

Use Of Segregation As A Weld Design Opportunity

Pfeif, E.A. and Howard, C., Tate, S., Liu, S., Mishra, B., Olson, D.L.
Colorado School of Mines, Golden, CO, USA
sliu@mines.edu, epfeif@mines.edu

Abstract

When formulating welding consumables the weld metal designer must consider the metallurgical segregation processes and microstructural evolution steps resulting in the cooling of the weld deposit from its liquid state. The designer needs to systematically address each of the necessary steps in the metallurgical evolution to achieve the preferred optimum weld metal microstructure and properties. The selection of the optimal Rare Earth (RE) element addition to achieve intragranular precipitation of inoculants for acicular ferrite formation in high strength low alloy steel weld metal is introduced here to demonstrate the application of fundamentals of microstructure evolution.

Keywords

Weld Metal Design; Weld Microstructural Evolution, Rare Earth Microstructural Control, In-situ Synthesized Inoculants

Introduction

On cooling of steel weld deposits through two and/or three phase regions, the resulting elemental partitioning can produce both detrimental and/or beneficial microstructural-property relationships. An understanding of elemental partitioning, thermal processing, microstructure-property relationships, and alloy design concepts are especially valuable when weld composition and thermal experience are to take full advantage of multiple phase transitions upon cooling. The first and most advantageous microsegregation events occur on cooling through the dual phase liquid-solid region. Microsegregation can result from dendritic and/or cellular growth with elemental partitioning of the solute between the center of the dendrite or cell, and their interdendritic region, commonly resulting in coring. The amount and direction of solute segregation and redistribution depends on the distribution coefficients of each solute.

The degree of solute segregation depends on the magnitude of the deviation of the partition coefficient from one. Most weldable engineering alloys have distribution coefficients less than one, which promotes solute segregation to the interdendritic region. Welding consumable developers can use the distribution coefficient of select elemental additions to react with other solutes in the remaining interdendritic liquid to form compounds and intermetallic phases. Dendritic growth in low carbon steels during arc welding processes typically produces four to five dendrites per prior austenite grain. The interdendritic intermetallic phase constituents

formed as a result of the distribution coefficient less than one produce heterogeneous nucleation sites within the solidified grains. Furthermore, welding consumable developers can further refine the microstructure of the welds by utilizing alloying elements that poison grain boundaries, inhibiting growth of ferrite at grain boundaries. Poisoning grain boundaries has been found to provide additional undercooling that encourages intragranular heterogeneous nucleation of acicular ferrite that provides improvements in weld toughness [1].

The best example of microstructural refinement with grain boundary poisoning is the microstructural evolution resulting from titanium-boron (TiBor) welding consumables for the welding of steel. Mori and Homma [1] used this method to promote a refined microstructure of acicular ferrite by utilizing titanium and boron-containing consumables in low carbon steels. A synergistic effect occurs during the solidification of the weld metal containing amounts of titanium and boron. The titanium provides two uses: (1) titanium in the arc plasma getters nitrogen preventing boron nitride formation, which in turn allows boron to poison the austenite grain boundaries, and (2) titanium oxide and nitride precipitates act as nucleation sites for acicular ferrite. The grain boundary poisoning prevents ferrite precipitation along the grain boundaries, which further encourages intragranular formation of titanium oxide intermetallic precipitates that act as nucleation sites for undercooled acicular ferrite formation. The amount of undercooling, enhanced by grain boundary poisoning, increases the number of nucleation sites within the grains and refines the microstructure resulting in acicular ferrite and/or martensitic weld metal microstructure [2,3].

Rare Earth (RE) elements as alloying additions to steel have been used to desulfurize as-cast steel, decrease Heat Affected Zone (HAZ) hot cracking susceptibility in welds, [4,5] and increase hot workability of steels [2,3]. Furthermore, alloying with RE elements has been shown to alter sulfide precipitate shape [6,7], getter hydrogen during welding [8], and decrease the amount of solute segregation in steels [2,3]. Research utilizing cerium has predominantly been done in papers when Rare Earths have been used. Rare Earth additions can modify weld metal chemistry and microstructure, and when properly understood and used can make significant changes in weld metal properties and performance.

Weld Consumable Design Background

The TiBor welding consumable example demonstrates that a good weld metal designer must consider the metallurgical segregation processes and microstructural evolution steps for

microstructural control during cooling of the weld deposit from its liquid state. The designer needs to systematically address each of the necessary steps in the metallurgical evolution to achieve the preferred optimal weld metal microstructure and properties. The specific steps to the design process and its fundamental basis are described in a process flow sheet in Figure 1. The use of Rare Earth elemental additions in the weld deposit during welding can be applied to demonstrate that with fundamental knowledge of solidification, chemical thermodynamics and kinetics, alloy theory, and the effects of specific alloying additions, predictable weld metal properties can be achieved.

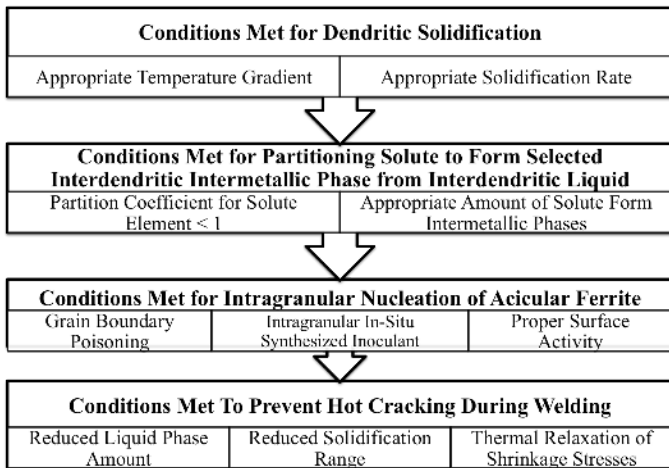


Figure 1: Steps to ensure grain refinement by the addition of Rare Earth elements to welding consumables.

Welding Microstructural Issues to be Addressed

Issues that need to be addressed for effectively using Rare Earth metals as consumable additions include selected elemental partitioning, selective nucleation sites by grain boundary poisoning, interdendritic reactions and designed undercooling. Further issues include: inoculant formation, intragranular nucleation, bead size and shrinkage, and the prevention of hot cracking by managing the residual stresses and chemical composition modifications during solidification. Rare Earth metals are extremely reactive with impurity elements (oxygen, sulfur, phosphorus, nitrogen, and hydrogen), iron and the other alloying additions (Chrome, Nickel, Manganese) within steels and their Heats of formation are typically large negative values; as such, rare earth elements are dominant in most chemical reactions. With proper selection of Rare Earth elements and proper content to address the multiple issues described in Figure 1, such additions can achieve the desired microstructural outcome in steel welds.

Weld Microstructural Evolution Fundamentals

To favorably impact the weld metal microstructure, the alloy system and solute(s) additions need to have the following specific attributes: (1) set the conditions for heterogeneous nucleation of a second phase during the solidification process (2) promote dendritic and/or cellular growth (3) promote solute partitioning to the interdendritic boundaries (4) promote formation of intermetallic interdendritic in-situ synthesized

inoculant (ISI) phases (5) exhibit proper temperature range for solidification to control the amount of interdendritic liquid (6) exhibit adequate solidification range that provides sufficient time during cooling to form thermodynamically stable interdendritic intragranular ISI particles and (7) promote the formation of desirable interfaces for later nucleation or epitaxial growth of second phases. To achieve these attributes, the specific solute(s) composition range needs to have: a) a distribution coefficient less than one, b) sufficient chemical reaction rates to accommodate the short times during cooling, and c) an active substrate surface. In this investigation, Rare Earths elements were primarily selected, as solutes for their rapid compound formation and ability to fulfill the other needed attributes.

Microstructural Evolution of Weld Metal

On solidification various intragranular microstructures can evolve depending on the solute concentration and type and the solidification parameter—the temperature gradient G over the solidification rate, R or $R^{1/2}$, as shown in Figure 2 [9,10]. Figure 2 illustrates the resulting dendritic or cellular microstructure as a function of chemical composition and welding parameters. It is the dendritic and cellular microstructures that experience solute partitioning. These behaviors give the alloy designer the ability to distribute desirable microstructural constituents for the evolution of optimal weld metal microstructure. It is clear that weld metal development requires knowledge of the metallurgical as well as a processing experience to achieve the beneficial contributions of each solute.

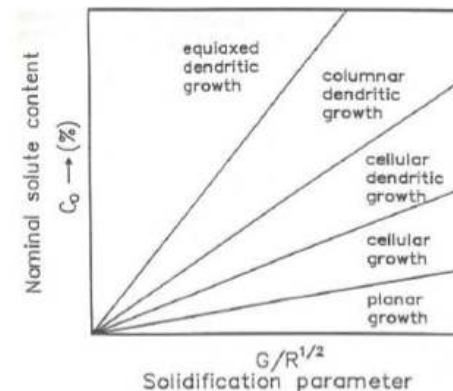


Figure 2: Interface Stability Diagram to determine solidification interfacial properties. [10]

The process of alloy solidification proceeds by the growth of either cells or dendrites, both of which result in the segregation of solutes on a fine scale. To understand the causes of this solute segregation phenomenon, consider a model binary alloy consisting of a concentration (C_0) of “B” atoms in metal “A” as shown in Figure 3. Upon cooling this molten alloy to the temperature T^* (which is below the liquidus), a solid forms with a composition of C_s . Since the newly formed solid has a solute composition lower than that of the liquid from which it formed, some solute atoms are rejected into the remaining liquid. As a result, the liquid becomes enriched to a composition of C_L . Upon further cooling of this liquid solidification resumes and the liquid is further enriched due to the growth of more solid [9].

The enriched boundary layer ahead of the solid-liquid interface experiences constitutional undercooling in that the freezing temperature of the liquid, T_f , increases with distance from the liquid-solid interface so that the undercooling increases with distance from the solid-liquid interface. This constitutional undercooling phenomenon is a direct consequence of the exponentially decreasing solute concentration ahead of the solid-liquid interface. Constitutional undercooling causes any perturbations in the solid-liquid interface to grow rapidly into the melt since these protrusions will encounter liquid with a higher freezing temperature.

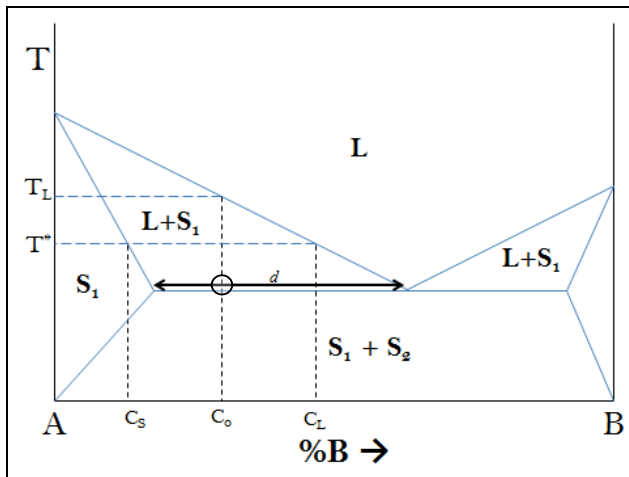


Figure 3: Model phase diagram illustrating a region in which the segregation coefficient is less than one.

The enrichment process continues until the dendrites begin to impinge upon each other. At this point, the remaining liquid between the dendrites is highly enriched in solute. In some alloy systems, the highly enriched liquid formed during dendritic solidification will precipitate intermetallic phase particles that can act as nucleation sites for subsequent phase transformations [11,12]. Therefore solute segregation is a potentially useful result of dendritic solidification. However, if dendritic solidification is desired, it is important to understand the requirements for this mode of solidification. It has been shown that the form of the solid structures that form during solidification is a function of two parameters: the solute concentration $[C]$ and solidification rate (R) . Therefore, both the composition and the solidification rate must be engineered to assure that dendritic segregation is sufficient to form nucleating particles.

Figure 4 illustrates the solidification-generated constituents (interdendritic oxides) in the middle of austenite decomposition microstructure. The ferrite veining delineates the prior austenite grain boundaries. These interdendritic oxides can serve as grain refiners and heterogeneous nucleation sites for subsequent solid-state transformation products. These particulates can also affect the mechanical properties of the weld metal. The coarse ferrite structure along the grain boundaries can be minimized using selected solutes for poisoning the grain boundaries, preventing grain boundary ferrite formation and thus promoting intragranular nucleation.

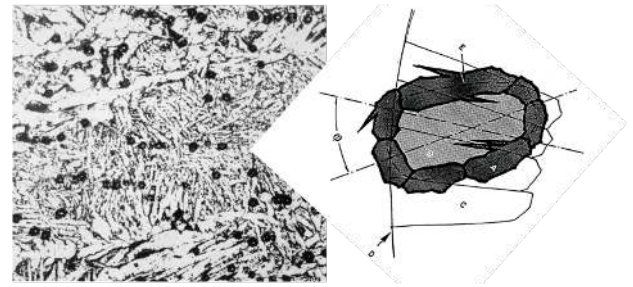


Figure 4: (Left) Interdendritic oxides forming within a prior austenite grain, with schematic illustration (Right). [11]

It has been shown that during the cooling of austenite, ferrite preferentially nucleates at austenite grain boundaries. The growth of grain boundary ferrite produces a relatively coarse microstructure that provides an easy path for crack propagation resulting in poor mechanical properties. The formation of intragranular ferrite results in a much finer microstructure than ferrite grown from grain boundaries. This finer microstructure provides greater resistance to crack growth. Therefore, it is desirable to add elements that poison the grain boundaries to prevent the nucleation and growth of ferrite along the prior austenite grain boundaries. If these poisoning agents prevent ferrite from nucleating at austenite grain boundaries, then the austenite grains will continue to cool until undercooling is sufficient for acicular ferrite nucleation to occur inside the grain. In the event that precipitates are present within the grains, these precipitates will act as nucleation sites for the formation of acicular ferrite.

Figure 5 illustrates how grain boundary poisoning elements can be used to refine acicular microstructure in welds. While one prior austenite grain boundary can be seen in the micrograph, the predominant portion of the micrograph illustrates star-shaped acicular ferrite laths produced from heterogeneous nucleation sites within the prior austenite grains. Elements used for grain boundary poisoning segregate to grain boundaries, decrease the likelihood of grain boundary ferrite nucleation and increase the activation energy for movement of grain boundaries in the material [1].

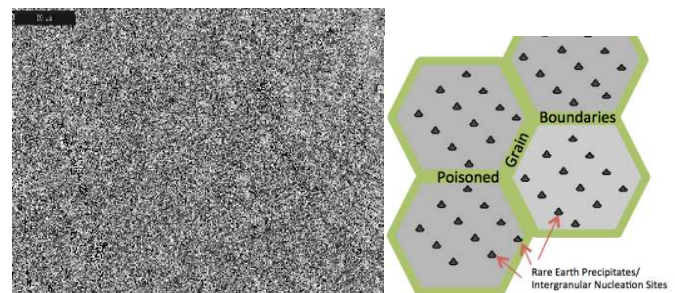


Figure 5: In contrast to Figure 4 the amount and distribution of intragranular star-nucleated acicular ferrite formation resulting from undercooling achieved by the use of grain boundary poisoning solutes. [13]

Acicular ferrite formation is favorable in welds for its high toughness that result from the “basket weave” organization of the thin lenticular grains formed at random orientations in the microstructure. The high aspect ratios around 10:1 and random orientation lead to crack arresting properties that increase the overall strength of weld metal. The formation of this

microstructure is a product of finely dispersed particles from which the ferrite can heterogeneously nucleate. Oxides, sulfides, and nitrides typically act as the nucleation sites of acicular ferrite in many low carbon steel welds.

Metallurgical Considerations for Weld Microstructural Refinement

The selection of intergranular precipitates for assisting grain refining and intragranular nucleation of phases that modify or enhance the mechanical properties of the weld metal requires understanding of the nucleation/epitaxial processes to promote fine intergranular product microstructure.

The epitaxial approach to inoculation is a technique commonly used to refine the grains of castings. The solid phase is able to grow directly off the intragranularly produced In-situ Synthesized Inoculants (ISI). Predicting the effectiveness of ISIs has been the subject of some contention. The more common theory assumes that each ISI particle plays the role of a substrate for epitaxial growth of the solid phase. Thus, lattice mismatch between the ISI particle and the solid is the predominating factor that determines the effectiveness of a given ISI.

However, it has been shown that the ISI particle size can play a more significant role in second phase formation [12]. In the heterogeneous nucleation approach, lattice mismatch becomes less relevant. This process is significantly affected by the amount of undercooling. Undercooling is directly proportional to the thermodynamic driving force for nucleation. It is, therefore, possible to compensate for even a relatively large lattice parameter mismatch simply by using small ISI particles [14].

As discussed in previous Sections, when poisons are present, grain boundaries cannot nucleate ferrite. Thus the undercooling of austenite grains continues until the point at which nucleation becomes favorable. If intragranular precipitates are present, then ferrite nucleation can occur at these precipitates before undercooling is sufficient to support nucleation at poisoned grain boundaries.

Solidification Cracking

During final solidification of welds, hot cracking along the weld centerline and/or in the interdendritic regions can occur. Solidification cracking can also occur in the heat affected zone (typically referred to as liquation cracking). Hot cracking occurs when the stresses across the solidifying weld are greater than the strength of the weld metal as the fraction of solid approaches one. This stress is generated by contraction due to thermal expansion, shrinkage due to solidification, or a mixture of the two. The decreasing integrity in the weld metal following solidification is due to the segregation of the elements that promote low melting temperature liquid formation at solidifying grain boundaries and interdendritic regions [15]. These low melting temperature liquids are typically eutectics formed with iron and impurities (such as sulfur and phosphorus) that segregate during solidification. Both mechanical and metallurgical factors must be considered

in mitigating solidification cracking, however, the weld metal consumable designer can only change the metallurgical aspects due to weld filler metal.

The last stage of liquid in the solidification process determines the susceptibility of a material to solidification cracking and the formation of microcracks within the weld. Three factors are of concern:

1. The amount of liquid relative to the amount of solid in the melt.
2. The temperature at which solidification happens.
3. The amount of shrinkage due to phase changes.

The estimated amount of liquid and solid can be determined from the lever rule. Those systems with wide proeutectic tie line lengths above the three phase reaction isotherms, indicated by “d” in Figure 3, will solidify with less liquid as well as being able to reject more solutes in the final stages of solidification for dilute solute alloys. Reducing the total amount of liquid reduces the amount of shrinkage that occurs in the interdendritic regions. Furthermore, reducing the amount of proeutectic liquid reduces the amount of liquid films that can develop to cause microcracks during further solidification under thermal stresses caused by cooling. However some liquid is beneficial for feeding or back-filling of solidification shrinkage to “heal” cracks [16].

The solidification temperature range affects the magnitude of the shrinkage strains that develop during cooling [16]. With large enough stresses and liquid phases present the process of solidification cracking is facilitated. Higher eutectic/intermetallic phase formation temperatures allow for less thermal expansion mismatch stresses and further stress relief in the solid as well as increase the mobility of chemical species in the solids. Additionally, higher intermetallic/eutectic temperatures allow for larger amounts of undercooling, thus encouraging dendritic growth, with more nuclei forming during solidification, finer dendritic structure and less solute partitioning.

Three-Phase Reactions

Three phase reactions are either peritectic or eutectic in the RE-iron systems for dilute solutions. The order in which they occur on cooling has a significant impact on the ability of a system to form intergranular intermetallic phase inoculants. The nucleation and growth of the intermetallic phases differ depending on the nature of the three-phase reaction. The evolution of the liquid phase in each instance varies producing two distinct liquid management problems. The different reactions are illustrated in the phase diagrams in Figures 6 and 7 with vertical lines at two atomic percent solute. In both instances upon cooling a dilute solution a peritectic reaction occurs at approximately 1400°C. The three-phase reaction after the first peritectic reaction in a given Rare Earth-iron system can be either peritectic or eutectic. The peritectic type reaction is of the form $L + \gamma \rightarrow RE-Fe$, and the form of the eutectic reaction is $L \rightarrow RE-Fe + \gamma$. Figure 6 presents a case where the peritectic reaction is followed by a eutectic reaction at 1338°C in the Iron-Holmium phase diagram. Figure 7 presents the case where two consecutive peritectic reactions occur for terbium and praseodymium.

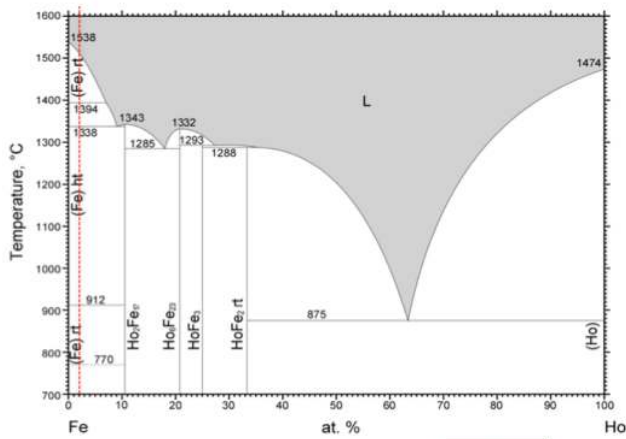


Figure 6: Iron-Holmium phase diagram [17]. An example of an Iron-Rare Earth pair that has a peritectic reaction followed by an eutectic reaction occurring for dilute solutions.

Since it is unclear whether the eutectic or the peritectic reaction will proceed at a faster rate, the relative importance of the nature of the second reaction in determining hot cracking is unclear. Although the RE-Fe product formed during the peritectic reaction may separate the remaining γ and liquid, thus reducing the reaction rate, the degree to which this product will slow the reaction has not been determined. As a result, it is not possible to determine the propensity of a given Fe-RE alloy to hot crack based on the type of reactions occurring (heat of mixing) and the remaining liquid (lever rule) prior to the second three-phase reaction. The question of which reaction is more effective in managing the liquid in the iron-rare earth system has yet needs to be determined for the selected rare earth element.

Weld Metal Microstructural Evolution with Rare Earth Elements in Iron

Consumable design must consider both the metallurgical factors and welding process parameters, such as solidification temperature range and the tendency of liquids formed by segregation to wet grain boundaries. The selection of a rare earth-iron system for consumable development should take the solidification temperature range into consideration and the weld cooling rate.

Selection Process for Rare Earth Metal Elements Components in Welding Consumables

Rare earth metals have partially filled d and f levels in their inner electronic structure facilitating conversion of valence and crystal structure by promoting d and f shell electrons into the outer valence electronic structure. This intrinsic characteristic also makes the elements favorable for getting oxygen, hydrogen, sulfur and the formation of multiple phases. In the application of welding, the inner electronic structure of the rare earth metals with d and f shell electrons allows for larger variation of volume and crystal structures, thus contributing to the evolution of microstructures. Figure 7 highlights the rare earth elements made up of the fourteen 4f

period elements and the elements of Column 3b on the periodic table.

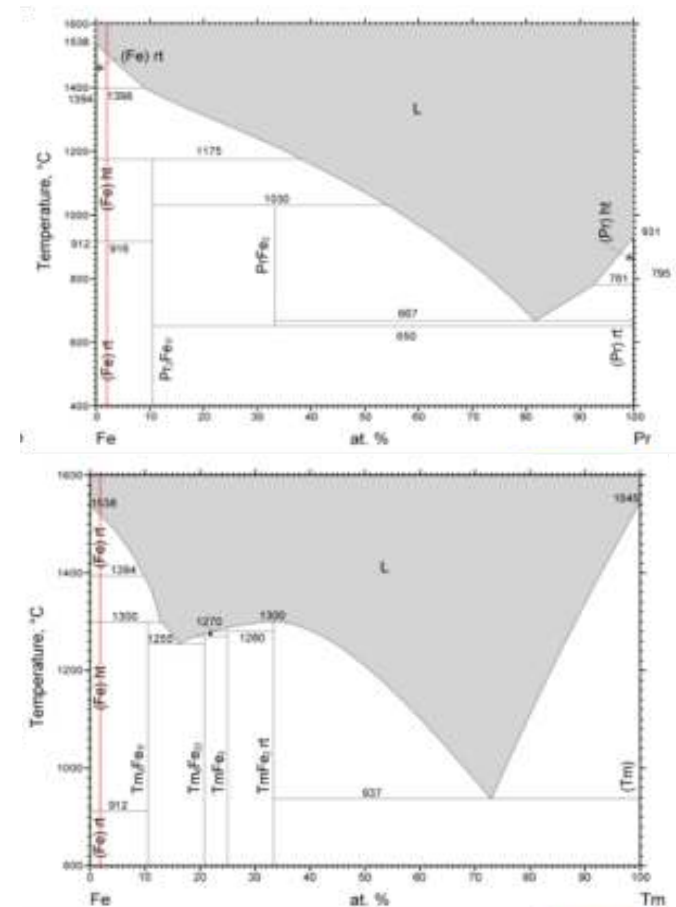


Figure 7: Phase Diagrams for Case IIA (top) with praseodymium [18] and Case IIB (bottom) elements thulium [19]. Case IIA will result in less eutectic liquid at dilute solutions as can be found from the lever rule using the tie line above the second peritectic reaction isotherm.

Preliminary selection of rare earth solutes for the proposed approach to welding consumable design requires considering the magnitude of the distribution coefficient relative to iron. Once a preliminary list of alloy additions has been assembled, the alloy designer should pare down this list by applying the following series of criteria. First, a negative heat of mixing is desired to promote the formation of an intermetallic compound that is desirable for grain refinement during welding. Secondly, the solidification temperature range should be minimized to reduce hot cracking susceptibility. These requirements are summed up by the following two cases, where the second case has two subcases, which provide guidelines for ranking candidate solutes:

CASE I: The solute has a peritectic reaction (negative heat of mixing) followed by a eutectic reaction (positive heat of mixing).

CASE II: The solute has two consecutive peritectic reactions (The first three-phase reaction is peritectic reaction with austenite and δ ferrite, the second reaction involves the formation of Iron-Rare Earth (Fe-RE) intermetallic phase).

CASE IIA: The alloy has two consecutive peritectic reactions and is expected to have tendencies towards shrinkage cracking due to intermetallic phase formation temperatures below 1300°C.

CASE IIB: The alloy has two consecutive peritectic reactions and is expected to have less tendencies towards shrinkage cracking due to intermetallic phase formation temperatures above 1300°C.

These three cases are applied to the Rare Earth elements in the paragraphs below to produce a list of candidate alloy additions for welding consumables.

For solute compositions in the Henrian range (less than 5 at. pct.), the distribution coefficients of the Fe-RE alloys found in

formation above 1300°C but contain a higher amounts of interdendritic peritectic liquid. The amount of liquid remaining prior to the peritectic formation of the Fe-RE intermetallic phase was determined by invoking the lever rule directly above the reaction isotherm as shown in Figure 8. By applying the lever rule to the two phase diagrams in Figure 8, it is possible to determine that the alloy in the phase diagram on the left will have less remaining eutectic liquid than the alloy on the right.

Selection of potential Rare Earth additions can consider elements from both Case IIA and IIB. The elements Gadolinium and Erbium both have solubilities in δ -iron greater than one atomic percent, reducing their overall economic efficiency as less of the elements would be partitioned during solidification in comparison to other elements. Furthermore, The Yb-Fe phase diagram is not well characterized at higher temperatures and could potentially have positive heat of mixing, so it can be ruled out as a candidate until the phase diagram is further elucidated.

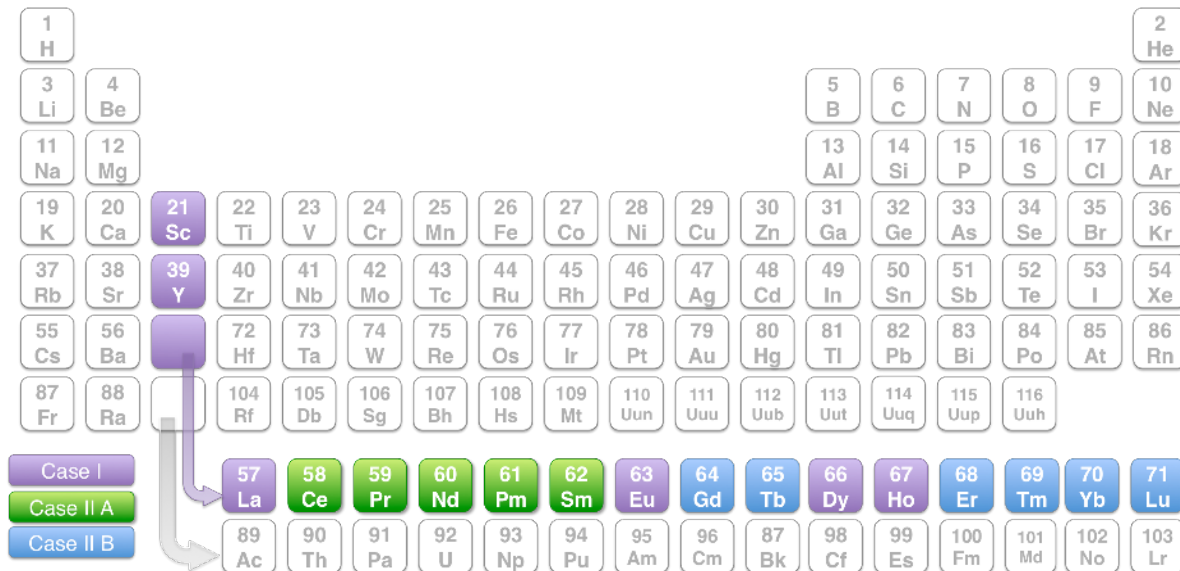


Figure 8: Periodic table of elements with the considered Rare Earth metals highlighted into three different categories depending on whether the element forms a compound with iron.

the literature were all less than one. Therefore, all Rare Earth elements are predicted to segregate to the solid-liquid interface during solidification of Fe-RE alloys. Thus, all Rare Earth elements pass the preliminary test. Next, by assessing the heat of mixing criteria, six elements (Sc, Ho, Dy, Eu, La, and Y) were excluded from further consideration. These elements, together with iron, will form eutectic reactions and are, therefore, identified as “Case I Elements” in Figure 7.

Case II elements display a difficult balance between the intermetallic phase formation temperature and the amount of eutectic liquid that must be achieved for hot cracking mitigation. Higher intermetallic phase formation temperatures reduce the amount of shrinkage stresses in the melt, which, in turn, decreases hot cracking susceptibility. In the case of the remaining Rare Earth elements, the high intermetallic phase formation temperatures coincide with larger eutectic liquid amounts. Case IIA elements exhibit intermetallic phase formation temperatures lower than 1300°C but less eutectic liquid. While Case IIB elements exhibit intermetallic phase

Furthermore, due to its radioactivity, Promethium should be ruled out of the possible alloying elements.

From the seventeen Rare Earth elements, the remaining seven from Case IIA and IIB are good candidates for additions to welding consumables: Ce, Pr, Nd, Sm, Tb, Tm, and Lu. From the remaining seven elements, the selection of potential Rare Earth additions must now consider epitaxial growth and hot cracking-related issues. For epitaxial growth the Fe-RE intermetallic phases need to possess a desirable interface for a later nucleation or epitaxial growth of a second phase—acicular ferrite in this case. As mentioned earlier, in cases where small precipitates are formed heterogeneous nucleation is known to occur independent of crystal structure; for larger precipitates lattice mismatch becomes more relevant for nucleation of second phases.

One consequence that occurs due to lattice mismatch that does not affect nucleation and growth but could play a role in hot cracking, is the strain energy associated with the lattice

disregistry of the precipitate and the solidified substrate. Increased strain within the lattice is accompanied with larger lattice mismatch between the precipitates. Higher intermetallic phase formation temperatures are advised to allow for strain recovery within the melt. Varying cooling rates and Rare Earth elemental addition contents alter the amount of undercooling experienced within the partitioned liquid phase. Altering the undercooling affects the amount of the ISI particles and can therefore alter the amount of acicular ferrite in the final weld metal microstructure.

Out of the remaining elements the solidification ranges must be considered for hot cracking. The elements in Case IIA have larger solidification ranges as illustrated in Table 1 compared to the Rare Earth Elements in Case IIB. Furthermore, the elements in Case IIB have higher intermetallic phase formation temperatures, which is beneficial to reduce shrinkage stresses. However, the Case IIB elements have shorter tie line length above the second three-phase reaction isotherm labeled d in Figure 3 compared to the Case IIA elements that would result in almost half the amount of liquid phase in the Case IIB. Prior research groups have found the beneficial effects of adding cerium to castings and weldments, however these do not address other RE elements that could prove more potent at grain refining and acicular ferrite nucleation. The other recommended RE elements have intermetallic formation temperatures almost 300°C higher than cerium.

Table 1: Rare Earth Selection Parameters

	Element	Symbol	Reason for Recommended Removal from Potential Elements	Second Three Phase Reaction Temperature (°C)	Tie Line length above Second Three phase Reaction, d, (at%)	
Case I	Scandium	Sc	Second three phase reaction involved with dilute solutions is eutectic	1200	8	
	Yttrium	Y		1255	7	
	Lanthanum	La		780	91	
	Europium	Eu		-	-	
	Dysprosium	Dy		1372	7	
	Holmium	Ho		1338	9	
Case II	Cerium	Ce		1063	41	
	Praseodymium	Pr		1175	38	
	Neodymium	Nd		1208	30	
	Promethium	Pm	Radioactive	1210	42	
	Samarium	Sm		1280	30	
	Case II B	Gadolinium	Gd	Solubility >1 at % in Fe	1338	12
		Terbium	Tb		1312	18
		Erbium	Er	Solubility >1 at % in Fe	1355	11
		Thulium	Tm		1300	13
		Ytterbium	Yb	Probable eutectic reaction for second three phase reaction involving dilute solutions	-	-
Lutetium		Lu		1320	13	

To investigate the effect of solidification temperature range and tie line length with the RE elements it would be advised to compare the results found prior with cerium to that of two other case IIA and two Case IIB elements. The two case IIA elements recommended would be praseodymium and samarium (or neodymium). Praseodymium would provide a tie line length comparable to cerium with an intermetallic phase formation temperature 100°C greater. Samarium would provide a higher intermetallic formation temperature with an intermediate tie line length. From Case IIB it would be suggested to use terbium as it has the highest tie line length from the case IIB elements and either lutetium or thulium depending on availability.

Rare Earth and Boron Preservation

To ensure that elemental boron can be available as an austenite grain boundary poisoning element, sufficient boron must be present to hinder ferrite nucleation at prior austenite grain boundaries after boron has reacted in the arc with the shielding gas. The amounts of each Rare Earth element addition must be adjusted to protect the boron. The seven Rare Earth elements identified in this work as potential candidates for incorporation into steel welding consumables are: Ce, Pr, Nd, Sm, Tb, Tm, and Lu. Finally the quantity of RE element available must be sufficient to form RE-Fe intermetallic phases for the intragranular formation of acicular ferrite formation.

In addition to the RE elements that will 1) control the oxygen and nitrogen potential in the weld metal and 2) form intermetallic compounds for intragranular acicular ferrite formation, boron is still being considered as the addition to poison the prior austenite grain boundaries. The presence of RE will protect boron from being consumed before fulfilling the mission of hindering the grain boundaries from allotriomorphic ferrite formation.

The development of a PHACOMP [20] type calculation for prediction of RE elemental compositions for welding consumables will be discussed in a further paper. This method will account for the use and preservation of RE element alloy additions through the various steps of microstructural evolution as indicated in Figure 1 to ensure the inoculation of intragranular acicular ferrite formation.

Conclusions

Alloy theory was used with solidification principles to predict intragranular nucleation of acicular ferrite based on Rare Earth element additions and boron additions to steel. Seven possible Rare Earth additions were deemed acceptable based on alloying and solidification and thermodynamic criteria. Proper amounts of these Rare Earths additions are needed to achieve a variety of functions.

- (a.) Protect the boron allowing for grain boundary poisoning, to hinder grain boundary ferrite from forming and promote intergranular acicular ferrite.
- (b.) Form Fe-RE intermetallic phase nucleation site for the acicular ferrite.
- (c.) Assist in hydrogen management by being (irreversible) hydrogen traps and
- (d.) Maintain and reduce traditional hot cracking tendencies due to the presence of sulfur and phosphorous.

Future Work

Although the design approach presented in this paper is based on sound theoretical knowledge, further investigation needs to address the optimization of the selection of the rare earth element addition and the technology issues of: welding process and parameters (plasma atmosphere), multiple pass, and out of position issues.

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References

- [1] Mori, N., Homma, H., Okita, S., and Asano, K. "The behavior of B and N in notch toughness improvement of Ti-B bearing weld metals," *International Institute of Welding*, IIW Doc: IX-1158-80, (1980).
- [2] Fu, H.G., Qu, Y. and Xing, J. "Investigations of Solidification Structures of High Carbon Alloy Cast Steel Containing RE-V-Ti," *Journal of Materials Engineering and Performance*, Vol. 18, No. 4, (2008), pp.333-338.
- [3] Woo, I. and Nishimoto, K., "Metallurgical Factors Contributing to HAZ Cracking Susceptibility in Cast Alloy 718 Welds and its Improvement by Cerium Addition," *Metals and Materials International*, Vol. 7, No. 3, (2001), pp. 241-249.
- [4] Tomita, Y. and Okawa, T., "Effect of Microstructure on Mechanical Properties of Isothermally Bainite-transformed 300M Steel," *Mater. Sci. Eng. A*, Vol.172, No.1-2, (1993), pp. 145-151.
- [5] Zhu, X.Y., You, T., Shi, Q., Zou, Y., and Lin, Q., "Effects of Cerium on Microalloying in Low Sulfur Nb-Ti-Bearing Steel," *J. Rare Earths*, Vol. 23, No. 6, (2005), pp. 742-746.
- [6] Fu, H.G., Xiao, Q., Kuang, J., Jiang, Z and Xing, J.D., "Effect of Rare Earth and Titanium Additions on the Microstructures and Properties of Low Carbon Fe-B Cast Steel," *Materials Science and Engineering A*, Vol. 466, No.1-2, (2007), pp. 160-165.
- [7] Yi, D. W., Xing, J.D., Fu, H.G, Ma, S.Q., and Liu, Z.X., "Effects of RE-Al Additions and Austenitising Time on Structural Variations of Medium Carbon Fe-B Cast Alloy," *Materials Science and Technology*, Vol. 26, No. 7, (2010), pp. 849-857(9).
- [8] Lensing, C.A., Maroef, I. S., Park, Y.D. and Olson, D.L., "Utilization of Yttrium Hydrogen Trap and Welding Parameters in Managing Hydrogen Content in Welding High Strength Low Alloy Steel," *Ph.D. Thesis Colorado School of Mines*, (2001).
- [9] Pfann, W., "Principles of Zone-Melting". *J. of Metals*, Vol. 4, (1952), pp. 747-754.
- [10] Savage, W.F., Nippes, E.F., and Miller, T.W. "Microsegregation in 70Cu-30Ni Weld Metal", *Welding Journal*, Vol. 55, No. 6, (1976) pp. 165s-173s.
- [11] Indacochea, J.E. and Olson, D.L., "Relationship of Weld-Metal Microstructure and Penetration to Weld-Metal Oxygen Content," *Journal of Materials for Energy Systems*, Vol. 5, No. 3, (1983), pp. 139-148.
- [12] Barbaro, F.J., Krauklis, P., and Easterling, K.E., "Formation of Acicular Ferrite at Oxide Particles in Steel", *Materials Science and Technology*, Vol. 5, No. 11, (1989) pp. 1057-1068(12).
- [13] Liu, S. and Olson, D.L., "The Role of Inclusions in Controlling HSLA Steel Weld Microstructures," *Welding Journal*, Vol. 65, No. 6, (1986), pp. 139s-150s.
- [14] Dvornak, M.J., Frost, R.H., and Olson, D.L., "Influence of Solidification Kinetics on Aluminum Weld Grain Refinement", *Welding Journal*, Vol. 70, No. 10, pp. 271s-276s, (1991).
- [15] Kou, S., *Welding Metallurgy*, John Wiley and Sons, (New Jersey, 2003), pp. 263.
- [16] Cross, C.E., "On the Origin of Weld Solidification Cracking," *Hot Cracking Phenomena in Welds I*, (Springer Publications, 2005), pp. 3-18.
- [17] Fe-Ho Phase Diagram (1990 Okamoto H.) ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenual, section editors; ASM International, Materials Park, OH, USA, 2006-2012.
- [18] Fe-Pr Phase Diagram (2000 Okamoto H.) ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenual, section editors; ASM International, Materials Park, OH, USA, 2006-2012.
- [19] Fe-Tm Phase Diagram (1990 Okamoto H.) ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenual, section editors; ASM International, Materials Park, OH, USA, 2006-2012.
- [20] L.R. Woodyatt, C.T. Sims, and H.J. Beattie, "Prediction of sigma-type phase occurrence from compositions in austenitic superalloys," *Trans. TMS-AIME*, Vol. 236, No. 4, (1968), pp. 518-527.