Predicting Sigma Formation in Mo-Bearing Stainless Steels

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INTRODUCTION

While many high alloy austenitic stainless steels employ molybdenum additions to increase their corrosion resistance, localized enrichment of Mo caused by solidification microsegregation can promote the formation of brittle intermetallics like σ and χ. The degradation of mechanical properties associated with these phases is also cause for concern in primary ferrite alloys, where the eutectoid decomposition of ferrite to austenite and σ can occur in the solid state. Thus, avoiding σ-formation during weld solidification is only part of the solution; the extent and mechanism of ferrite decomposition *on cooling*, which relies on composition and cooling rate, must also be considered.

TECHNICAL APPROACH

In order to provide a quantitative description of microstructural development in Mo-bearing stainless steels as a function of composition and cooling rate, 64 Fe-Ni-Cr-Mo compositions with Mo-contents ranging from 0-10wt% were chosen over a broad range of Ni and Cr contents characteristic of commercial stainless steels. Arc button melting was used to create small heats of each alloy for experimental purposes. Laser welds were prepared at travel speeds from 4.2 to 42mm/s to provide cooling rates from approximately 10^4-10^5°C/s. EBSD analysis was used for phase identification. Multi-component phase diagrams were also calculated to describe the observed microstructural development.

RESULTS/DISCUSSION

The mechanism of σ formation in the Fe-rich corner of the Fe-Ni-Cr-Mo system was experimentally determined to be the product of the eutectoid decomposition of ferrite to austenite and σ, regardless of solidification mode. Sigma was observed in primary austenite alloys above 2.5 wt%Mo and in primary ferrite alloys above 6wt%Mo. The higher threshold Mo-content for primary ferrite alloys is attributed to the higher solubility of Mo in this phase. The compositional range (Cr_{eq}/Ni_{eq}) of σ stability broadens with increasing nominal Mo content, and is more pronounced for primary austenite solidification because of the strong segregation of Mo during solidification.

Calculated pseudo-binary vertical phase diagrams demonstrated the existence of thermodynamic stability of σ for many alloys at each Mo-content, though the solvus temperature for σ-containing phase fields increases dramatically with increasing Mo-content. This trend coincides with the experimental data, as alloy compositions that enter a phase field with σ-sigma stability at higher temperatures have an increased likelihood to possess the necessary atomic mobility for the transformation to nucleate and/or complete. Thus, while equilibrium phase diagrams provide no explicit kinetic information, a modicum of kinetic information may be inferred on an empirical basis when these calculated phase diagrams are combined with the experimental observations in this study. When the σ onset temperatures were calculated as a function of alloy composition, a critical onset temperature range was found for the button melts to exist between 1140°C and 1171°C above which σ-sigma forms and below which it does not. Multi-component isothermal sections calculated at these threshold temperatures were superimposed on the corresponding calculated liquidus projections, resulting in experimentally validated process-microstructure maps that describe the potential for σ formation in single pass arc welds for Mo-bearing stainless steels. These diagrams accurately delineate broad composition ranges that will solidify as primary ferrite without σ formation.

CONCLUSIONS

The process-microstructure maps presented here can be a useful tool in developing conventional arc welding consumables and schedules that ensure primary ferrite solidification to avoid solidification cracking, and also avoid σ formation on cooling that could significantly impair the mechanical properties of the weld. The working space identified in this study could be used to choose or design filler metals in this alloy system and tailor dilution levels to achieve desired fusion zone properties. This thermodynamic modeling methodology can also be extended to other alloy systems where solid state transformation behavior on cooling is a significant engineering concern.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.