Developing Corrosion Resistant Alloys Using Big Data

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Abstract

Utilizing big data to govern decisions is becoming increasingly valuable and corrosion resistant alloy design is no exception. This paper will discuss how big data techniques can be employed to design disruptive materials technology. Big data material informatics can significantly accelerate the discovery of new alloy solutions. More than 100 years of experimental research underpins the science employed, but modern computational tools and materials informatics principles enable new decision strategies to be utilized. The big data approach relies on calculations which predict the microstructure of millions of alloy compositions and utilizing proprietary data mining algorithms to identify unique materials spaces which would never be discovered experimentally. Several examples will be used to demonstrate this novel technique, specifically the development of corrosion resistant coatings for refinery and power generation equipment as well as laser cladding alloys for the protection of marine hydraulic rods.

Keywords

“Big Data” “ICME” “Thermal Spray” “Laser” “EHLA”

Introduction

Integrated Computational Materials Engineering (ICME) is a developing technology whereby the performance of materials and systems can be predicted across multiple length scales. One segment of ICME is the Calphad method, which utilizes experimental data to calculate phase diagrams of potentially complex alloys. Such techniques are relevant to the design of corrosion resistant materials which are being driven into ever more demanding and customized applications. This paper discusses several corrosion resistant materials developed using a proprietary software platform, the rapid alloy development (RAD) system, to design customized alloys for emerging applications and processes. The RAD approach marries the utilization of thermodynamic calculations with a big data approach [1].

The big data approach enables the evaluation of millions of alloy compositions in a quick efficient manner. Such an approach enables the development timeline of novel materials to be significantly reduced from years to months on average. With the reduction in development timeline, it is possible to design more customized alloys tuned to both performing in specific applications and to functioning in specific processes. An example of the latter, process specific alloy design, is presented in the development of alloy technologies intended for two different process technologies: 1) laser or extreme high speed laser (EHLA) deposition, and 2) twin wire arc spray deposition.

The RAD methodology is constantly evolved via a feedback loop to improve accuracy and interpretation. Three products will be presented in various stages of development. Firstly, the development of nickel-based alloys for hydraulic rods are presented. In the case of this alloy family, the relationship between microstructure and performance was less understood at project initialization. Therefore a thorough study of experimental alloys with different microstructural features was conducted to identify the optimal product. Alloy N4 is the outcome of this study and experimental results are presented. Secondly, the development of iron-based alloys, also for hydraulic rods, is
presented. In this case, the RAD software has been embedded with predictive algorithms for iron-based hardfacing alloys from previous related projects. As such, the development of the iron-based alloy required fewer experimental iterations and less uncertainty on the desired final microstructure. Alloy F1 is the outcome of this second study. Both alloys N4 and F1 are intended for hydraulic rod applications but are experimental at the time of publication. Thirdly, the incorporation of learning from the development of a now commercialized product, Metco 8453 are presented. In this example, the development of a Ni-based alloy for high temperature corrosion protection yielded useful learnings which has now been fed into the RAD model for future development. Alloys F1 and N4 and the RAD technique are patent pending, Metco 8453 is covered under US patent # 9802387 and pending international filings.

**Big Data Mining**

All the alloys presented here were developed using big mining processes. One example of utilizing RAD for the design of a Nickel based abrasion and corrosion resistance resistance is shown in Figure 1. Figure 1 plots 56,231 different alloy compositions, whereby each alloy is represented by a single dot according to the predicted abrasion and corrosion resistance. The abrasion resistance is governed in part by the volume fraction of hard phases, such as chromium carbide, in the microstructure. The corrosion resistance is governed by the chemical composition of the Nickel matrix as opposed to the composition of the alloy itself. From this visualization interface, a series of alloys can be selected to meet the desired performance criteria. While, Figure 1 depicts a simple two dimensional analysis of the data, it is possible to control additional performance aspects such as crack sensitivity, weldability, and alloy cost simultaneously.

*Figure 1 : Visualization of 56,231 alloys according to their predicted abrasion and corrosion resistance utilizing the Rapid Alloy Development technique*
**Experimental**

Experimental alloys, F1 and N1-N5, were atomized into 45-105 μm powder to be deposited via laser. A 2kW Laserline Laser was used to do the deposition of the samples. Each powder was used to make a 100mm x 100mm and 3mm thick sample which was used to measure crack susceptibility, corrosion resistance, abrasion resistance and conduct microstructural analysis.

Dye penetrant testing was conducted in accordance to ASTM E165 on all samples to determine whether any stress cracking had occurred during or after the laser cladding process. Microstructural analysis was conducted using either a Zeiss Axio Observer.D1m optical microscope or a Tescan scanning electron microscope. Matrix chemistries were measured using energy dispersive spectroscopy. Abrasion resistance was measured via ASTM G65 procedure A (6,000 revolutions) at an outside laboratory.

**Marine Applications – Ni-Based Alloys for Hydraulic Rods**

In order to combat the corrosion seen in marine applications, more expensive and more alloyed materials have been used such as duplex stainless steels or Ni-Cr-Mo superalloys. Although these alloys are sufficiently corrosion resistant for many applications, they tend to be soft and have poor abrasion resistance. Elevated abrasion resistance is often required for hydraulic cylinder rods. In both dynamic hydraulic systems where the rod is cycling several times a minute, and systems that are exposed to sand and silt, duplex steels and common superalloys have a reduced life due to abrasion.

Several alloy compositions where selected as shown in Figure 2A-E in order of increasing hard phase fractions, Alloy N1 (Figure 2A) being the lowest, Alloy N5 ((Figure 2E) being the highest. Per design using Figure 1 and similar RAD plots, each alloy has a similar matrix chemistry with only hard phase fraction being the microstructural variable. Alloy N4 was selected for further study as it produced the best combination of crack, abrasion, and corrosion resistance in early experiments. Figure 2F shows the liquid dye penetrant testing of Alloy E as a 5 layer laser clad overlay, which indicates zero cracking in the overlay.

**Table 1 : Comparison of Alloy N4 with Conventional Abrasion and Corrosion Resistant Alloys via ASTM G65 Procedure A Dry Sand Abrasion Testing**

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>ASTM G65A Volume Loss</th>
<th>Microhardness HV&lt;sub&gt;300&lt;/sub&gt;</th>
<th>Cr, Mo Content in Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimet</td>
<td>452 mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>305</td>
<td>Cr: 26%, Mo: 5%</td>
</tr>
<tr>
<td>Stellite 6</td>
<td>277 mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>423</td>
<td>Cr: 21%</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>232 mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>282</td>
<td>Cr: 21%, Mo: 9%</td>
</tr>
<tr>
<td>Alloy N4</td>
<td>201 mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>389</td>
<td>Cr: 20%, Mo: 11%</td>
</tr>
</tbody>
</table>

The performance of Alloy N4 was benchmarked against several standard materials common for use in combined abrasion/corrosion environments: Ultimet, Stellite 6, and Inconel 625 as shown in Table 1. As shown Alloy N4 exhibits the best abrasion performance and high hardness. The matrix composition is a good indicator of the corrosion behaviour of the material in various environments, and suggests Alloy N4 should perform similarly to Inconel 625. One concern is the potential microstructural galvanic interaction between the hard
phases and the matrix itself. However, early test results show no accelerated galvanic corrosion occurring between the matrix and hard phase precipitates.

Non-Marine Applications – Fe-Based Alloys for Hydraulic Rods

A similar methodology was used to design an Fe-based alloy with stainless steel level corrosion resistance. In this example, a pre-existing thorough understanding of Fe-based alloys was utilized in the design, and a multi alloy study was unnecessary. As such, the RAD technique could be immediately transitioned into product development without much iterative

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**Figure 2:** Optical Micrographs of experimental Nickel alloys designed in this study. A) Alloy N1, B) Alloy N2, C) Alloy N3, D) Alloy N4, E) Alloy N5 and F) dye penetrant test of alloy N4 of this study as a laser clad weld indicating a crack free overlay.
experimental feedback. Table 1 shows an abrasion and corrosion comparison of Alloy F1 against several commercially available alloys. Again, based on matrix composition, it is expected Alloy F1 will perform similarly to 431 stainless steel in corrosive environments. It is interesting to note, that Alloy F1 possess a lower hardness yet a higher abrasion resistance than both 431 stainless steel and RockIt 401.

**Table 1 : Comparison of Alloy F1 with Conventional Abrasion and Corrosion Resistant Alloys via ASTM G65 Procedure A Dry Sand Abrasion Testing, **converted from Procedure E**

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>Process</th>
<th>ASTM G65A Volume Loss</th>
<th>Microhardness HV300</th>
<th>Cr Content in Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy F1</td>
<td>PTAW</td>
<td>103 mm³</td>
<td>354</td>
<td>Cr: 18%</td>
</tr>
<tr>
<td>431 Stainless Steel</td>
<td>PTAW</td>
<td>251 mm³</td>
<td>539</td>
<td>Cr: 17%</td>
</tr>
<tr>
<td>RockIT 401*</td>
<td>EHLA</td>
<td>360 mm³**</td>
<td>510</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Experimental Feedback Loop**

**High Temperature Corrosion – Ni-Based Alloys for Refinery and Power Generation**

A component of the overall RAD methodology is the incorporation of an experimental feedback loop. This feedback loop occurs during and at the end of RAD enabled product development. Metco 8453 was designed by identifying compositions with a low melting temperature under the theory that such properties would enhance adhesion and reduce porosity in the material [2]. However, further learnings were gained from evaluating Metco 8453 coatings which were then coded into RAD algorithms for future development. The additional analysis and subsequent addition to the RAD software involved the oxidation of the material during the spray process.
The microstructural analysis of the Metco 8453 is shown in Figure 4. Energy dispersive spectroscopy (EDS) measurements were taken to measure the composition of the oxide particles and the metallic splats separately. Those measurements are charted in Figure 5, which indicate the preferential oxidation of Al, Si, and Cr in comparison to Ni and Mo. Such preferential oxidation affects the chemistry of the metallic splats in the coating, which drives the corrosion behavior. Analysis of 8453 and other experimental alloys considered in the 8453 product developed enabled a RAD module to be constructed around predicting the oxidation behavior of the alloy during the spray process. The additional RAD module was utilized in order to design a portfolio of Fe-based twin wire arc spray materials for corrosion resistance including Metco 8280, Metco 8293, and Metco 8294 [3].

In previous studies, Metco 8453 (previously branded as Nicko-Shield 200) was compared against Hastelloy C276 arc spray coatings [2]. Those studies demonstrated that Metco 8453 had substantially improved adhesion even under the non-optimal spray conditions which are common in on-site spray operations. Refinery vessel corrosion protection is commonly an on-site application. The Metco 8453 alloy has been used successfully since its development in a variety of refinery vessels due to its enhanced sprayability and adhesion coupled with the inherent corrosion resistance of the coating.
Conclusions

Typically corrosion materials are developed for and therefore well suited for bulk processes such as drawing, casting, or forging. Nevertheless, it is common to transition such bulk process designed metals to be used in coatings for laser, EHLA, PTA, or thermal spray. Generally, the performance of a coating can be further improved if they utilize an alloy specifically designed for such process. This paper highlights the design of three materials currently underway in three stages of a big data driven methodology for alloy design, termed the Rapid Alloy Development (RAD) platform. Metco 8453 is a Ni-based corrosion resistant wire used today in refinery and power generation applications among others for high temperature corrosion resistance. The development and subsequent analysis of the product acts as an experimental feedback mechanism into the RAD platform. Alloy F1 is an Fe-based alloy intended for PTA/laser/EHLA cladding. In this case, built in modules predicting the behaviour of Fe-based materials was utilized for rapid alloy design with few experimental iterations. Alloy D was the born of a more comprehensive study investigating the behaviour of Ni-based alloys intended for PTA/laser/EHLA. While the RAD software previously had no existing module to predict the behaviour in this space, the experimental results have now been incorporated for future product development.

References
