HENRY GRANJON PRIZE COMPETITION 2006
Winner, Category C
"Design and structural integrity"
NON-DESTRUCTIVE DETERMINATION OF INTERSTITIAL NITROGEN CONTENT IN AUSTENITIC STAINLESS STEEL WELD METAL UTILIZING THERMOELECTRIC POWER

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ABSTRACT

Electronic properties of an alloy correlate directly to its microstructure. The thermoelectric power coefficient has been determined in this investigation to be a rapid and accurate measurement, which can be utilized for microstructural assessment and correlated to achieve maximum material performance of structural alloys. In high nitrogen-strengthened stainless steel welds, nitrogen partitions into solid solution nitrogen and nitrides during the welding thermal cycle. The formation of nitrides results in a degradation of mechanical properties and corrosion resistance. Thermoelectric power measurements offer a means to assess the weld interstitial nitrogen content allowing for a better correlation between nitrogen content and weld metal microstructure and properties. The thermoelectric power coefficient has been measured on plasma gas-tungsten arc welds on nitrogen-strengthened austenitic stainless steel alloy 1.4565, which has been interstitially strengthened with nitrogen for enhancement in mechanical properties and corrosion resistance.

IIW-Thesaurus keywords: *Nitrogen; Gases; Nitrides; Austenitic stainless steels; Stainless steels; Steels; Weld metal; Microstructure; Mechanical properties; Corrosion; Thermodynamics; Measurement; Practical investigations; Simulating; Reference lists.*

Through the application of solid state physics concepts, a non-destructive surface contact probe utilizing thermoelectric power has been developed to conveniently assess and quantitatively map soluble nitrogen content in nitrogen strengthened austenitic stainless steel weldments. The thermoelectric power coefficient is very sensitive to microstructural changes but with careful correlation to standards, thermoelectric power can be used as a rapid, non-destructive technique for assessment of alloy composition, phases, and microstructure variations.

The thermoelectric power coefficient has been measured on plasma gas-tungsten arc welds on nitrogen-strengthened austenitic stainless steel alloy 1.4565, which has been interstitially strengthened with nitrogen for enhancement in mechanical properties and corrosion resistance.

Austenitic stainless steels are generally considered to be the most weldable of all the stainless steels. Additions of nitrogen in austenitic stainless steel promote austenite and enhance mechanical properties and corrosion resistance leading to the importance of maintaining the nitrogen content of the base metal during welding throughout the heat-affected zone and the weld metal. Nitrogen influences austenitic stainless steel deformation

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Doc. IIW-1750-06 (ex-doc. V-1335-06) recommended for publication by Commission V "Quality control and quality assurance of welded products".

by affecting planar dislocation slip and pronounced twinning. The preferred deformation mode is determined mainly by properties of individual dislocations, in particular by the splitting of dislocations into partials, thus affecting the dislocation mobility and dislocation interactions with obstacles, cross-slip, and climb. Nitrogen in austenitic stainless steel is also shown to shift the breakdown potential of pitting corrosion to more positive values, thus retarding the passive film breakdown (lower corrosion).

Normally austenitic stainless steels can accommodate significantly higher levels of nitrogen in the metal matrix; however, during welding nitrogen adsorption/desorption to the welding arc atmosphere occurs leading to an increase/decrease in nitrogen content upon solidification. Changes in the nitrogen content can lead to both beneficial and/or detrimental results. For example, an increase in nitrogen content can cause suppression of delta-ferrite and result in an increased hot-cracking susceptibility during welding. Once the nitrogen is in solution in the steel, it is important to make sure that subsequent solidification can occur without the formation of pores. Porosity is one of the most serious issues when alloying steel with nitrogen. In welding of high nitrogen austenitic stainless steel, it is essential to avoid weld defects, nitrogen losses, nitride precipitation, etc., that may reduce the steel's corrosion resistance and mechanical properties.

Nitrogen solubility in weld metal is affected by alloying additions, as well as other welding parameters such as the weld speed, current, voltage, and shielding gases. For weld metal, one must consider that the liquid has approached equilibrium and then upon solidification, the nitrogen partitions from the solidifying dendrite or cells into the interdendritic liquid. It is important to know when and which secondary phases form under particular conditions, because formation of secondary phases can have profound effects on the mechanical properties and corrosion resistance. There are two types of precipitates (secondary phases) that have been found in austenitic stainless steel: intermetallic phases and nitrides/carbides making it important to understand the role of nitrogen in austenitic stainless steel weldments and determine the effects of partitioning of nitrogen into interstitial nitrogen and nitrides on such mechanical properties as tensile strength and toughness, and corrosion resistance. The solubility of nitrogen in austenitic stainless steel, the effects of additional alloying elements, changes in nitrogen content and solubility due to welding, and the effect of variations in nitrogen contents on mechanical properties and corrosion resistance must be taken into consideration.

An understanding of the weld microstructure is important because the solidified weld metal has two different regions (dendritic and interdendritic) both possessing unique mechanical and corrosion properties. The use of a composite model best describes the combined effect of both regions, thus making it more important to develop and understand the use of composite models to describe the solidified weld metal, in combination with the utilization of thermoelectric power assessment. The equilibrium partition coefficient plays an important role during solidification because, whether the equilibrium partition coefficient is less than one or greater than one, will delineate whether solute is pushed or rejected into the interdendritic region. The non-homogenous distribution of alloying elements associated with segregation reveals a "corrugated" microstructure. The nature and amount of sequential transformation occurring upon cooling is dependent upon the phase stability of the regions and the thermal stability. One way of expressing the austenite stability in cored materials such as weld metal is to assume that a sinusoidal distribution function can be applied to each of the segregating elements.

The equilibrium partition coefficient controls the direction and extent of segregation during solidification [1]. Micro-segregation during solidification results in an increase in the concentration of alloying elements and precipitates (carbides, nitrides, and intermetallic phases) and possibly porosity in the interdendritic liquid. The natural tendency of iron and nitrogen is for the partition coefficient to be less than one ($k < 1$) so that nitrogen gets rejected into the liquid interdendritic region during solidification. Micro-segregation is normally caused due to insufficient diffusion in the solid state adjacent to the interdendritic liquid. The diffusion coefficient of nitrogen is orders of magnitude above that of substitutional alloying elements, so that nitrogen is normally not prone to generate segregation [2]. As the substitutional alloying elements begin to segregate, nitrogen becomes attracted to areas with higher chromium, manganese, and molybdenum contents and the nitrogen is repelled by areas with higher nickel, cobalt, and carbon content, which can be estimated from the sign of the equilibrium partition coefficient.

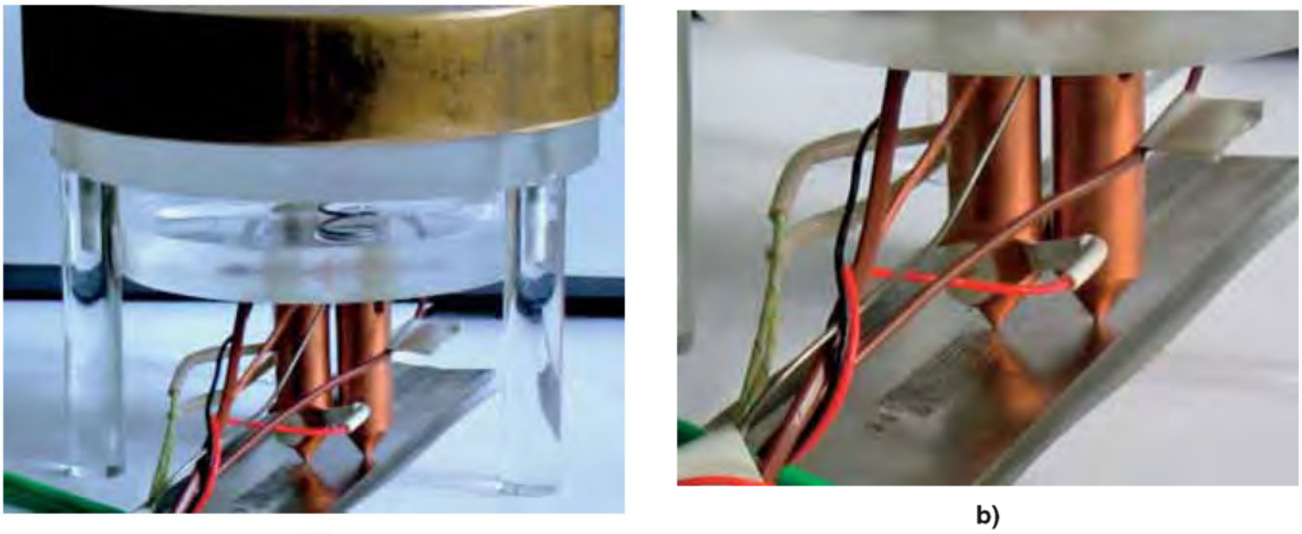
Because nitrogen is an interstitial solid solution strengthener in austenitic stainless steel, it is necessary to quantitatively determine the nitrogen content that is in solid solution, and the nitrogen associated with formed nitrides, which allows a correlation to mechanical properties and corrosion resistance. From the literature it became apparent that the high nitrogen steel industry relates properties and material behaviour only to the total nitrogen content, and that this practice is most likely due to the lack of a convenient method to determine only the interstitial nitrogen content. If microstructure and properties are to be properly correlated and estimated, it is essential that both the solid solution nitrogen and the nitride nitrogen contents can be easily and rapidly determined.

The thermoelectric power coefficient can be used for an assessment of nitrogen content (residual strain) because the thermoelectric power coefficient is a function of the electron concentration, electronic effective mass, and scattering parameters. The Fermi energy value (Fermi energy surface in the k-space) changes with electron filling in the conduction band due to the electron donation by nitrogen atoms. When nitrogen enters the metal matrix as an interstitial atom it prefers to occupy octahedral sites because the occupation of a tetrahedral site requires outward displacement of all four neighbouring iron atoms, whereas the irregular octahedral site can be occupied with the displacement of only two iron atoms parallel to the cube edge. This displacement of the iron atoms leads to lengthening of the lattice in the direction causing the lattice distortion or residual strain, resulting in a change in the amount of d-orbital electron overlap. The amount of d-orbital overlap affects the number of electrons in the d-band because of the Pauli-exclusion principle and the shape of the d-band. The effective mass of the electron is a measure of the curvature of the d-band at the Fermi energy level, so that as the nitrogen strains the lattice it alters the d-electron orbital of the lattice, thus altering the curvature of the d-electron band at the Fermi energy level and giving a measurable shift of the thermoelectric power coefficient. Through the use of a thermoelectric power surface contact probe as shown in Figure 1, with proper standardization and calibration, the interstitial nitrogen content can thus be calculated in austenitic stainless steel weldments [3-8].

Thermoelectric power assesses interstitial nitrogen content in austenitic stainless steel weldments because nitrogen induces strain in the crystal lattice. The welding thermal experience also induces residual stress (strain) in most cases. The welding residual stress conditions will be measured and mapped using the thermoelectric power coefficient surface probe measuring technique. The welding of dissimilar metal combinations can be assessed utilizing this new technique. By using a number of methods to measure residual stress on specimens, a calibration practice will be established which will allow for the development of a technique to achieve quantitative residual strain (stress) values. Preliminary investigations were previously performed at Colorado School of Mines to determine the relationship between thermoelectric power and tensile stress induced by an Alliance tensile tester. The ability to separate constitutional and thermal experience contributions to residual strain (stress) is a major challenge that needs to be addressed if thermoelectric power is to predict residual strain (stress) for nitrogen-strengthened stainless steel welds.

Experimental testing for this research was performed at the Federal Institute of Materials Research and Testing (Berlin, Germany) and the Colorado School of Mines. Autogenous plasma gas tungsten arc welds were performed on austenitic stainless steel alloy 1.4565 plates utilizing an argon-5 % nitrogen shielding gas. Changes in the nitrogen content are made by utilizing variations in the number of weld beads with all other parameters held constant. To standardize and calibrate the thermoelectric power surface contact probe for determination of interstitial nitrogen content in austenitic stainless steel weldments, analytical techniques must be used to determine both the total and interstitial nitrogen contents. Techniques utilized for determination of total nitrogen content include emission spectroscopy, Leco gas chromatography, and micro-Kjeldahl digestion. Techniques for determination of interstitial nitrogen content were much more difficult to locate. X-ray diffraction can be used for determination of interstitial nitrogen content, however the residuals stress due to welding must be accounted for to obtain an accurate measurement. Fortunately, in 1942 an analytical chemist named Beeghly [9-11] developed an ester-halogen digestion technique to quantify nitrides, carbides, and oxides in steel. For this research, the Beeghly ester-halogen digestion technique has been modernized. The ester-halogen digestion technique dissolves out the metal matrix leaving behind a nitride, carbide, and oxide residue. This residue is then put into the Leco Nitrogen Determinator to determine the nitride content. The interstitial nitrogen content is then calculated from the difference between the total nitrogen content (Leco Nitrogen Determinator) and the residue nitride content.

Austenitic stainless steel alloy 1.4565 weldments were thoroughly analyzed using optical microscopy, electron microscopy, x-ray diffraction, energy dispersive x-rays, and various chemical techniques. To thoroughly understand the thermoelectric power measurement, it was also important that the interstitial nitrogen and formed nitride contents in nitrogen-austenitic stainless steel weldments be thermodynamically modelled. Also, the thermodynamics of precipitation of nitrides and the role of solidification on the formation of nitrides have been investigated.



a)

b)

Figure 1 – Thermoelectric power probe measuring device for austenitic stainless steel weldments [3-8]

In conclusion, thermoelectric power has been experimentally shown to be a linear function of interstitial nitrogen content in austenitic stainless steel alloy 1.4565 weldments. From the change in Gibb's free energy, ΔG, which relates to external work (thermoelectric power), the thermoelectric power coefficient as a function of interstitial nitrogen content was determined as:

$$\Delta Z_\alpha = -\frac{\Delta G^0}{nF\Delta T} - \frac{RT}{nF\Delta T}(\ln [a_N]^2 - \ln [p_{N_2}]) \qquad (1)$$

Then, a composite model was applied to understand the properties associated with the dendritic and interdendritic regions in the austenitic stainless steel weldments. The thermoelectric power equation given above was derived using a composite concept with the rule-of-mixtures, and Figure 2 shows a direct correlation between thermoelectric power coefficient and interstitial nitrogen content in alloy 1.4565 weldments [3-8].

Microstructural analysis and thermodynamic calculations indicate the formation of nitrides in the interdendritic region of stainless steel alloy 1.4565 weldments. The results from electron microscopy (Figure 3) also indicate that high nitrogen steels suffer sensitization due to chromium depletion adjacent to the nitrides. The formation of nitrides in the interdendritic region takes interstitial nitrogen out of solution, resulting in a decrease in corrosion resistance and mechanical properties in the interdendritic region of stainless steel alloy 1.4565 weld metal.

Thermodynamic modelling and experimental results indicate that the thermoelectric power coefficient measures the change in the interstitial nitrogen content in the interdendritic region of stainless steel alloy 1.4565 weldments. The Ellingham-Richardson diagram was modified for alloy 1.4565 (base metal composition) to determine the order of formation of nitrides as shown in Figure 4.

The significance of having a non-destructive analytical thermoelectric power tool, which can be used to rapidly assess the interstitial nitrogen content in nitrogen-strengthened stainless steel welds is important. This thermoelectric power assessment can be applied both in the laboratory and also on large stainless steel technical assemblies. The thermoelectric power procedure can be applied to as-fabricated welds as well as to verify proper post-weld heat treatment procedures, and can also be used for selection of welding consumables. This practice can be applied to any nitrogen-strengthened stainless steel as long as proper calibration and standardization has been established. This thermoelectric power practice does not replace existing technology as there is no present method to non-destructively measure interstitial nitrogen content, especially if nitrogen content is high enough to also form nitrides.

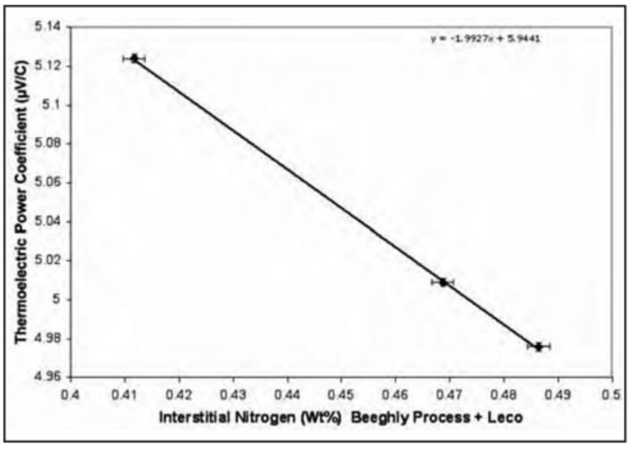


Figure 2 – Thermoelectric power as a function of interstitial nitrogen content for plasma welded stainless steel alloy 1.4565 with argon-5 % nitrogen shielding gas [3-8]

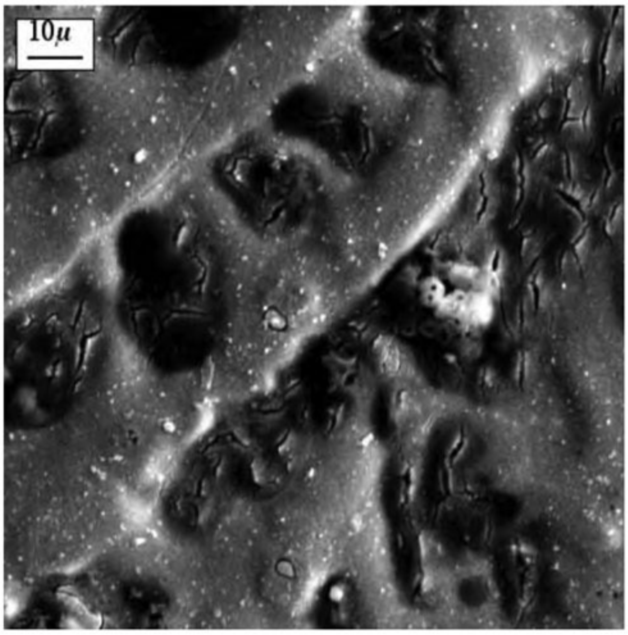


Figure 3 – Scanning electron microscope images at 2000X for plasma-welded stainless steel alloy 1.4565 with an interstitial nitrogen content of 0.487 wt. pct [3-8]

The use of thermoelectric power to assess interstitial nitrogen content in austenitic stainless steel weldments has lead to many possibilities in future research topics. Recently, the Albany Research Center has shown that high level alloy additions of carbon (> 0.3 wt %) to nitrogen enhanced (> 0.4 wt %) manganese stainless steels result in a precipitation free (no carbides or nitrides), high strength, austenitic stainless steel. Comparison

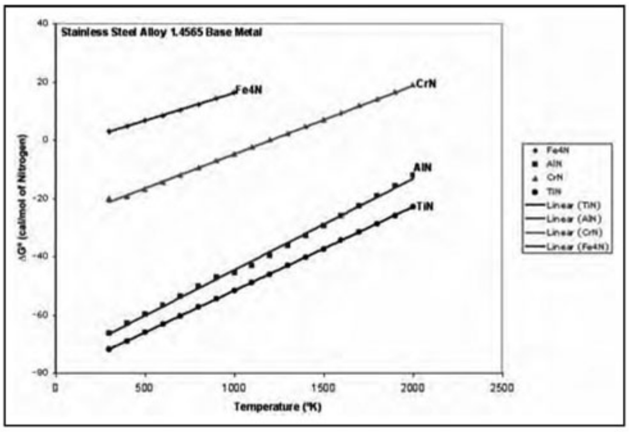


Figure 4 – Ellingham-Richardson diagram modified to take into account alloying elements in stainless steel alloy 1.4565

between Nitronic, 15-15, Hadfield stainless steels and these high-carbon and high-nitrogen stainless steels (N-C) show that these new N-C stainless steel alloys have up to a 40 % increase in yield strengths and a 25 % improvement in reduction-of-area at failure. These new alloys also have increased wear resistance, improved corrosion resistance, reduced creep, increased hardness, and increased high temperature strength. These new high nitrogen/carbon alloys and filler materials can potentially be used for oil and gas pipelines, hydrogen transport pipelines, drill collars, etc.

Colorado School of Mines, Devasco International, and Albany Research Labs are working together on the joining performance and the development of new high nitrogen, high carbon weld filler materials and in the development of a proper welding technique to maintain both the carbon and nitrogen content in the steel during welding. In these high-nitrogen, high carbon steels it is especially important to maintain and monitor both the carbon and nitrogen contents. An increase or a decrease in the interstitial nitrogen content due to welding will lead to the formation of nitrides or carbides. The tools developed in this thesis will be utilized to characterize and monitor the high carbon/nitrogen stainless steel welds using thermoelectric power to assess the interstitial nitrogen and carbon contents, and the Beeghly ester-halogen digestion method will be used to assess nitrides or carbides present in the steel due to welding.

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