thermal and mechanical stability of the displacive martensitic transformations.

Each sample was strained to failure in tension at constant test temperature, measured with thermocouples along the gauge volume. A laser dilatometer provided the projection of sample cross section at the gauge center. This was used to calculate the strain during mechanical deformation. Diffraction data was recorded in three-second intervals during each tension test. Phase analysis was performed using custom peak-

\(^1\)More details are available at: [http://lnnano.cnpem.br/laboratories/cpm/facilities/xtms/](http://lnnano.cnpem.br/laboratories/cpm/facilities/xtms/)
fitting algorithms for the IgorPro® [11] and MATLAB® programming suites. Data from the extensometer, load cell, thermocouples, and diffraction setup were correlated and used for the structural analysis described above. The martensite transformation in both alloys was quantified using the integrated peak intensities of the (111) peak for FCC, the (101̅1) peak for HCP in the Co-alloy, and the (110) peak for BCC in NOREM02.

The volume fractions of the individual phases were computed from the integrated intensity of a diffraction peak (Dickson [12])

\[ I_{i}^{hkl} = \frac{K_2 R_{i}^{hkl} X_i}{2\mu} \]  

(1)

Here, \( K_2 \) is an instrument factor, \( \mu \) is the absorption coefficient, \( X_i \) is the volume fraction of a particular phase, and the theoretical intensity is given by

\[ R_{i}^{hkl} = \left( \frac{1}{V^2} \right) (|F^2| \cdot p) e^{-2M} \]  

(2)

\( V \) is the volume of the unit cell, \( F \) is the crystal structure factor, \( p \) is the multiplicity of the lattice plane reflection, and \( e^{-2M} \) is the Debye-Waller temperature factor. The temperature factor is neglected here because the tension tests were all performed at constant temperature with little deformation-induced heating. If the additional constraint

\[ \sum_i X_i = 1 \]  

(3)

is imposed, then the above equations furnish the volume fraction of each phase \( i \),

\[ X_i = \frac{I_{i}^{hkl}}{R_{i}^{hkl}} \frac{1}{\sum_i \frac{I_{i}^{hkl}}{R_{i}^{hkl}}} \]
In-situ diffraction during a thermal-resetting heat treatment for (a) Stellite 6 and (b) NOREM 02 alloys. The colored images show the diffraction intensities (red = high, blue = background) as a function of time and 2θ.

Due to surface polishing and machining, these alloys showed a significant amount of strain-induced martensite in diffraction prior to the beginning of the test. To examine the inherent strain-induced mechanics of the materials, therefore, a short-time thermal-resetting treatment was performed to revert the matrix phases to a purely austenitic state, free of surface strain-induced martensite. Figure 19 shows the results of the thermal-
resetting experiment. Prior to thermal resetting, the $(10\bar{1}0)$ and $(10\bar{1}1)$ diffraction peaks from the Co-alloy (Fig. 2a) indicate that strain-induced ε-HCP martensite was present. The data also confirms that the FCC phase and carbides ($M_7C_3$ and $M_{23}C_6$) were present. On heating above 846°C, the HCP diffraction peaks disappeared. On cooling back to room temperature, the relative ratio of diffraction peaks from the FCC and carbides did not change. Thus, the initial microstructure before the tension experiments consisted of only FCC and carbides, similar to actual service conditions prior to wear.

The diffraction data from NOREM02 () confirms that FCC, $M_{23}C_6$ and martensite were present prior to thermal resetting. The broad martensite peak arose since the diffraction geometry was not optimized to differentiate between the $(101)$ and $(110)$ peaks; this peak is termed the BCC $(110)$ peak hereafter. During heating, this broad peak initially moved to lower $2\theta$ position due to lattice thermal expansion, in agreement with the diffraction peaks from FCC and carbides. At around 560°C, however, the BCC $(110)$ peak shifted to higher $2\theta$ values, suggesting a reduction in lattice parameter. This reduction is interpreted as the onset of tempering, when carbon diffuses out of the BCC martensite structure [13]. Above 660°C, the BCC $(110)$ peaks shifted to lower $2\theta$ with increasing temperature. They also became sharper at higher temperature, consistent with a reduction in defect density. Above 900°C, the BCC $(110)$ peak decreased with increasing temperature. At 1000°C, only the diffraction peaks corresponding to FCC and carbides were present. During cooling, the diffraction data show that thermal martensite formed below 127°C.

Thus, the NOREM02 samples had predominantly FCC, carbides and small amount of
martensite prior to tensile testing. The thermal-resetting treatment therefore removed the surface effects related to sample preparation and enabled investigation of the deformation-induced martensitic transformation.

Figure 20
In-situ diffraction data during straining at RT of (a) Co-Alloy and (b) NOREM 02 Alloy. Blue corresponds to background counts and the red color corresponds to high intensity at peak position. The color scale is modified to highlight low intensity peaks.
Figure 20 shows typical data from thermomechanical straining of Co- and NOREM02 alloys at RT. The raw diffraction data vs. time is plotted as an intensity color map, with corresponding force, laser displacement and temperature vs. time. The straining results for the Co-alloy (Figure 3a) show the onset of the FCC→HCP transformation at 1000 s. In contrast, the NOREM 02 alloy shows some thermal FCC→BCC transformation before loading. The extent of transformation increases with plastic strain. Although the above data qualitatively demonstrate the strain-induced transformations, a quantitative analysis is needed to determine whether large differences in transformation behavior exist between the alloys.
Figure 21: Summary of diffraction and stress-strain analyses for all the data measured from (a) Co alloy and (b) NOREM 02. The experiments were not performed above 350°C for NOREM02 samples due to cessation of the FCC to BCT transformations.

Figure 21 presents a quantitative summary of thousands of diffraction spectra. Stellite 6 displayed large work hardening and less ductility at RT and 350°C, compared to 700 and 825°C (Figure 4a). This is rationalized in terms of both defect generation (measured by increases in peak width), and by the FCC→HCP transformation (measured by increases in HCP fraction) during plastic deformation. During initial straining, the observed work hardening correlates with defect generation in the FCC phase. The increases in FCC (111) peak width indicate that the defect generation was largest at RT and 350°C and
diminished to nearly zero at 825ºC. At larger strain (~3% for RT and 350ºC and ~6% for 700ºC), the FCC→HCP transformation was detected by diffraction. The rate of transformation, \( df/d\varepsilon \), was greatest at RT and 350ºC and it diminished to zero at 825ºC. The defect generation in the HCP phase was also largest at RT and 350ºC. Thus, the larger strain hardening at RT and 350ºC is attributed to higher defect generation in the FCC and HCP phases and the earlier onset of the FCC→HCP transformation, relative to 700 and 825ºC.

In Stellite 6, the HCP volume fraction was zero initially and it achieved a rather modest maximum volume fraction of ~0.02 to 0.03 for the RT, 350, and 700ºC cases. The low volume fraction is attributed to a thin (less than 50 nm thick) platelet morphology. This morphology co-deformed with the FCC matrix, as evidenced by the large increases in peak width with strain. The onset of the transformation occurred only after substantial defect generation in the FCC matrix. There was less defect generation at higher temperature and accordingly, the onset of the transformation was delayed. Overall, the stacking fault energy in Co-base alloys is relatively small [14] and this aids the formation of plasticity-induced defects. These defects are known to serve as nucleation sites for the transformation [15].

The Fe-base NOREM 02 alloy also displayed large work hardening at RT and 350ºC (Figure 4b), although it was smaller compared to the Co-base alloy. For example, the true stress increased to approx. 1 GPa in the Co-base alloy compared to approx. 0.7 GPa for
NOREM 02, during initial straining to 0.02. In this regime, both the Co-base and NOREM02 showed comparable increases in FCC (111) peak width at RT. NOREM 02 had pre-existing BCT (6 to 10%) that formed during cooling without load. Upon straining at RT, the FCC→BCT transformation commenced at < 0.5% (earlier than for Co-base) and the increase in BCT volume fraction was more than an order of magnitude larger than that for the HCP volume fraction in the Co-base alloy. The BCT phase acquired an abrupt increase in peak width in the 0.5-1% strain regime. Beyond that, the peak width remained constant, suggesting that the martensite acted as a non-deforming phase in a softer FCC matrix. This differs from the HCP/Co-base phase, which continued to deform and acquire defects over the duration of the test. At 350°C, NOREM02 did not exhibit any strain-induced FCC→BCT transformation and increases in FCC peak width were more modest. The NOREM 02 stress-strain curves at RT and 350°C diverged as the FCC peak widths for the two temperatures diverged. At 350°C, the modest reduction in BCC peak width was likely due to peak shifts from elastic loading. Overall, the work hardening at 350°C was smaller, the martensitic transformation was absent, and the defect generation in the FCC phase was reduced compared to RT.

*In-situ XRD Tensile Experiment Summary*

The in-situ diffraction investigation shows that the temperature-dependent galling resistance of Co-base and Fe-base (NOREM02) alloys correlate with the temperature-
dependent phase transformations and strain partitioning in these materials. In Co-base Stellite alloys, good galling resistance is exhibited from RT to 700°C, where a strain-induced FCC→HCP phase transformation is observed. At 825°C, the transformation is absent and galling resistance is poor. In NOREM 02, good galling resistance is exhibited at RT, where a strain-induced FCC→BCC/BCT transformation is observed. At 350°C, the transformation is absent and galling resistance is poor. Both alloys show decreasing strain hardening with increasing temperature. This correlates with a reduction in peak width broadening in both the FCC and martensite phases and a delayed onset and reduced magnitude of transformation. During straining of Stellite 6 between RT and 700°C, the initial hardening is associated with defect storage (peak broadening) in the FCC matrix with carbides, and subsequent hardening derives from the FCC→HCP transformation and defect storage in both the FCC and HCP phases. In NOREM 02, however, retained (6-10 vol.%) martensite (BCC/BCT) is present at the outset. Although defect storage monotonically increases in the FCC matrix, it is non-uniform and often negligible in the BCC/BCT phase, suggesting that it does not co-deform easily with the matrix.

Characterization of Everit 50 Galled Samples

The Everit 50 alloy, a fully martensitic stainless steel alloy with significant (approx. 30 vol %) chromium carbides, shows favorable wear properties in most of the ASTM G98
tests. This is primarily due to the high hardness of the martensite plus carbide microstructure, which favors small asperity deformations and crack formation at the surface, leading to small wear particles and a reduced overall steady-state wear. This same high hardness, however, makes part fabrication and durability difficult, as the many cracks seen in the following micrograph attest. These cracks run both through the part thickness and form over the surface of the part, potentially acting as initiation sites for later catastrophic crack growth.

![Micrograph of wear and cracks](image)

**Figure 22**

Everit 50 G98 Galling button cross-sections tested at RT and 350 MPa. Small wear debris and relatively flat surfaces attest to the excellent wear properties of the alloy. At high load, however, extensive cracking is observed, both at the surface (from wear action) and through-thickness cracks.

At high loads and elevated temperatures, however, a transition to a tribofilm wear mechanism takes place. As is shown in the figures below, a thin layer of material devoid of carbides is formed over the surface of the galled sample at high loads and temperatures.
(350°C at 40kN of normal load). This layer appears to be relatively uniform over the entire contact surface, and appears to have a similar lathe-like morphology presented in the SEM backscatter micrograph below.

Figure 23
Everit50 G98 galling button cross-section tested at 350 C and 350 MPa in a) Optical differential Interference contrast and b) SEM backscatter. A layer of carbide-free material, approximately 10 um thick, is observed at the wear surface. A lath morphology is observed in SEM backscatter.

This lath morphology is indicative of a martensitic transformation, which is corroborated by X-ray diffraction of the sample surface. In the figure below, the surface is confirmed to be BCC at high loads and high temperatures, with a peak shift to higher angle (i.e. a smaller lattice parameter) and the disappearance of carbides. This is consistent with a high temperature phase transformation, with the BCC matrix transforming to FCC
austenite at high temperature and ‘lubricating’ the surface. At these temperatures carbon
is a mobile species and may diffuse out of the tribofilm layer. As the sample is cooled to
room temperature after the test, the surface tribofilm would then be undercooled past the
Ms temperature and transform back to a carbon-depleted martensite phase. The high
temperature experienced during the formation of the tribofilm is also supported by the
appearance of a significant oxide peak on the Everit 50 galled sample surfaces.
Figure 24
X-ray diffraction of Everit50 G98 galled surfaces tested at 350°C with increasing load. At 40kN load (350 MPa) a shift in the BCC peak is found, along with the elimination of carbides and the formation of an oxide layer. This is consistent with a high-temperature austenite tribofilm formed during wear, subsequently transforming back to a carbon-depleted martensite upon cooling to RT.

The resulting wear mechanism is depicted schematically below. The tribofilm wear mechanism results from a phase transformation to a soft high temperature phase at the wear surface, which then preferentially shears and absorbs the mechanical energy of the sliding wear surfaces. This is analogous to the phase transformation mechanism that makes ice-skating possible. The tribofilm wear mechanism offers several advantages for engineering wear surfaces. The film is self-healing, as any exposed surface is quickly
loaded and transforms into soft austenite. The overall wear rate is actually decreased for many wear geometries, as the soft austenite retains wear debris. Because the shear is localized to the tribofilm layer, the mechanism of galling is eliminated by the inability of deformation to propagate into the base material.

Several challenges remain for implantation of such an alloy in a valve application process, however. The tribofilm wear mechanism results in an increase in the frictional force due to mechanical mixing at the wear surface, and may thus require larger motors in a real valve. The increase in friction, however, is predictable and less than an order of magnitude, typically. As the tribofilm observed here transformed back to martensite after the galling test, the effect of cycling temperatures on the wear mechanism in this alloy would be necessary to investigate. Finally, the effect of tempering on the wear mechanism must be understood so that manufactured parts will have acceptable toughness while still retaining excellent wear and galling properties.
To examine the applicability of the martensitic Everit 50 alloy to a valve hardfacing component, PM-HIP and tempering studies were performed. After the onset of tempering, the alloy hardness drops by a small amount. The tribofilm wear mechanism however, disappears, and the TGS drops from >340 MPa to less than 10 MPa. This loss of galling resistance is hypothesized to be correlated with the loss of interstitial content from the matrix due to tempering. As the matrix would have less interstitial content, the softer surface layer would experience less heating and may not reach temperatures sufficient for the BCC to FCC transformation. Pronounced strain-softening would then not occur, and the tribofilm would not be able to spread across the wear surface.
Characterization of GallToughPlus,

To investigate galling mechanisms, morphology, and properties in a fully austenitic stainless steel, similar wear specimen preparation was done on galled buttons of the GallToughPlus alloy. One of these specimens, tested at a 1kN load on the button sample, is shown in Figure 26. A large plowed trough is evident behind a region of pile-up behind the original asperity interface. The counter-surface sliding direction is roughly to the right in this figure. As the original small asperity reaches a critical condition, it rapidly grows, plowing into the surface and pushing up material behind in its wake. Examination of the mating surface (not shown here) shows evidence of a nearly identical process occurring on the mating surface (as might be expected in self-mated tribological couples).
Figure 26

Gall scar on GallToughPlus alloy a) top view (SEM) and b) cross-section after a RT ASTM G98 test at 1kN load. The original gall scar in a) was electrocoated with copper and ground to take the cross-section at approximately the dotted line. The original asperity interface with the pile-up behind it is evident in b).

This sample was the subjected to EBSD analysis to examine grain structure and orientation. Selections take to the left of the galling scar asperity interface in the trough, at the asperity interface, and to the right of the interface at the pile-up are shown in Figure
27. The severe nature of the surface deformation is evident in the EBSD patterns, with few indexable grains within 200 microns of the surface.

Of particular interest is the grain structure behind the asperity interface in the pile-up region in Figure 27f. Although heavily deformed, some grains can be indexed that show elongation along the vertical loading direction, indicating that they have been compressed by the moving and growing asperity interface. Furthermore, these grains near the surface are separated from the base material by a deformed band approximately 100µm thick, indicating inhomogeneities in the strain field. **It is proposed that these features are a characteristic of a strain localization process.**
Figure 27
SEM (a, b and c) and EBSD (d,e, and f) imaging of sections of the gall scar in Figure 26. Images to the left of the original asperity interface in the trough of the gall scar (a, d), at the interface (b, e), and to the right of the interface at the pile-up (c,f) are shown. Note the grains in the pile-up, although heavily deformed, can be indexed, separated by a dark band of un-indexable material approximately 100 µm wide.
Finally, nanoindentation of the galled surface was performed to examine the effect of this extreme surface processing on the hardness of the material. Nanoindentation to 500 nm depth was performed in an array, and the average hardness of the material was taken between 200 and 300 nm. Microscopy of the indents was then performed to measure distances to the affected wear surfaces. This was done across the gall scar and far away in the unaffected base material. The results are shown in Figure 28 below.

Material deformation during the ASTM G98 test clearly indicates a large effect of hardening, with the average hardness 5.4 GPa approximately 10 µm from the wear surface, raised from a bulk value of 3.5 GPa. No discernable difference in the location of the indents with hardness was observable based on these tests.
Figure 28
Hardness vs. Depth below the wear Surface for GallToughPlus ASTM G98 sample cross-section tested at room temperature.

Summary

The transition to severe adhesive wear behavior, termed galling, is a distinct and separate process in different stainless steel systems. It depends on both external loading conditions, and on inherent material properties, like yield strength, as well as phase stability and microstructure. In a particular duplex stainless steels, a softer austenite phase preferentially deforms to form a tribofilm on the surface, with a sublayer of primarily ferrite underneath. The transition to severe wear is then controlled by interface de-bonding between these two layers and the unaffected base material underneath.
In martensitic stainless steels filled with carbides, the significant hardness of the material in the untampered state prevents large surface deformations and lowers wear rate. At very high loads, the transition to severe adhesive wear may be characterized by a transformation from BCC to FCC at high temperature, which forms a soft, uniform tribofilm on the surface of the sample. This tribofilm can act as a solid-phase lubricant, taking up shear strain and retaining wear debris. The formation of this tribofilm however is dependent on surface heating from adiabatic deformation. As a consequence, after tempering treatments that lower the hardness, tribofilm formation is no longer observed and the galling properties of the alloy are significantly degraded.
A schematic of the hypothesis for galling initiation in austenitic stainless steels. Note that only one strain localization is shown here for simplicity; for catastrophic asperity growth, multiple events would be necessary for 3 dimensional asperity contact enlargement.

Austenitic stainless steels show a tendency to form larger and more seizure prone galling scars which are controlled by a catastrophic growth of single asperities (or equivalently coalescence of several asperity junctions into a single contact). Based on metallographic examination of gall-scar cross-sections of simple austenitic stainless steels (GallToughPlus and 316L) the hypothesis was developed that this catastrophic growth is mediated by a strain-localization process under the highly deformed wear-affected surface. This process zone in front of a localized shear zone has relatively low accumulated strain and lower temperature rise compared to the wear surface. The
propagating strain-localization event must overcome the strain-hardening and geometric tendencies toward homogeneous deformation to cause the galling process. It is therefore proposed that this process zone controls the initiation of the galling process. Thus by engineering the inherent material properties in this region, the tendency toward strain-localization (and thus galling threshold stress) may be affected.
Chapter 5: Investigation of the Temperature Dependence Hardfacing Alloy Properties

**EBSD**

**Figure 30**

a) EBSD orientation image map and image quality map of room temperature Norem02 sample showing an un-indexable region of ~2 µm below the galled surface and b) EBSD orientation image map of high temperature tested Norem02 sample with an un-indexable region

In the case of the Norem02 sample tested at elevated temperature (Fig. 17b), this un-indexed region appears to be larger and ranges to ~15 µm below the galled surface of the sample. Within this highly deformed layer, there appears to be a mottled presence of
carbide particles (~2 µm), which have been clearly indexed. Furthermore, the matrix away from the galled surface clearly shows the austenite grains. Just below the deformed layer, these austenite grains seem to indicate grain growth phenomenon (~15 µm) with an aspect ratio of 2:1, along with an apparent preferred orientation of the grains. From the SEM and EBSD analysis it is clearly evident that the size of the highly deformed layer formed underneath the galled surface of the two samples are different. The elevated temperature sample seems to show an increase in the size of the deformed layer by a factor of 7. This behavior could be due to a decrease in the yield strength of the material at elevated temperature. In order to further understand the phases present in these deformed layers of the galled room and high temperature samples, XRD analysis was carried out on the galled surfaces.

Figure 31 shows a comparison of the XRD results from Norem02 samples tested at room and high temperature at a load of 20kN, under which both set of samples exhibited galling. From the results, both the samples show the prominent peaks of FCC [(111) and (200)] and M$_{23}$C$_6$ carbides, which is similar to the phases seen in the monolith Norem02 alloy obtained from the powder processing. However, both alloys show the presence of martensite phase, as is evident from the martensite peaks in the XRD. The conspicuous difference between the two samples is the change in the peak intensities of FCC and martensite phases. In the room temperature tested sample, the peak intensity of FCC phase (both (111) and (200)) is lower than that from the sample tested at higher temperature, which could indicate that the amount of FCC phase in the room temperature
sample is higher. Furthermore, the amount of martensite phase in the room temperature tested Norem02 sample appears to be higher than that in the high temperature sample as is evident from the increase in the peak intensity of martensite phase in the XRD analysis of the room temperature sample. From the XRD analysis, it appears that martensite formation takes place when Norem02 samples are subjected to galling conditions, which was not present in the powder processed sample of Norem02. To investigate the microstructure formed at the deformed regions and examine the location of martensite formation, the two samples were studied under a transmission electron microscope.

Figure 31
XRD analysis results of room and high temperature galled Norem02 samples tested under a load of 20kN, showing peaks of martensite. The amount of martensite in the room temperature sample seems to be higher than in the high temperature sample. The trend in FCC peak changes is reversed.
Figure 32 shows the extraction of a TEM sample from the room temperature galled surface of the Norem02 sample using a focused ion beam sample extraction. The image shows the electroplated layer of Cu located on the left. The extracted sample spans a depth that ranges from galled surface (as indicated on the image) to well into the interior of the sample. Fig.19b is an image of the extracted sample in a TEM with a small portion of Copper still attached to the sample as shown in the image. On this TEM sample, two regions of interest were closely examined: 1.) close to the galled surface that low-index, highly deformed region in EBSD (i.e. <2µm from the surface as marked in Figure 32 and 2.) away from the surface (~10 µm from the surface).

Figure 32
a) Image showing the location of TEM foil extraction just below the galled surface cross section and b) the same extracted sample observed in TEM marked with the region of interest.
Figure 33 is a magnified bright field image of the region shown in Figure 32. The image shows a distribution of very fine grains (<100nm) in the highly deformed region formed near the galled surface. This region could not be indexed by EBSD most probably because of the grains being much finer than the electron beam size in SEM (~ 0.1µm). It is believed that formation of fine grains just below the galled surface is because of recrystallization of highly deformed grains resulting from the galling behavior of the contacting surfaces. Evidence for the formation of such a nano-grained region has been shown by other researchers [22,23]. Figure 33b shows a diffraction patterns obtained from the nano-grain region of Figure 33a. The presence of sharp concentric rings in the diffraction image confirms the presence of nano-grains near the galled surface. Upon indexing the diffraction rings, it was found that this region consists of both austenitic and ferritic crystals as indicated in the diffraction pattern. In a similar fashion, the region farther away from the galled surface was also studied.
Figure 33
a) A bright field image showing presence of nano-grains in the high deformed region marked in Figure 30 just below the galled surface and b) diffraction pattern obtained from the same region showing discrete concentric rings indicative of very fine grain size and indicating the presence of both FCC and BCC phases by indexing
Figure 34

a) Extracted TEM foil showing a second area of interest farther from the highly deformed region shown in Fig.17b and b) bright field image from this region showing parallel lath type structures which appears to be martensite.

Figure 34 shows the microstructure at a distance ~12µm from the galled surface. The magnified bright field image taken from this region shows the presence of lath type structures that is indicative of the presence of martensitic microstructure (Figure 34 b). The diffraction pattern obtained from the region in Figure 34 b is shown below in Figure 35c. The diffraction pattern was indexed as that belonging to a BCC structure. Figure 35a and Figure 35b show dark field images that were taken by selecting the two of the bright diffraction spots as shown. From the dark field images, the two chosen spots in the diffraction pattern seem to be originating from different variants of martensite. Similar TEM investigation was carried out on Norem02 high temperature sample to understand the changes in the microstructural features occurring at high temperature.
Figure 35
Dark field images a) and b) taken from region (shown in Fig. 19b)) showing different variants of martensite indicated by the diffraction spots (20c)).

From the SEM and EBSD analysis, the elevated temperature Norem02 galled sample showed evidence of a larger plastically deformed region than that formed in the room temperature galled sample. SEM images show a ~15 µm region underneath the galled surface where the grains of the matrix were not clearly distinguishable. The EBSD analysis showed an un-indexed region, which was about 7 times larger than that seen in
the room temperature Norem02 sample (~20 µm). For these reasons, the size of the TEM sample that was extracted for analysis was larger than that of the Norem02 room temperature tests. The sample spanned a depth of ~20µm from the galled surface. The microstructure of this sample was studied closer to the galled surface and at a region away from the galled surface.

Figure 36 shows a bright field image taken from a region close to the galled surface (<1µm). The image appears very similar to that of Norem02 room temperature microstructure taken from the highly deformed region. The diffraction pattern obtained from this region (Figure 36b) also shows concentric rings, which upon indexing showed the presence of both FCC and BCC crystals similar to the room temperature Norem02 sample (Figure 33). Hence, the microstructure in the deformed region of Norem02 sample tested at high temperature also consists of very fine nano-grains of austenitic and ferritic grains. The development of similar phase makeup and grain size at both temperatures corroborates the hypothesis that this nanolayer is formed in a manner similar to phase-reversion steel microstructures. However, as the exact loading and temperature cycle are unknown, and this test is ex-situ, this remains an open question.

However, farther away from the interface, the elevated temperature test sample did not show an evidence of martensite formation unlike the situation observed in the room temperature sample. The grain structure observed from this region consisted primarily of deformed austenite grains where banding was observed, but no BCC phase or orientation
changes were found in diffraction patterns. It is therefore hypothesized that at high temperature NOREM02 deforms by shear banding (or similar strain localization process) as the original unaffected material is loaded during wear testing.

Figure 36

a) Bright field image taken from the highly deformed region in high temperature tested Norem02 sample showing very fine nano-grained region similar to that seen in low temperature sample (Figure 33) and b) Diffraction pattern from this region showing discrete rings indicating the presence of very fine grains, upon indexing show the presence of both FCC and BCC crystals

The plastically deformed regions formed because of the galling action can be divided into two regimes: 1.) A very fine nano-grained region that forms just below the galled surface (<2µm), and 2.) A deformed region that lies farther away from the galled surface, where hardening is evidently achieved by strain-induced martensitic phase transformation. It is hypothesized that the formation of this strain-hardened region limits the plastic
deformation to a thickness of few microns below the surface and prevents the bulk of the materials from being affected by the surface loading. These results also corroborate well with the reported martensite formation in Norem02 alloys by other researchers [8,24], who also arrived at a similar hypothesis of surface deformation limited by transformation induced strain hardening. Furthermore, the highly deformed regions of samples tested at both room and high temperature showed very fine nano-grain structures that were found to have both austenitic and ferritic grains. It has been shown that a thin region of very fine microstructure is formed just beneath the wear surface during relative motion of contacting surfaces [22,23]. It is believed that the BCC rings obtained in the TEM diffraction patterns could be from small martensitic grains, which shares microstructural similarities with high-pressure torsion and phase-reversion induced nanocrystalline steels. However, because of the very fine size of the grains present in these regions, distinguishing between martensite and ferrite and the origin of the BCC phase was not possible here.

The formation of this deformation-induced martensite, below the nano-grained region in the room temperature tested Norem02 alloy, is attributed to the meta-stable nature of the austenitic matrix in the as-processed Norem02 samples. As mentioned previously, thermodynamic equilibrium dictates that at room temperature, the expected amount of ferrite in Norem02 is ~65% by volume, which was not observed in the as-processed sample. There is thus a large driving force for the formation of a BCC martensite phase that allows formation of martensite upon deformations of the surface.
Figure 37
Schematic representation of the changes in the microstructure occurring during galling conditions in Norem02 during low and high operating temperatures

Summary

Norem02 stainless steel hardfacing alloy shows good galling resistance (TGS> 300 MPa) at room temperature due to the formation of deformation induced martensite during testing, which restricts the deformed region to a small zone (~2µm) below the galled surface. The presence of BCC martensite lathes under the wear surface was confirmed by post-test XRD and TEM. Large (>5 µm long) laths are found under the highly deformed layer (3-5 µm below the surface), while nanoscale (<50 nm) sized BCC phases are found within the highly worked nanocrystalline surface region.
However, as the operating temperature increases, the driving force for this martensitic transformation is expected to decrease. This expectation is confirmed by in-situ XRD tensile deformation, which detects no strain-induced martensite transformation in NOREM 02. This reduces or eliminates the extent of martensite transformation taking place at higher temperature leading to a larger (~20 µm) deformed layer and promotes the onset of galling at lower loading conditions, thereby reducing the galling threshold.
Chapter 6: Characterization and Optimization of Nitromaxx, a Nitrogen-modified Stainless-steel Hardfacing Alloy

The effects of nitrogen alloying on stainless steel hardfacing was studied by adding nitrogen to the melt composition during the manufacturing process of powder-metallurgy manufactured stainless-steel hardfacing alloys. The alloy powders were then vacuum packed and hot isostatically pressed (HIPed) at 100 atm. at 1000°C to densify the metal compact according to standard PM-HIP specifications. The interstitial content and thermodynamic stability of the precipitates are known to be a strong function of temperature[21]. Various heat treatments were then performed to determine the effect on the microstructure stainless steel hardfacing alloyed with nitrogen.

The previous investigations of existing hardfacing alloys (NOREM02 and Stellite 6) were evaluated along with other candidate alloys to gain insight into the process of galling and the dependence on material microstructure. Key conclusions from this activity are: 1) PM-HIP processing is superior to weld cladding for hardfacing part fabrication because fewer defects are generated and weldability and galling properties are decoupled; 2) a different optimization approach is required for each alloy as the mechanism of severe
adhesive wear differs among alloys; and 3) galling in austenitic stainless steels shows massive, non-uniform strains at the wear surface and in gall scars.

These insights were then used to identify several compositions and heat treatment processes for a 2nd generation of hardfacing alloys. Austenitic stainless steels were chosen as a primary focus for development since NOREM02 displays good room temperature galling behavior and the alloy system well understood. Alloying compositional changes as well as thermodynamic databases are therefore more predictable. *Alloy design objectives emerged from the hypothesis that strain localization controls the onset of galling.* These objectives included:

1) Decrease the stacking fault energy to increase the strain-hardening rate in the metal matrix,

2) Increase interstitial strengthening to decrease the depth of surface deformation, and

3) Increase the volume fraction of hard, non-deforming phases (e.g., carbides and nitrides).

These alloying strategies follow from known dependencies of metals[16] and cermet-type materials [30] on strain localization properties[29].

These specific goals can be met with nitrogen modification of existing stainless steel alloys to affect the galling properties, as shown schematically in Figure 38. By adding nitrides to the material microstructure, the propagation of strain-localizations is made more inhomogeneous, raising the overall energy necessary for the process. Adding
interstitial nitrogen to the austenitic matrix phase is expected to raise the yield strength by impeding dislocation movement. Large amounts of matrix nitrogen may also lower the SFE in stainless steels, which can affect the plastic deformation processes and result in higher strain-hardening by a variety of mechanisms (as discussed above). Partitioning of nitrogen with alloy content and heat treatment is first discussed for optimization, followed by wear morphology and deformation mechanism changes in the alloy due to nitrogen content.
Figure 38
Alloy design approach for increasing galling threshold stress in stainless-steel hardfacing alloys. Based on a phenomenological hypothesis that galling initiation is controlled by strain-localization properties, nitrogen alloying can affect the microstructure and properties of the alloy to delay this process.

**Microstructure of Nitromaxx Alloy**

The initial strategy for alloy engineering was to mimic basic attributes of Stellite 6, which is a proven materials system with excellent galling-resistance for hardfacing applications. An austenitic (FCC) metal matrix, as found in both Stellite and Nitromaxx, is desirable
for corrosion, temperature stability, and material compatibility with base metals for valve bodies (typically 316L stainless steel). Second, the underlying thermodynamics and deformation mechanisms are understood well. Third, the matrix exhibits a large strain hardening rate over a large temperature range, in part due to relatively low stacking fault energy[12]. Finally, additions of hard secondary phases have been shown to provide abrasive wear-resistance and resistance to surface strain-localization[27].

Table 4
Nominal Composition of Nitromaxx Alloy

<table>
<thead>
<tr>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>25</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>3.5</td>
<td>1.2</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Nitromaxx is a new alloy developed to mimic these basic attributes of Stellite 6 but in a cobalt-free form. The composition of Nitromaxx is shown in Table 3-1. It is similar to NOREM02 but has additional nitrogen. The SEM micrographs in Figure 3-1 demonstrate that a matrix phase is surrounded by secondary phases. The identity of these phases and their structures were quantified using Reitveld refinement of X-ray diffraction patterns. The results in Table 4-1 indicate that Nitromaxx consists of an austenitic matrix plus 35 vol% M\textsubscript{23}C\textsubscript{6} carbides and 15 vol% Cr\textsubscript{2}N nitrides, for a total of 50 vol% hard secondary phases. Thus, one result of nitrogen alloying is a significant increase in the fraction of nitride phases. These hard phases are expected to suppress surface
deformation during wear and contribute to galling performance by promoting strain hardening in the matrix phase and disrupting shear bands (see Section 2.3).

Figure 39
Comparison of Alloy Microstructures: a) Stellite 6, b) NOREM 02, and c) Nitromaxx

Nitrogen alloying was shown to increase the proportion of hard secondary phases, via nitrides, but the phase fraction of these nitrides were not a strong function of annealing temperature. This is also born out through thermodynamic modelling of Nitromaxx using the ThermoCalc software package. The molar fraction nitrides and carbides are not a strong function of temperature over the range of 1000 to 1200°C, as shown in Figure 39. This was also born out in metallographic studies of the alloy using point counting methods (Figure 40).
Microstructures of stainless-steel hardfacing modified with nitrogen. Samples etched with Vilella’s etchant, and subsequently boiling NH$_4$OH. Carbides are light grey, and nitride phases are colored black. Nitrogen content, and subsequently nitride content, increases to the right.

Thermodynamic modelling of the system, however, shows that heat treatment can affect the matrix composition and interstitial content. The interstitial nitrogen content in equilibrium is shown in Figure 42 below as a function of temperature, increasing monotonically with annealing temperature. This is consistent with work on similar stainless steel compositions. The complex compositional equilibria exhibited between
the carbide and nitride species is a possible source of this nitrogen. Even small amounts of nitrogen can increase the lattice parameter (approximately 0.0009Å per atomic fraction of N[31]) and provide significant increases in yield strength (up to 120 MPa per wt% N) and strain-hardening rate[32]. Heat treatment studies to determine the effect of annealing temperature on the structure and properties of the Nitromaxx alloy were therefore performed.

Table 5
Phase balance of Hardfacing Alloys

<table>
<thead>
<tr>
<th></th>
<th>Matrix</th>
<th>% Volume Fraction</th>
<th>Secondary Phases</th>
<th>% Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stellite 6</strong></td>
<td>FCC</td>
<td>70</td>
<td>M₁₂₃C₆</td>
<td>30</td>
</tr>
<tr>
<td><strong>NOREM 02</strong></td>
<td>FCC</td>
<td>65</td>
<td>M₁₂₃C₆</td>
<td>35</td>
</tr>
<tr>
<td><strong>Nitromaxx</strong></td>
<td>FCC</td>
<td>50</td>
<td>M₁₂₃C₆</td>
<td>35</td>
</tr>
<tr>
<td>(HT1 and HT2)</td>
<td></td>
<td></td>
<td>Cr₂N</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 41
Thermodynamic Phase Equilibrium for Nitromaxx Alloy as a Function of Temperature. The phase balance results in an FCC matrix and carbide and nitride phases. The FCC matrix is meta-stable at low temperature. Note: the amount of phase is shown in molar fraction.
Interstitial nitrogen in FCC vs. equilibrium temperature, as predicted from thermodynamic simulations (CALPHAD). The Nitromaxx chemistry was simulated at each equilibrium temperature in the ThermoCalc ® software after suppression of non-observed phases (M₇C₃).

**Heat Treatment Optimization**

Initially, both NOREM02 and Nitromaxx samples were hot isostatically pressed (HIP) at 1000°C, and then characterized using X-ray diffraction. The results showed that the lattice parameter of the FCC matrix was nearly identical for the as-made samples at 3.585±0.005 Å. This is significant as the lattice parameter is known to increase linearly...
with interstitial (including nitrogen and carbon) content in the FCC matrix. The data therefore suggest a similar interstitial matrix composition in both Nitromaxx and NOREM02, after HIP processing.

In principle, an increase in matrix interstitial nitrogen may be an avenue to increase matrix strain hardening and increase wear and galling resistance (Section 4.1). Therefore, Nitromaxx samples were annealed for 2 hours at temperatures ranging from 1000 to 1200°C. This is the recommended range of annealing temperature for 316L stainless steel, the most common valve gate base material. Results are reported for a 2 hour annealing time since longer times did not quantitatively change the Nitromaxx alloy structure or microstructure. The annealed samples were then investigated with a microhardness indenter and X-ray diffraction. Thermodynamic simulation of the alloy using the ThermoCalc suite was also performed to compare expected phase compositions as a function of heat treatment.
Figure 43
FCC Lattice Parameter of Nitromaxx vs. Annealing Temperature. Nitromaxx samples were heat treated at temperature for 2 hours and water quenched.

Figure 4-2 shows that the lattice parameter of the FCC matrix in Nitromaxx increases monotonically with annealing temperature. Table 4-3 shows that the corresponding hardness values also increased monotonically with annealing temperature. This increase in alloy hardness is attributed to an increase in matrix hardness as the volume fraction of nitrides remained relatively constant (10-15 vol%) for all heat treatment temperatures. Based on thermodynamic simulation and known effects of nitrogen, these measurements are hypothesized to be due to increased matrix nitrogen in the FCC matrix. The results also suggest that this trend extends to even greater annealing temperature, although 1100°C is the maximum annealing temperature for the base valve gate material 316L, per ASTM specifications[33]. An 1100°C anneal for 2 hours is recommended as it achieves
significant increases in lattice parameter and hardness of the FCC matrix phase while remaining within the specification of the valve gate material.

Table 6
Hardness vs Annealing Temperature of Nitromaxx

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>HVN</th>
<th>HRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOREM02 1050 °C</td>
<td>419 ±8</td>
<td>43 ±0.7</td>
</tr>
<tr>
<td>Nitromaxx 1050 °C</td>
<td>405 ±6</td>
<td>41 ±0.5</td>
</tr>
<tr>
<td>1100 °C</td>
<td>444 ±6</td>
<td>45 ±0.5</td>
</tr>
<tr>
<td>1200 °C</td>
<td>468 ±9</td>
<td>47 ±0.8</td>
</tr>
</tbody>
</table>

_Alloy Optimization Summary_

The addition of nitrogen to a NOREM base alloy results in a microstructure with an increased number of hard second phases, including both Cr$_2$N and M$_{23}$C$_6$. During heat treatment to the original Norem02 specification of a 1050°C annealing temperature, the matrix showed a very similar lattice parameter, indicating that the matrix interstitial nitrogen was not changed by the melt nitrogen addition. Heat treatment studies were thus
carried out to increase the matrix nitrogen composition. Higher annealing temperatures and resulted in an increase of the FCC matrix lattice parameter, indicative of increased matrix nitrogen concentration. Additionally, macro-hardness of the Nitromaxx alloy increases with increasing annealing temperature, supporting the conclusion that nitrogen matrix content increases with higher temperature. An optimized temperature of 1100°C was chosen as a compromise between hardfacing properties and the heat treatment specification for 316L type stainless steels.

Galling Sample Characterization

The Nitromaxx samples annealed at 1100°C (HT2) showed improvement in Threshold Galling Stress (TGS) and wear rate as compared to the original annealing temperature HT1(1050°C) and especially compared to other stainless steel hardfacing alloys, such as NOREM02. Table 4-1 summarizes the galling properties based on the ASTM G98 galling test. Details of the study are available in EPRI Report 3002003923. Stellite 6, NOREM02, and Nitromaxx exceed Threshold Galling Stresses (TGS) of 300 MPa at 25°C, yet at 350°C (PWR operating conditions) NOREM02 degrades significantly while Stellite 6 and Nitromaxx maintain a high galling stresses.

The Nitromaxx alloy with HT2 annealing treatment (1100°C) shows galling characteristics comparable to or better than Stellite 6. This is also evident on galled surfaces after high temperature testing, as shown in Figure 4-4 below, where Nitromaxx
HT2 and Stellite6 both have similar surface features at similar size scales, namely, limited surface deformation, original surface machining visible, and surface oxide formation. In contrast, the elevated temperature NOREM02 sample shows much larger and extensive galling scars and ‘prow’ formation, indicative of deep surface deformations and resulting mechanical locking. The results of nitrogen alloying and heat treatment optimization thus lead to better galling resistance which is both quantifiable and readily apparent in tribological applications.
Table 7
ASTM G98 Galling Properties

<table>
<thead>
<tr>
<th>ASTM G98 Threshold Galling Stress (MPa)</th>
<th>Test Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>25°C</td>
</tr>
<tr>
<td>Stellite 6</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Nitromaxx (HT2)</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>NOREM02</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>GallTough Plus</td>
<td>15</td>
</tr>
<tr>
<td>316L</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 44
Sample Surfaces in the ASTM G98 test at high temperature (350°C) and 15ksi (100 MPa) in a) NOREM02, b) Nitromaxx, and c) Stellite 6. Note scale differences in a), where large scale galling scars require larger field of view. These gall scars are eliminated in the Nitromaxx alloy and Stellite 6, where more uniform deformation and oxidation are observed. Surface deformation is limited enough to see the original ground surfaces in b and c.
For alloy modification, the chemical, microstructural, and deformation mechanics contributions underlying the galling performance are of interest. To study these effects, samples taken from the ASTM G98 galling test were prepared for metallographic examination. Buttons tested under the highest applied load (15 ksi) were electrodeposited with a layer of copper (to protect the wear surface for microscopic examination). They were then sectioned, and polished to below 50 nm surface roughness. The samples were then investigated with optical and SEM microscopy for surface morphology, wear particle formation, and metallographic structure.

Figure 45
Gall scar cross-sectioning sample preparation for the ASTM 98 test

The results of this cross-sectioning are shown below. In Error! Reference source not found., the galled surfaces of NOREM 02 tested at RT and 343°C are shown with SEM backscatter imaging. Severe plastic deformation is observed in all galled surfaces, with
the depth of deformation increasing with temperature. In NOREM 02, the deformed layer increases significantly from approximately 3 to 15 µm when the temperature is elevated. This is indicative of lower hardness due to loss of yield strength and strain hardening. In contrast, Figure 4-6 shows the high-temperature (343°C) cross-sections of the Nitromaxx and Stellite 6 alloys. Both alloys show very similar (<3 µm) plastic zone depths, within which there are high densities of lath microstructures. This indicates that the nitrogen addition increases the galling threshold stress by preventing plastic deformation into the depth of the contacting surface. This is a likely consequence of an increase in work hardening and hardness at high temperature. The possible deformation mechanisms to achieve these increases are thus investigated using in-situ diffraction techniques and ex-situ TEM microstructural investigations.
Figure 46
ASTM G98 galling button cross-sections of NOREM 02 tested at a) RT and b) 343°C with SEM backscatter imaging. The depth of the plastically deformed region increases significantly at high temperature, from approximately 3 to 15 µm.
Microstructure of ASTM G98 button cross-sections in a) Nitromaxx and b) Stellite 6, tested at 343°C. Nitromaxx retains a small plastically deformed surface region (< 3 µm) even at high temperature.

**Surface Oxides on Galling-resistant Hardfacing Alloys**

A final similarity observed in Nitromaxx and Stellite 6, the hardfacing alloys with acceptable high temperature wear performance, is the presence of surface oxides on high-temperature ASTM G98 specimens. These oxides can be observed in Figure 44b and c as dark regions along the outer periphery of the samples. Note that these oxides are not observed on worn surfaces of alloys with poor galling performance. They are indicative of the high temperatures experienced by the contacting surfaces even after very short sliding distances and times (the G98 test imposes a single revolution of the surfaces).
The lack of gall scars and the presence of oxides further indicate the extreme conditions of wear and galling, due to mechanical work in the near surface layers. These oxides result from the increased temperature at the surface due to deformation. (As the mechanical work being imposed on the surface remains the same for equal frictional conditions, the local flash temperature must increase[34]).

Figure 48
SEM and EDS (XPS) micrographs of oxides on the surface of high-temperature ASTM G98 specimens of a) Nitromaxx and b) Stellite 6. The surface layers show increases in oxygen content.
The oxides are composed, in both cases, of fine lamellar debris interspersed with a phase that has high oxygen content. Both surface layers are approximately 3 - 5 µm thick, depending on location, and are surface-adherent. These layers show low intensity in electron backscatter microscopy, indicating a lower effective atomic density. They also show no contrast or coherent electron-backscatter diffraction, and are not observed in X-ray diffraction, indicating a structure that is either amorphous or highly faulted. All of these observations are consistent with an amorphous or faulted oxide formed in a near surface layer on the samples.

These oxides are observed here on an austenitic stainless steel hardfacing alloy for the first time in literature (although they have been previously observed in Stellite alloy tests[35]). Such layers have been connected to the good wear and galling properties of these alloys, but definitive mechanisms for their influence remain elusive, primarily due to the difficulty of in-situ tribological characterization. Their mechanism of formation is also uncertain, being formed either from debris re-deposition and mixing[35], or an enhanced surface diffusion process resulting in a thicker than expected (from steady-state oxide kinetics[34]).

Summary

Nitrogen modification of a stainless-steel hardfacing alloy increases the wear resistance and increases the galling resistance (Threshold Galling Stress) as measured in the ASTM G98 test compared to NOREM02. The difference is pronounced at elevated temperature
(350°C), where the wear and galling properties of NOREM02 are substantially lower. The Nitromaxx alloy annealed under the same conditions as NOREM02, with similar matrix properties, showed increases in elevated temperature TGS. This shows the influence of additional nitride precipitates alone on the galling properties of the stainless steel hardfacing alloy. Heat treatment of the Nitromaxx alloy at 1100°C increases the wear and galling properties to a level comparable to Stellite 6, especially at elevated temperature. This improvement in high-temperature wear properties is attributed to an increase in interstitial nitrogen content in the matrix, as correlated to FCC lattice parameter and thermodynamic simulation. Compositions and heat treatment conditions that optimize the matrix nitrogen concentration and volume fraction of hard secondary phases result in a stainless steel hardfacing optimized for elevated temperature galling conditions.
Chapter 7: Mechanistic Study of Nitrogen Alloying in Stainless-steel Hardfacing

In-situ XRD

A central theme of this effort is to increase galling resistance by increasing both the strain-hardening of the matrix and the volume fraction of hard phases. A mechanism that provides the highest level of strain-hardening achievable in FCC metals to induce the formation of martensite (SIM) during straining. SIM has been correlated with the galling properties of NOREM02 at room temperature\[15\]. Above 200°C, the amount of SIM in NOREM02 is reduced significantly and the galling resistance decreases catastrophically from >300 MPa to 30 MPa as shown in Table 7 ASTM G98 Galling Properties.

The FCC to BCC strain-induced martensite transformation (SIM) in stainless steels is initiated by the formation of high-energy defect sites during plastic deformation. Martensite nucleates at these sites, which include places where shear bands and stacking faults intersect\[36\]. The addition of nitrogen is proposed to increase the generation of defect sites during plastic deformation, by lowering the stacking fault energy (SFE) in the Nitromaxx alloy\[37\]. In particular, the Olson-Cohen model of SIM suggests that a greater rate of defect site generation should increase the rate of martensite nucleation and
also increase the temperature at which a given amount of SIM transformation occurs[36]. Thus, the conditions under which the FCC to BCC SIM transformation occurs are dependent on the underlying plastic deformation during straining of the FCC matrix. This includes not only crystallographic slip (dislocation motion) but also twinning. For example, greater rates of FCC to BCC SIM have been measured in stainless steels when twinning and SIM were observed to occur simultaneously[24]. In those cases, greater strain-hardening rates were also observed.

Plastic deformation mechanisms in Nitromaxx were studied using in-situ diffraction at the National Nanotechnology Laboratory (LNNano) at the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. A Gleeble thermomechanical simulator was set-up in the path of a synchrotron X-ray beam at the XRD-1 beamline. An X-ray beam energy of 12 keV (wavelength 1.033Å) and a reflection geometry were used as schematically shown in Figure 49. Information on the structure and amount of various phases was then collected during tensile testing under chosen temperatures under vacuum. More details of the experimental setup are available at: http://lnnano.cnpem.br/laboratories/cpm/facilities/xtms/.
Figure 49
LNLS In-situ diffraction schematic. Temperature and tensile load are applied concurrently during a powder θ-2θ diffraction experiment.
Figure 50

Example In-situ data collection during RT tensile test of the Nitromaxx alloy. Diffraction patterns, temperature, force, and area contraction (measured by laser extensometer) are all collected as a function of time.

Figure 5-2 shows an example of the resulting data for Nitromaxx HT2 during tensile testing at RT. The force (kN), change in cross sectional dimension (mm), sample temperature (°C), and diffraction peaks as shown as a function of increasing time during tensile straining at a rate of 0.01/s. During straining at room temperature, the FCC (111) and (200) peaks diminish from an large initial intensity (red) to a smaller intensity (green), while the BCC (220) peak increases in intensity. Thus, the FCC to BCC SIM is observed qualitatively. To quantify this diffraction intensity change, the peaks were fit.
using a custom algorithm in the IgorPro and Matlab programming suites and normalized. The fraction of FCC and BCC phases in the matrix were quantified by calculating the normalized intensities of the (111) and (110) peaks, respectively. More information about the experiments and data reduction is available in Smith et al. (2014).

Table 8
Volume % of Hard Phases and FCC Lattice Parameters in Stainless Steel Hardfacing Alloys

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>A. NOREM02</td>
<td>1050 °C</td>
<td>3.585</td>
<td>0.12 wt% N</td>
</tr>
<tr>
<td>B. Nitromaxx (HT1)</td>
<td>1050 °C</td>
<td>3.582</td>
<td>0.45 wt% N</td>
</tr>
<tr>
<td>C. Nitromaxx (HT2)</td>
<td>1100 °C</td>
<td>3.602</td>
<td>0.45 wt% N</td>
</tr>
</tbody>
</table>

Lattice parameters of the FCC phase were primarily a function of annealing temperature, while the volume fraction of hard secondary phases is primarily a function of melt nitrogen composition (due to nitride formation). The results of Reitveld refinement at RT prior to tensile testing are shown in Table2. FCC matrix lattice parameters are similar for similar annealing conditions (NOREM02 and Nitromaxx annealed at 1050°C), and larger at higher annealing condition (1100°C), regardless of nitrogen alloying content. Conversely, the volume fraction of hard secondary phases (carbides and nitrides) is greatly increased with increased nitrogen content regardless of annealing temperature.
These results are consistent with the effects of heat treatment studies in Section 4.2 above.

The deformation behavior of these structural effects is shown in Figure 5-3, the fraction of matrix that transformed to BCC vs. straining at room temperature. Nitromaxx and NOREM02 had a similar SIM response when both alloys were heat treated at 1050°C for 2 hrs. The similar response of the matrix occurred even though Nitromaxx had 15 vol% of nitrides (vs. 0 vol% for NOREM02). The lattice parameters and transformation behavior thus suggest that the matrix composition and deformation kinetics are similar and do not depend on overall alloy composition.

The amount and rate of martensite evolution with strain can be seen to increase however with annealing temperature. Figure 5-3 shows an increased amount of SIM when the Nitromaxx was annealed at 1100°C rather than 1050°C. From Table 5-1, the lattice parameter of the matrix is also increased with higher heat treatment temperature. The results demonstrate that increasing the nominal melt nitrogen composition alone is insufficient to change the rate of SIM in the matrix, and that increasing heat treatment temperature can increase the rate of martensite evolution with strain. It is hypothesized, therefore, that matrix composition and underlying deformation mechanisms are primarily controlled by equilibrium heat treatment temperature in the Nitromaxx alloy.
Strain-induced martensite kinetics (FCC to BCC transformation) at room temperature in NOREM 02 (HT1) and Nitromaxx annealed at 1050 (HT1) and 1100 °C (HT2). The SIM kinetics are identical for NOREM 02 and Nitromaxx HT1, whereas Nitromaxx HT2 evolves more martensite per unit strain. This is most likely due to differing SFE from matrix composition differences, such as nitrogen.

Although the matrix composition and properties can be controlled by heat treatment temperature, the temperature stability (thermodynamic potential) of the SIM transformation does not appear to be significantly affected by nitrogen alloying or heat treatment. Figure 5-4 shows the results for tensile straining at elevated temperature up to 350°C, for NOREM02 heat treated at 1050°C and Nitromaxx heat treated at 1100°C. Figures 5-4 (b, d) show that both alloys suffer a significant reduction in SIM with
increasing test temperature. The results suggest that the excellent galling resistance of Nitromaxx at 350°C (Table 4-1) cannot be attributed to SIM. The benefit of the nitrogen addition and elevated annealing temperature (1100°C) to the SIM is modest. In particular, the equivalent Md₅₀ temperature (the temperature at which the matrix is 50 vol% martensite at 30% strain) is only 15°C greater for Nitromaxx HT2 vs. NOREM02.

However, increased matrix nitrogen may still alter the underlying plastic deformation mechanism (through SFE), leading to improved high temperature properties. Figures 5-4(a, c) demonstrate a difference in the temperature dependence of the stress-strain response between NOREM02 and Nitromaxx. In particular, NOREM02 displays a continuous decrease in flow strength and strain hardening with increasing test temperature. However, Nitromaxx HT2 shows a decrease in strength and strain hardening from RT to 150°C. From 150°C to 350°C, a large desirable strain hardening is maintained. The maintained strain-hardening rate can serve to suppress strain localization during wear testing and it suggests a change in deformation mechanism in Nitromaxx HT2 above 150°C. This is also supported by quantitative differences in the peak broadening of the FCC diffraction patterns during high temperature deformation, which is indicative of a change in stacking fault energy and/or deformation mechanism. To summarize, nitrogen addition appears to alter the deformation mechanisms across all test temperatures. It enhances SIM at RT but does not alter the temperature stability of the transformation at elevated test temperatures. In this elevated temperature regime, the
larger strain hardening suggests a fundamental change or enhancement in deformation mechanism other than SIM (such as twinning).

The resultant strain-hardening rate (and thus the ultimate tensile strength) is larger at high temperatures for Nitromaxx than for NOREM02, as shown in Figure 5 4c. The strain-hardening rate drops appreciably in NOREM02 from 150°C to 350°C, but the stress-strain response of Nitromaxx remains very similar over the same temperature range. This is the same temperature range over which the strain-induced martensite transformation is small or non-existent. A separate change in the deformation mechanism of the matrix is thus necessary to explain this increased strain-hardening rate (e.g. twinning).
Figure 52
Elevated temperature In-situ Tensile Testing of NOREM 02 (a, b) and Nitromaxx (c, d). The temperature stability of the FCC to BCC SIM transformation is not increased, but the tensile test maintains a higher level of strain-hardening at 350°C

Summary

In-situ diffraction testing shows that in the original heat treatment condition, the strain-induced martensitic phase transformation in Nitromaxx HT1 at room temperature evolves with nearly the same strain kinetics as the original NOREM02. This indicates that strain induced defects have similar energies in the two alloys, and the improved wear and
galling of Nitromaxx at the original heat treatment is due primarily to the additional hard second phase constituents (nitrides). Nitromaxx heat treated at higher temperatures shows faster strain-induced martensite strain kinetics, which is consistent with a change in defect density behavior from fitting to the Olson-Cohen model of SIM. This is consistent with nitrogen lowering the stacking fault energy in the FCC matrix, and corresponds to the higher strain-hardening rate observed through high temperatures. This work confirms that nitrogen acts to introduce more hard second phases, increases hardness, and increases strain hardening rate in the matrix, and that these mechanisms correlate to the galling behavior as outlined above. Although the strain-induced phase transformation was not observed at high temperature (e.g. above 200°C), the change of strain kinetics indicates an underlying alteration of the defect behavior and resulting mechanical properties up through high temperature. In the following, TEM investigation of tested galling samples is done to confirm the change in deformation mechanism with alloying content.

**TEM Investigation of Galled Surfaces**

As SIM was not observed in elevated temperature testing, alternative hypotheses for the effect of nitrogen and heat treatment were investigated through microstructural studies of wear specimens. The plastic deformation mechanisms were investigated using transmission electron microscopy (TEM) of galled surface cross-sections. The investigation focused on samples from ASTM G98 testing at elevated temperature
The galled button cross-sections, in Figures 5-2 and 5-3 were used for TEM foil extraction. Figure 5-5 depicts a process by which focused ion beam (FIB) milling was used to trench, undercut, and then thin small sections of material from under the galled surface of tested Nitromaxx samples. These electron-transparent samples were then characterized using TEM.

![Diagram of FIB foil machining from ASTM G98 gall button wear surface cross-sections.](image)

Figure 5-6 shows a representative result from the TEM investigation of Nitromaxx (at the optimized 1100°C heat treatment). Extremely fine grains (<50 nm) are observed at the wear surface as a result of severe plastic deformation during the galling test. At a distance 3 µm below the wear surface, deformation is reduced enough so that fine-scale (10 nm or less) thick lathes can be observed in the FCC matrix. Selected-area diffraction patterns
(SADP) show a clear twinning orientation along the (110) zone axis, confirming that these lathes are indeed deformation twins. Specifically, the diffraction pattern shows doubling of general diffraction spots, except those of type (hhh). These peaks correspond to a twin invariant plane of (111), the expected invariant plane in FCC materials like stainless steels[38].

Figure 54
Morphology and Structure Confirmation of Deformation Twinning in Nitromaxx gall button sample tested at 343°C. Selected area diffraction patterns of lath microstructures confirm twinning orientations (right) in material under the wear surface.

Subsequent sampling of different grains indicates this is a general deformation mechanism for Nitromaxx at elevated temperature. Additional diffraction patterns confirm that deformation twinning structures are observed between 2 and 5 µm below the
wear surface (Figure 5-7 below). Closer to the wear surface, the grain size is nanocrystalline (< 50 nm, due to severe plastic deformation). Nanometer-scale lathes are observed consistent with twinning, but the resolution of the selected area diffraction patterns is insufficient to confirm deformation twinning by individual crystallite structure. No fine-scale twinning structures are observed at distances > 5 μm from the wear surface. The increased deformation twinning is consistent with a decrease in the stacking fault energy at test temperatures. The hypothesis is supported that a reduction in stacking fault energy is caused by the added matrix nitrogen in Nitromaxx. This deformation mechanism, as well as the interstitial strengthening due to matrix nitrogen, is also hypothesized to cause the decrease in wear depth observed in Figure 46.
Figure 55
Total extent deformation twinning in Nitromaxx AST G98 sample tested at high temperature.

Further observations indicate that the twinning observed in Figure 5-8 is due solely to the mechanical deformation of the material during the ASTM G98 galling test, and was not a pre-existing artifact of machining or sample preparation. A similar morphology was observed in TEM samples harvested from the opposing (block) surface of the same Nitromaxx HT2 specimen, after ASTM G98 testing at 343°C. Figure 5-8 shows TEM results from material in the as-prepared state that was not deformed during the G98 test. These samples were harvested from a portion of the block surface outside of the test area.
Near-surface deformation is observed, consistent with the surface machining process but no twining morphology or BCC phase was observed in the diffraction pattern in the deformed layer. Twinning has yet only been observed in areas affected by the elevated temperature ASTM G98 test itself.

Figure 56
a) TEM sample from outside the G98 Worn Surface of Nitromaxx; b) dark field images showing the fine FCC grains observed at ~1µm depth form the surface with no diffraction evidence for twins; (c) similar dark field images from a deeper region showing only shear bands at 70° to each other. The zone axis of this image is close to <110>.

TEM Measurement of Stacking Fault Energy
The stacking fault energy of the alloys can be determined by imaging dislocations with transmission electron microscopy (TEM). Dislocations with a perfect lattice Burgers vector can dissociate into two partial dislocations that repel each other. This repulsion is balanced by the energy of the stacking fault between the two bounding partials. If the partial dislocations are able to achieve equilibrium, then the stacking fault energy (SFE) can be estimated from the equilibrium distance between the two partial dislocations. The character of the dislocation and the elastic constants of the crystal are required.

Figure 57
Transmission Electron Microscopy imaged in Weak Beam Dark Field conditions of stacking faults in stainless-steel hardfacing alloys a) Nitromaxx and b) NOREM02
Figure 57 shows images from TEM foils that were extracted from under wear surfaces deformed at elevated temperature, using FIB milling techniques (as described above). The samples were imaged under bright field (BF) and weak beam dark field (WBDF) conditions. A near [111] zone axis tilt was used to observe dislocation pairs on {111} slip planes (typical of FCC materials), using <−220> type diffraction vectors. Following the approach of Pierce et al. [39], a g(4g) diffraction condition was adopted for partial dislocation imaging, with ‘inside out’ diffraction condition reversal to determine the position of the partial dislocations bounding a stacking fault. Approximately 20-25 pairs of partial dislocations were imaged in each sample. An average and standard deviation was determined for the partial separation distance (stacking fault width) in each material.

The experimental partial spacing measurements can be related to stacking fault energy based on a formalism by Aerts et al [40]. This is determined from the equilibrium separation width of the two partials using approximations for crystalline anisotropy and image distortion due to local stress fields:

\[ d_{\text{eff}} = \frac{\mu_{\text{eff}} b^2}{8 \pi \gamma} \left( 1 - \frac{2 \nu_{\text{eff}} \cos 2\beta}{2 - \nu_{\text{eff}}} \right) \]

The stacking fault energy is \(\gamma\), \(b\) is the partial dislocation burgers vector (equal to \(a/6<112>\) in FCC stainless steels), \(\beta\) is the total dislocation character angle, and \(\mu_{\text{eff}}\) and \(\nu_{\text{eff}}\) are the effective shear modulus and Poisson’s ratio on the \(\{111\}\) slip planes that contain the stacking faults. The effective constants are used to approximate the fully
anisotropic expressions. They have been shown by Timoshenko to be an excellent fit to experimental data in FCC and BCC metals[39]. The preceding in-situ diffraction studies of in-situ tensile testing yield a value of $\mu_{\text{eff}} = 73$ GPa, with a value of $\nu_{\text{eff}}$ taken as 0.31 from literature (typical of austenitic stainless steels) [12]. The dislocation character angle (the angle between the Burgers vector and dislocation line direction) was not determined from the experiments. This is due primarily to a variation in strain and thickness contours so that the extinction criteria ($g \cdot b$ analysis) could not be achieved reliably. This uncertainty in character produces bounds on the stacking fault energy as the character angle rotates from 0 to 90 degrees. For calculation of the stacking fault energy, $\beta$ is taken as 90 degrees to give an upper estimate of the SFE.

The results in Table 7 indicate that the higher matrix nitrogen content in Nitromaxx increases the average stacking fault width and thereby decreases the average stacking fault energy. These measurements may be indicative of elevated temperature properties, as the induced defects were imposed at elevated temperature (343°C). This assumes that the stacking fault width did not change during cooling. The SFE of Nitromaxx is < 20 mJ/m², the empirical range [41] below which twinning becomes accessible in FCC alloys.

A complication is that the standard deviation is comparable is large. An interpretation is that all partial dislocations were not at the equilibrium value of $d$ prescribed in the above equation. This could arise, for example, from internal stress from nearby defects, free surfaces, sample bending, and lattice resistance to dislocation motion. These effects could
in principle cause deviations in $d$ that are larger or smaller than the equilibrium value but in principle, these deviations should be centered about the equilibrium value if the internal stress fluctuates around zero. Under this assumption, the difference in *average* stacking fault width is used to distinguish between the two alloys. The effect of internal stress could be addressed in part by performing measurements in regions with a smaller dislocation density and by heating and cooling the sample to attempt to allow dislocation configurations to equilibrate.

Table 9
Summary of TEM SF Measurements of HT Deformed Hardfacing Alloys

<table>
<thead>
<tr>
<th></th>
<th>SF Width (nm)</th>
<th>SF Energy (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norem02</td>
<td>8 ± 6</td>
<td>30 ± 20</td>
</tr>
<tr>
<td>Nitromaxx</td>
<td>14 ± 5</td>
<td>10 ± 20</td>
</tr>
</tbody>
</table>

*Summary*

TEM investigations of Nitromaxx HT2 samples show fine scale (<10 nm width) twins in regions 2-5 µm below surfaces that were deformed during ASTM G98 tests at elevated temperature (343°C). These features are consistent with deformation twins. Several samples were analyzed to ensure that the observations are representative within the sample to confirm a generalized behavior. No fine scale twins were observed at a
distance > 5 µm from the wear surface, nor were they observed in TEM samples taken from outside the worn area. Thus, this twinning deformation mechanism is directly correlated with surface deformation during high temperature wear.

Direct measurements of SFE using separations of dislocation partial pairs confirm that the addition of nitrogen and heat treating the sample for <give the conditions> reduces the mean value of stacking fault energy. The reduction in stacking fault energy is consistent with the creation of defects during deformation that can serve as nucleation sites for martensite. The reduction can also promote the formation of deformation twins. The reduction in SFE is consistent with the creation of defects during deformation that can serve as nucleation sites for martensite. The reduction can also promote the formation of deformation twins.

The reduction in SFE is can be used to rationalize the observed increased martensite formation during straining at room temperature (Section 5.1) and the pronounced deformation twins observed in samples deformed at 343°C. Nitromaxx therefore benefits from strain-induced martensite formation at room temperature and strain-induced twins at higher temperature. Although the errors in measurement are large (due to the high density of defects from large strains), the measurements support a reduction in stacking fault energy from approximately 30 mJ/m² to 10 mJ/m².


Chapter 8: Discussion

The transition to severe adhesive wear or galling behavior at elevated temperature has found to occur in this work via different mechanisms depending on alloy system. Depending on microstructure, phase stability, and deformation mechanism in the alloy, deviation from steady-state surface contact regimes (separate independent asperities) can occur by formation of surface layers over a wide area, or catastrophic growth of single asperities. Specifically, in a duplex stainless steel alloy the softer phase (austenite) deforms preferentially, forming a tribolayer across the sample. Severe adhesive wear occurs when this deformed layer de-bonds and tears from the surface. A tribofilm forms in an un-tempered martensitic stainless steel by phase reversion to the high-temperature stable austenite, which preferentially deforms as a kind of solid-state lubricant.

In contrast to these film-forming behaviors, austenitic stainless steels undergo a process of asperity growth and coalescence, where a single surface contact point grows several orders of magnitude in size in an avalanche process, taking up all surface loads. Based on metallographic and microscopic characterization, this catastrophic asperity growth process is hypothesized to be initiated and propagated by a strain-localization or load instability process, similar to shear banding. Proceeding from this hypothesis, increasing the galling threshold stress in austenitic stainless steels should be increased by

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microstructural and property alloy modifications that make strain-localization processes more difficult (i.e. require higher stresses). Additions of hard second phases in a material microstructure are known to make shear band propagation more difficult, as long as the particles are at least as large as the shear band width. Higher strain-hardening rates are also known to directly oppose strain-localization processes. Higher hardness decreases the average asperity size and depth of highly deformed material at the wear surface, which decreases the adhesive bond driving force for the strain-localization process. Finally, nitrogen alloying is proposed as a method to achieve all three of these goals through nitride formation, stacking fault energy modification, and interstitial hardening in an austenitic stainless steel hardfacing alloy.

Nitromaxx is a stainless steel hardfacing alloy that has been modified by increasing the nominal nitrogen content by adding 0.45wt% nitrogen, and subsequent heat treatment to increase interstitial content in the matrix. It achieves the proposed goal to match the wear and galling resistance of a cobalt-base alloy, Stellite 6, over a temperature range from RT to 350°C. The wear morphologies of Nitromaxx and Stellite 6 were similar, showing surface oxides and no large excrescences or gall scars up through 350°C. Deformation depth into the affected surfaces of galled buttons showed similar morphology and deformation depth, 3-5 µm for samples tested at high temperature. This compares with NOREM 02 which had affected depths greater than 15 µm at high temperature.
Both hard secondary phase additions and alteration of matrix properties showed empirically beneficial effects on galling properties. First, modification of the stainless steel hardfacing by adding nitride hard phases showed an increase in threshold galling stress. XRD and in-situ XRD studies showed that additions of nitrogen for the same annealing conditions as the original alloy (1050°C), however, resulted in an FCC matrix with the same structure and similar lattice parameter, mechanical properties, and deformation mechanism. The increase in threshold galling stress at high temperature between NOREM02 and Nitromaxx annealed at the same temperature is therefore attributable to the addition of nitrides alone.

Secondly, increasing the annealing temperature of Nitromaxx to 1100°C also showed a measurable increase in galling properties and qualitative difference in wear surface morphology. Increased annealing temperature was shown to increase the matrix lattice parameter. This observation is consistent with thermodynamic models that show that interstitial content increases with annealing temperature. This annealing condition also increases the formation of martensite during straining at room temperature, and the formation of twins during straining at elevated temperature. The latter correlates with improved elevated-temperature galling resistance in stainless steel hardfacing.

These observations of the effects of nitrogen alloying and processing are consistent with the hypothesis that galling is initiated by a strain-localization process. At elevated temperature, the observation of deformation twinning correlates with increased strain.
hardening. The latter is expected to suppress strain-localization. Also, the volume fraction of secondary hard phases and hardness increase. These effects, coupled with increased strain hardening, are consistent with the reduced depth of surface deformation observed at elevated temperature. Galling properties may be improved by preventing asperity growth from reaching a critical value for the initiation of strain-localization. At the same time, the critical stress and necessary asperity size is increased by the increased strain hardening rate of the matrix and path complexity of the strain-localized region caused by the large hard phases in the microstructure. The result is a much more uniform surface deformation with few localized deformation spots, and no gall scar initiation. This results in similar macroscopic qualitative and quantitative wear behavior to Stellite 6.

While this work is highly correlative in nature between the structure, material properties, and wear and galling performance of hardfacing alloys, it does not attempt direct measurements of the galling type process in stainless steels, primarily due to the high complexity of such experiments. Direct measurement of the nitrogen modified stainless-steel matrix composition has not been attempted in this work, instead relying on correlations with XRD measurement and previously established relationships. Nitrogen compositions of stainless-steel hardfacing alloys would be desirable with a high-resolution probe, e.g. Electron Energy Loss Spectroscopy. The measurement of mechanical properties has so far been done under conditions unlike that of the wear surface; although the temperatures are the same, the strain-rates and stress states are
unlike those expected at the wear surface and contacting asperities. For example, while many material mechanical properties were measured in tension at low strain-rate, asperity deformation and sliding is expected to be high-strain rate with complex, reciprocating compression-tension stresses (Chapter 1). The exact state of stress at the wear surface is also expected to have large gradients, and evolving microstructure and properties, which are not fully known especially in cases of severe adhesive wear. One reason for this is directly related to the degree of difficulty in direct observation of two surfaces in contact. Correlation of galling properties with mechanical properties measured in compression and torsion over a range of temperatures (RT to 500°C) and strain rates ($10^{-3}$ to $10^4$ s$^{-1}$) would help to resolve this unknown. Finally, direct measurement of shear banding strain-localization tendencies in austenitic stainless steel hardfacing alloys would be desirable for direct correlation with galling properties. Split-Hopkinson hat specimens or torsional impact loading would be desired to most closely mimic the high-strain-rate shear stress expected to be experienced by the gall test sample surface.
Chapter 9: Summary and Conclusions

Rapid alloy development of a 2nd generation hardfacing alloy has produced Nitromaxx, a PM-HIP, nitrogen-modified stainless steel alloy. It has excellent wear and galling properties from room temperature to 350°C but does not have the concerns of cobalt contamination associated with Stellite 6.

The mechanism of galling was investigated metallographically and differentiated into distinct phenomena in different alloy systems. In the austenitic stainless steels, observations of galled samples developed the hypothesis that strain-localization behavior is the controlling mechanism for galling behavior initiation (Figure 29). Nitrogen modification was targeted at the deformation mechanisms and phase balance to suppress strain-localization.
Nitrogen modification of an austenitic stainless steel-based hardfacing alloy successfully improves high-temperature wear and galling properties. Addition of nitrogen (approximately 0.45 wt% N) to the melt results in 15-20 vol% of nitrides (along with ~35 vol% M_{23}C_{6} carbides, Table 1) in a matrix with similar lattice parameter to NOREM02, correlated with thermodynamic simulations of lower interstitial content (Figure 42). Similar matrix lattice parameters and RT strain-induced martensite were
confirmed with in-situ X-ray diffraction (Table 8). These microstructural and compositional effects reduced the depth of surface plasticity (Figure 46), resulting in a change in the wear scar morphology and higher threshold galling stress.

Studies for alloy heat treatment optimization were carried out. Increasing the annealing temperatures up to 1200°C monotonically increases the matrix lattice parameter (Figure 43). This experimental result is consistent with an increase in matrix interstitial nitrogen with increasing annealing temperature. This trend is also supported by thermodynamic modeling. The higher annealing temperature increased macro-hardness (Table 6), reduced wear depth (Figure 47), and increases threshold galling stress (Table 7) also resulted from higher annealing temperature. An optimized heat treatment temperature of 1100°C was chosen to meet the annealing schedules of the base 316L stainless steel, the upper temperature allowed in the ASTM specification for 316L.

A higher annealing temperature was shown to affect the dominant deformation mechanisms and properties. X-ray diffraction measurements during in-situ tension testing showed that at room temperature, the matrix phase of Nitromaxx (annealed at 1100°C) undergoes a pronounced FCC to BCC strain-induced transformation (SIM). The volume fraction of transformed product is greater than Nitromaxx alloyed at 1050°C and an unmodified stainless steel alloy, NOREM02, also annealed at 1050°C (Figure 51). When Nitromaxx and NOREM02 are both annealed at 1050°C, they exhibit a nearly identical but relatively reduced SIM formation with strain. This indicates that annealing...
temperature can control the interstitial content and this in turn controls the matrix deformation behavior.

Further studies with X-ray and transmission electron microscopy (TEM) showed that wear at elevated temperature (350°C) induces deformation twinning in the matrix in the highly-deformed, near-surface region. Thus, the strain-induced transformation that is present at room temperature is not observed above 200°C. However, Nitromaxx also shows superior at elevated temperature compared to NOREM02 (Figure 52). Evidence for the high-temperature twinning deformation mechanism in Nitromaxx was confirmed by TEM, using FIB foil cross-sections taken from ASTM G98 galling test specimens tested at 343°C (Figure 54). Direct measurements of stacking fault energy (SFE) were made in both Nitromaxx and NOREM02 samples deformed at elevated temperature (343°C). The results show that that average SFE decreases from ~30 mJ/m² for NOREM02, to ~10 mJ/m² for Nitromaxx (A complication is that the standard deviation is comparable is large. An interpretation is that all partial dislocations were not at the equilibrium value of $d$ prescribed in the above equation. This could arise, for example, from internal stress from nearby defects, free surfaces, sample bending, and lattice resistance to dislocation motion. These effects could in principle cause deviations in $d$ that are larger or smaller than the equilibrium value but in principle, these deviations should be centered about the equilibrium value if the internal stress fluctuates around zero. Under this assumption, the difference in average stacking fault width is used to distinguish between the two alloys. The effect of internal stress could be addressed in part
by performing measurements in regions with a smaller dislocation density and by heating and cooling the sample to attempt to allow dislocation configurations to equilibrate.

Table 9). This is consistent with literature values for transition to twinning induced plasticity in stainless steels (see 135). Conversely, no twinning deformation has yet been found in NOREM02 G98 galled samples tested at high temperature.

These investigations correlate the excellent galling performance of Nitromaxx with higher hardness and strain hardening at elevated temperature from nitrogen modification. High melt nitrogen and heat treatment result in microstructural modifications (hard second phases) and changes in the deformation mechanism in the matrix. These mechanisms include an increased strain-induced phase transformation at room temperature and a change in strain hardening rate and mechanism at elevated temperature. Specifically, deformation twinning observed in at elevated temperature (350°C) test samples is consistent with a change in deformation mechanism through SFE modification. The higher hardness and strain hardening effects are consistent with the hypothesis that galling in stainless steels is dependent on a strain-localization mechanism. The optimized Nitromaxx alloy shows that improving properties which suppress strain-localization in stainless steels can yield a stainless-steel hardfacing with optimized performance at room and elevated service temperatures.
References


Rolls-Royce and Associates, Ltd.: Great Britain.


23. Fang, X.F.a.D., W., *Strain hardening and transformation mechanism of


and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications. 2014.


46. Magee, J.H., Two galling resistant stainless steels used for bridge hinge pins, Carpenter Technology Corporation: Reading, PA. p. 6.
56. Ocken, H., The galling wear resistance of new iron-base hardfacing alloys: a


75. Wadman, B.e.a., *Influence of surface texture on the galling characteristics of lean duplex and austenitic stainless steels,* in Duplex World 2010 Conference and Exhibition. 2010: Beaune, France.

Metallurgical and Materials Transactions A, 1996. 27A.
