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ROBUST QUANTIFICATION OF PHASE FORMATION POTENTIAL OVER A WIDE CHEMISTRY SPACE

D. Purdy
Electric Power Research Institute, Charlotte, NC, USA

ABSTRACT

Due to a high degree of mixing between substrate and weld deposit, fusion welding of dissimilar metal joints functionally produce new, uncharacterized alloys. In the power generation industry, such mixing during the application of cobalt-based hardfacing has led to a disconcerting number of failures characterized by the hard overlay welds disbonding. Investigations into this failure mechanism point to the unknown alloy beneath the surface of the hardfacing layer transforming, hardening, and becoming brittle during service.

This research describes a methodology for exploring a chemical space to identify alloy combinations that are expected to be safe from deleterious phase formation. Using thermodynamic modeling software and a stepped approach to potential chemistries, the entire phase stability space over the full extent of possible mixing between substrate and weld material can be studied. In this way diffusion effects – long term stability – can also be accounted for even in the case where mixing during application is controlled to a low level.

Validation of predictions specific to the hardfacing system in the form of aged weld coupons is also included in this paper. Though the application of this methodology to the hardfacing problem is the focus of this paper, the method could be used in other weld- or diffusion- combinations that are expected to operate in a high temperature regime.

INTRODUCTION

Following industry observations of disbonding of hardfacing in power generation – predominantly valve – applications [1], research began to understand the driving mechanisms of disbonding. Many operational and service life factors were considered alongside numerous ex-service samples which were evaluated destructively. In these observations, material combinations of non-austenitic steels, especially grades 11, 22, 91, and 422, with cobalt-based Alloy 6 and Alloy 21 produced a hardened microstructure susceptible to cracking and disbonding after exposure to significant operation (15-60,000 h) at temperatures above 535°C (1000°F). These findings were consistent across several manufacturers, weld processes, plants, components, etc., each with considerable accumulated service life prior to disbonding. Ultimately, the disbonding issue was treated as a metallurgical problem that required a metallurgical solution.

The disbonding issue was identified to be the result of deleterious phase formation in the microstructure, first appearing as significant hardened zones (above and beyond the hardness of the applied hardfacing) at the first weld bead. In some instances, the unstable microstructure was a consequence of the degree of mixing during welding; in other combinations with lower weld mixing, diffusion played a rate-limiting role for intermetallic precipitation. For example, at the interface of grade 91 and Alloy 21, there was evidence [1] of diffusion-controlled homogenization of the alloy chemistry at the interface leading to a narrow band of iron-rich cobalt-based hardfacing which produced an embrittled zone at the weld interface.

Table 1: Chemistry of alloys affected by disbonding (weight %).

Specification	Fe	C	Mn	Si	Ni	Cr	Mo	V	Other
ASTM A 182, Grade 11	Bal	0.10 - 0.20	0.60 - 0.80	0.50 - 1.00	--	1.00 - 1.50	0.45 - 0.65	--	--
ASTM A 182, Grade 22	Bal	0.05 - 0.15	0.30 - 0.60	0.50 *	--	2.00 - 2.50	0.87 - 1.13	--	--
ASTM A 182, Grade 91	Bal	0.08 - 0.12	0.30 - 0.60	0.20 - 0.50	0.4 *	8.0 - 9.5	0.85 - 1.05	0.18 - 0.25	Nb+Ta: 0.06 - 0.10 N: 0.03 - 0.07
ASTM A 565, Gr 616 (422 SS)	Bal	0.20 - 0.25	0.50 - 1.00	0.50 *	0.50 - 1.00	11.0 - 12.5	0.9 - 1.25	0.20 - 0.30	W: 0.9 - 1.25
AMS 5387B & 5373C (Alloy 6)	3.0 *	0.9 - 1.4	1.0 *	1.5 *	3.0 *	27.0 - 31.0	1.50 *	--	W: 3.5 - 5.5 Co: Bal
ASTM A 732 Gr 21; AMS 5385F (Alloy 21)	3.0 *	0.20 - 0.30	1.0 *	1.0 *	1.75 - 3.75	25.0 - 29.0	5.0 - 6.0	--	Co: Bal

*maximum

The intermetallic phase hardening the uncharacterized alloy comprised of the mixture of cobalt-based hardfacing and iron-based non-austenitic steels was identified as sigma, σ, a (Fe,Co)-Cr close-packed tetragonal phase known for its very high hardness and low toughness [2]. This phase was found regardless of the constituents in the hardfacing or base material, within the limitations of Table 1. The presence of this phase was observed to cause dramatic increases in local hardness and reduced toughness in the zone of highest mixing [1]. All sub-surface cracking in these ex-service welds favored these hardened zones. The proposed solution to this unknown alloy with a propensity to form sigma was to eliminate the possibility of high levels of iron dilution in the cobalt-based hardfacing with a metallurgical barrier, or butter layer, of a different chemistry. This research did not consider the option of abandoning cobalt-based alloys for other hardfacing options.

METHODOLOGY

To eliminate the formation of sigma phase in this welded combination, while accounting for a broad range of possible dilution levels (5-50%) [1,3-7] and the long-term effects of high temperature operation (i.e. diffusion), all thermodynamic potential for sigma phase has to be eliminated. Further, the introduction of additional alloys – still at potentially high levels of mixing – needs to add no new risk for unexpected phases lest they also embrittle the weld. The challenge this posed was how to analyze the high number of possible butter materials versus the assortment of common base materials as they reach thermal equilibrium to identify combinations that were safe.

The method for analyzing this wide combination of materials required the use of predictive software. This study utilized JMatPro [8], a thermodynamics and kinetics package based on the CALculation of PHAse Diagrams (CALPHAD) method and databases. CALPHAD looks at the free energy contributions of each element in the mixture and their potential to form a wide array of phases. In thermodynamic equilibrium, elements are assumed to migrate into a configuration of the overall lowest total energy (most stable). This is an approximation of the service conditions these components see: given years of operation at high temperatures, constituents are relatively free to move into the phases of lowest energy.

For a given combination of materials, such as from Table 1, a base material and weld material were selected and combined by applying a simple fractional degree of mixing between the two materials on a per-constituent basis.

$$wt\%_i^{mixture} = n * wt\%_i^{weld\ metal} + (1-n)wt\%_i^{base\ metal} \tag{1}$$

Where $wt\%_i$ is the weight percent of constituent i, and n is the degree of mixing. The summation of these mixed constituents produces a new alloy representative of some fraction of the hardfacing weld zone. The model does assume complete mixing during welding for any given analysis which is another reason why the entire spectrum of compositions needs to be evaluated. If any fraction of a weld shows stability for hard phases, then given time and temperature it will harden, crack, and potentially contribute to disbonding.

Each potential material combination from 100% base metal to 100% weld metal can be analyzed in this fashion through an analytical thermodynamic tool. It is critical to examine the entire field because macrosegregation can occur due to the nature of welding and microsegregation can occur on the level of dendrites and lamellae which can also be a source of non-uniformity in the microstructure. Even though a bulk measurement of a region of a component may purport to be one composition, solidification behavior is far from ideal and there will be local variation. This approach offers controlled rigor to exploring a chemistry space for the potential unexpected interactions that may lead to deleterious phase formation. Given the possibility for all of these combinations actually occurring during manufacturing and service life, the ideal candidate materials combination will show no possibility of undesirable phase formation over the entire mixing range.

RESULTS

Thermodynamic Predictions

This methodology has been applied to the cobalt-based hardfacing system specifically to identify material combinations that would be predicted to be immune to the deleterious precipitation of sigma phase and other brittle intermetallics as observed during high temperature operation of valve components in the power generation industry. To this end, several alloys were evaluated in pairs from 100% substrate to 100% weld metal in increments of 10% mixing using nominal compositions in Equation 1. Analyses are presented at 600°C (1112°F), a representative temperature for high efficiency power generation systems (HRSGs and traditional boilers).

The added complexity of considering the use of butter layers required additional combinations be analyzed: where there had been one alloy-mixing space to consider, base metal to hardfacing, now there are two for any given scenario. The generation of these phase stability predictions created a wide understanding of the influence of alloy mixing in this system. Specifically, it is believed that iron mixing into the cobalt-based hardfacing, alloys 6 and 21, produces a global chemistry favoring the stability of sigma phase. While in most instances that mixing was dominated by the weld process, in at least one instance diffusion played a significant role. As temperatures in these power generation components continues to increase, it becomes imperative to provide a physical barrier between the iron-based substrates and the cobalt-based hardfacing.

As a baseline, Figure 1 shows the combination of materials that may result from welding or diffusion between the iron-based bainitic grade 22 and the cobalt-based Alloy 6, two of the most common alloys in this application in the industry and two most frequently impacted by disbonding. Over a wide range of possible chemistries, from about 30% to over 90% Alloy 6, the brittle intermetallic sigma is predicted to be stable. Evaluations of ex-service components show a common degree of mixing is 70% Alloy 6, which correlates to 20% sigma predicted. This phase is expected to be stabilized by compositions high in iron and chromium; cobalt substitutes for iron readily as illustrated in Figure 2, a ternary phase diagram of the Fe-Cr-Co system at 600°C. The experimental observations of sigma phase formation in the ex-service failed components validate this propensity at several different degrees of alloy mixing but the prediction shows just how wide that space is.

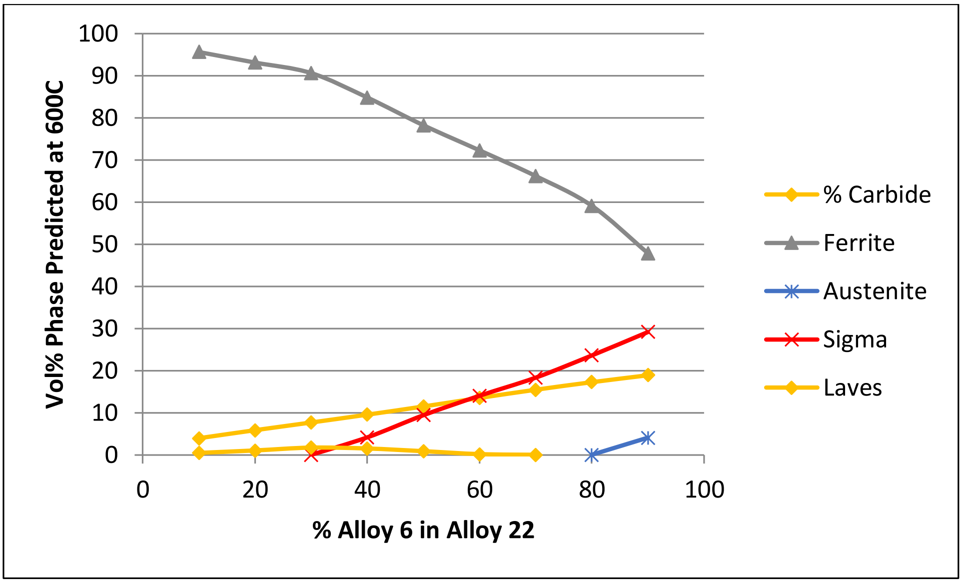

Figure 1: Phase stability predictions at 600°C for the F22-Alloy 6 system over a spectrum of mixing.

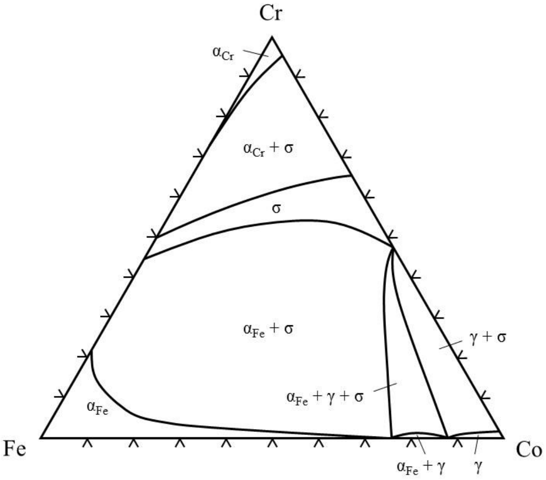

Figure 2: Ternary diagram for the Fe-Cr-Co system as predicted by JMatPro at 600°C.

This pattern of wide sigma-stable ranges extends to a number of common valve applications in the power generation industry, mirroring the observed failures in combinations between grades 11, 22, 91, and 422 when combined with both Alloy 6 and Alloy 21. These predictions are summarized in Figures 3 and 4. Even austenitic stainless steels show similar susceptibility, though nickel content is known to suppress sigma stability, see Figure 5 for a ternary of the Fe-Cr-Ni system, and retard sigma formation [9]. This combined with the limited high temperature applications of austenitic stainless steels in hardfaced applications begins to explain why no failures in this pairing had been reported.

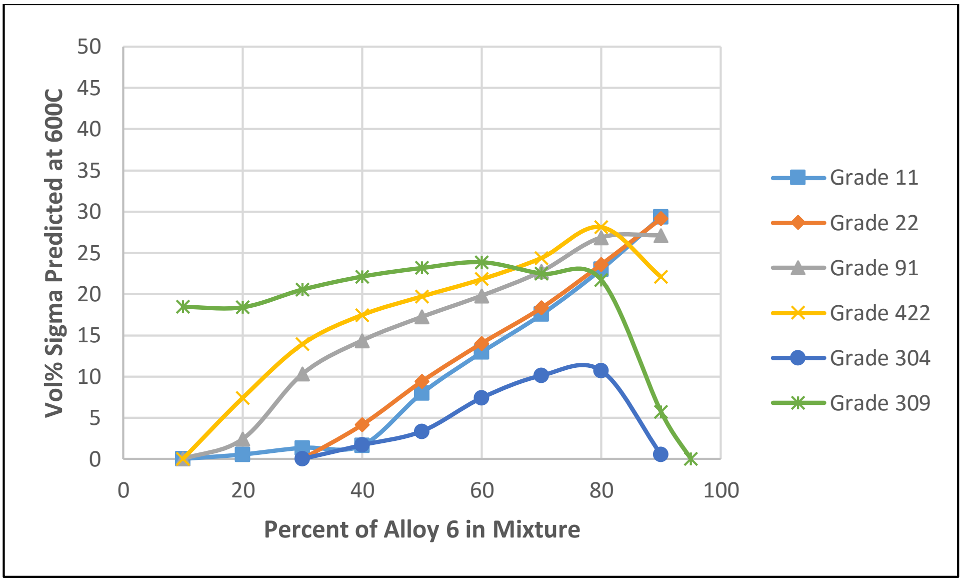

Figure 3: Sigma stability prediction at 600°C for alloys common to the power generation industry as mixed with Alloy 6.

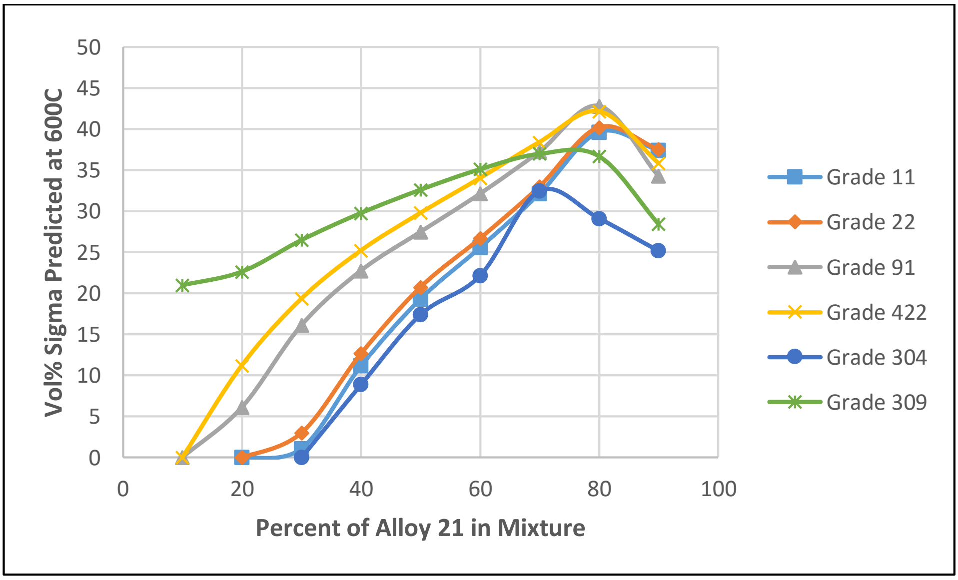

Figure 4: Sigma stability prediction at 600°C for alloys common to the power generation industry as mixed with Alloy 21.

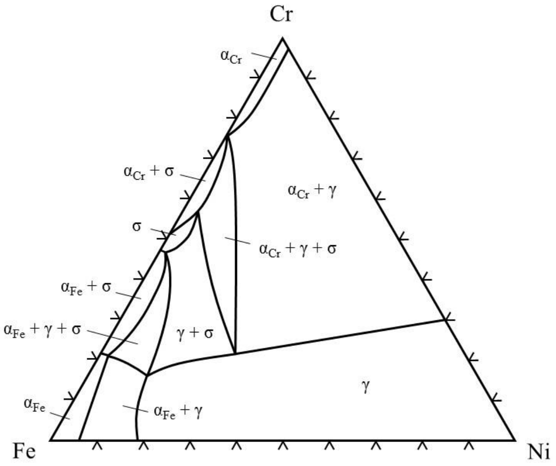

Figure 5: Ternary diagram for the Fe-Cr-Ni system as predicted by JMatPro at 600°C.

Weld Validation

This sensitivity of sigma phase to nickel content led to the predictions that use of a nickel-based butter layer could effectively reduce or even eliminate the potential for deleterious phase formation at any degree of mixing. Several commercial candidate alloys were examined using the above method and the results were encouraging, for example when grade 22 steel is protected with a barrier of filler metal 82, iron dilution in Alloy 6 is prevented and with it all potential sigma formation, Figure 6.

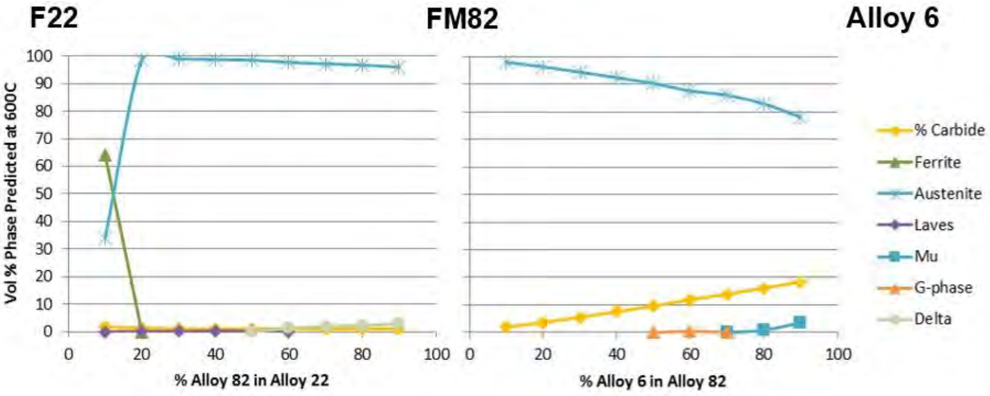

Figure 6: Composite predicted phase stability for the weld between grade 22, a butter layer of filler metal 82, and Alloy 6.

Validation of the predictions in Figure 6 was accomplished through thermally aged laboratory welds between grade 22 to Alloy 6 with and without a filler metal 82 butter layer. Welds were produced using GTAW for the nickel-based filler metal and PTAW cobalt-based hardfacing. The welds received no post-weld heat treatment but were aged at 620°C (1148°F) for 4,000 hours. This value represents an equivalent exposure to over 12,000 hours at 600°C (1112°F) or 100,000 hours at 570°C (1058°F); these time-frames are commensurate with transformation and failure in the ex-service components. After ageing, the welds were examined by cross-sectional hardness mapping as well as electron microprobe to examine the specimens for fine, hardening phases.

The ageing of the weld samples was interrupted after 4,000 hours to examine sub-surface characteristics as evidence of transformation, or lack thereof. Microhardness indentations were taken along the weld interface as well as the surrounding area and some limited microscopy was used to characterize any phases present. At the 4,000 hour interval, evidence of hardening at the interface of the grade 22-to-Alloy 6 weld was observed with peak hardness values exceeding 600 HV (500g). Ex-service samples showed values as high as 700 HV [1], but both are well above the target Alloy 6 hardness range of 400 – 450 HV. Electron microprobe and electron dispersive spectroscopy of this area was inconclusive but the morphology of the particles was consistent with sigma phase, Figure 7. At this same interval, the test coupons manufactured from grade 22, filler metal 82, and Alloy 6 saw peak hardness values at the interface of 320 HV (500g). Microscopy of this sample revealed a fine dispersion of low-atomic number particles.

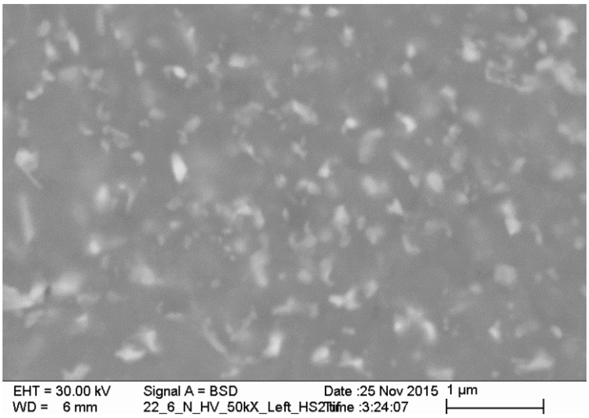

Figure 7: Backscattered electron image near the weld interface between grade 22 and Alloy 6 after 4,000 hours at 620°C.

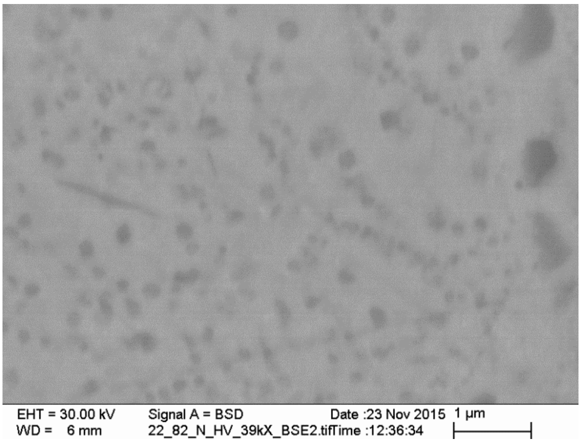

Figure 8: Backscattered electron image near the interface between grade 22 and filler metal 82 after 4,000 hours at 620°C.

DISCUSSION

The consistent implementation of an analytical model through thermodynamic calculation software has provided a framework for analyzing a large array of material combinations. The concerns addressed in this research focused on the observed hardening and delamination of hardfacing in power generation valves as caused by the formation of the undesired phase, sigma. By producing a database of predicted stable phase concentrations over a wide array of alloys in use in the industry, the technique illustrated possible combinations that would be devoid of the risks observed in the field. Installation of components manufactured using these alternate methods began in 2015.

Rapid deployment is a strong advantage to the analytical side of any engineering discipline. In materials science, thermodynamics has become a strong, trusted tool for optimizing chemistry space in alloy design. By some standards, this method is an offshoot of that idea. In the instance described in this paper, thermodynamic tools were utilized to examine un-optimized chemistry spaces caused by an uncontrolled degree of mixing during welding. These findings helped in explaining the observed valve disbonding failures. Left to their own devices, these unstudied alloys had unintended consequences in the form of secondary phase precipitation. The tools described herein were part of discovering why disbonding occurred as well as turning the question on end to discern how the causes could be prevented. Given the scope and duration needed to evaluate all the possible combinations in real applications, thermodynamic predictions were an imperative tool in examining the options and downselecting for physical trials and validation.

The findings in the hardfacing disbonding case study pointed to the use of nickel-based filler metals as affording a strong negative influence on sigma formation. Additional alloys discussed previously [2] showed similar behavior to the use of filler metal 82 detailed here and especially in Figure 6. Thus it is not the only solution though it provided a strong illustration. The use of the thermodynamic tools allowed for a robust interrogation of a number of chemical and thermal factors in this complex space.

It is important to stress that this thermodynamic analysis only accounts for composition, temperature, and, indirectly, crystal structure. Residual stresses or those from operation or thermal transitions can certainly affect secondary phase formation potentials and specifically stress has been tied to encouraging sigma formation in stainless steels [9]. Kinetics also plays a strong role in why austenitic stainless steels were perhaps less impacted by sigma formation. Figures 3 and 4 do show that austenitic alloys, such as 304 and 316, also have a range of mixing with cobalt-based hardfacing alloys that show sigma phase stability. This was an unsuspected discovery out of the predictive model as disbonding in these alloy combinations have not been observed in the field. In undiluted stainless steels, sigma phase is generally expected but only ever appears at very high temperatures because of how sluggish the transformation can be at moderate temperatures. In fact, microstructural analysis, specifically for sigma phase, is a valuable technique in determining real operating temperatures of overheated boiler tubes [10] where thermally enabled kinetics of sigma precipitation can be used to calculate conditions through a TTT method. Boiler tube over-temperature conditions are significantly hotter than those observed in steam valves and even so transformation takes some time. Stress- and kinetic- effects are currently not considered in the above analysis as the software is not currently capable and databases are insufficient to account for factors such as stress.

While the method to analyze a chemical space over all degrees of mixing ultimately shows only the thermodynamically stable “end-state”, given the elevated temperature regime at which some power generation components operate there is certainly sufficient atomic mobility to approach the predicted stability of phases. The increasing temperature of these components over their progenitors – which have been featuring the same material combinations and manufacturing processes for decades – has been identified as the most significant contributor to the occurrence of disbonding of hardfacing in valves. Given global trends, steam temperatures, which have a strong beneficial impact on thermal efficiency, will only continue to increase and with that comes increasing rapidity with which materials can approach thermodynamic stability.

This method was able to quickly analyze a wide spectrum of alternate weld chemistries to explore candidate alloys that would prevent the formation of deleterious phases. In this particular instance, simple nickel-based alloys offered a viable solution from a technical and commercial perspective. More complex nickel-based alloys with other constituents complicated the resulting microstructure and could result in new phase formation. These tools could be beneficial to other alloy systems in offering options for optimizing dissimilar metal joints especially when phase precipitation is part of the concern – either avoiding precipitation as in this example or promoting it in other potential scenarios (e.g. gamma prime).

CONCLUSIONS

A technique for quickly analyzing wide swaths of chemistry when examining dissimilar metal weld combinations was deployed to offer solutions for addressing the disbonding of cobalt-based hardfacing from high temperature steam valves in the power generation industry. The technique employed JMatPro to predict thermodynamic phase stability of material combinations of various base materials and weld materials over the entire spectrum of possible mixing with the goal of identifying combinations free of not only the experimentally observed sigma phase but also other potentially deleterious intermetallic phases. It was necessary to examine entire spectrum of mixing due to the potential for different degrees of bulk mixing during welding, the possibility for microsegregation during solidification, as well as diffusion affecting local chemistry (especially at weld interfaces) over the course of the expected long service life at elevated temperature.

In the example reported on in this paper examining the overlay welding of cobalt-based hardfacing alloys in power generation valves, alternate fabrication techniques using nickel-based butter layers were demonstrated through analytical prediction as well as representatively-aged weld coupons to be free of the embrittling sigma phase while traditional manufacturing processes were demonstrated to produce the same symptom as in ex-service samples. This example demonstrates the effectiveness of the methodology to explore the interactions of different alloys without the need to manufacture samples and wait for several years of service life, regardless of the application.

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