

# CHARACTERIZATION OF INDIGENOUSLY DEVELOPED 22Cr-8Ni-0.022S-0.031P MODIFIED 304 L AUSTENITIC STAINLESS STEEL

RATI SALUJA<sup>1</sup>, K M MOEED<sup>2</sup>

<sup>1</sup>Mechanical Engineering Department, Goel Institute of Technology and Management, India

<sup>2</sup>Mechanical Engineering Department, Integral University, India

## Abstract

The severe and hostile operating conditions of nuclear reactors demand the development of new Grade 304 L austenitic stainless steels that possess higher resistance to hot cracking. As when a latest coil or heat of steel is put in production various types of problems arises. The problems can be embrittlement, hard spots, cracking, hot tears, poorer weld penetration, oxidation or a multitude of other troubles. The customary method to determine the source of the problem is to investigate the sample through various destructive or non descriptive testings. Sometimes the source of the problem is marked, but most often nothing out of the ordinary is found. In these cases the problem lies in the composition of the steel even when the alloy is within the specified composition of the steel. Hence the present investigation evaluates the hot crack susceptibility of 304L type austenitic stainless steels to the chemical composition of the alloying material with the implementation of Response Surface Methodology. The propensity for hot cracking is determined primarily by the hot cracking susceptibility factor.

**Key Words** : Austenite Stainless Steel, hot cracking, weldability, nickel equivalent, chromium equivalent.

## 1. Introduction

Austenite steels make up over 70% of total stainless steel production. The most widely used austenite steel is the 304 grade or A2 stainless steel. Austenitic stainless steels are designed to give corrosion resistance in many environments, resistance to hydrogen and 885° F (475° C) embrittlement, good strength, good ductility and low hardness [1]. Austenitic stainless steels have a relatively high level of alloying elements compared to carbon steels. Alloying additions tend to lower the diffusion rates of atoms within the crystal lattice at a given temperature which slows down the softening, recrystallization and creep deformation mechanisms which control strength and plasticity at elevated temperatures [2]. This grade of austenite steel is widely used in reactor vessels and other components for nuclear systems [3]. To prevent hot-cracking, austenitic stainless steel welds generally contain a small percent of delta ferrite. Although ferrite has been found to effectively prevent hot-cracking, it can lead to embrittlement of welds when exposed to elevated temperatures. Thus hot cracking is a significant problem due to transformation of retained ferrite into sigma phase, which results in preferential corrosion of ferrite [4].

Hot cracking in 304L is amplified by low-melting eutectics containing impurities such as S, P, Si, and N [5]. All standard specifications in current use for the procurement of 304L allow for the possibility of receiving material overly rich in austenite stabilizers such that weld solidification as primary austenite could occur and lead to hot cracking in a production weld [6].

For arc welding processes, the cracking tendency can be predicted by considering the relative amounts of the ferrite stabilizers to the amount of austenite stabilizers i.e. chromium equivalence ( $Cr_{eq}$ ) to nickel equivalence ( $Ni_{eq}$ ). The ratio of nickel equivalence ( $Ni_{eq}$ ) while

chromium equivalence ( $Cr_{eq}$ ) i.e., equivalency ratio is based on the actual chemical composition of the steels involved, and can be used as a quantitative indicator for predicting the primary mode of solidification for arc (fusion) welded 304L series stainless steel. Since a small but finite amount of ferrite in the finished weldment is desired, weld pool solidification as primary ferrite is preferred to prevent the likelihood of encountering hot cracking during welding [7].

The severe and hostile operating conditions of nuclear reactors demand the development of new Grade 304 L austenitic stainless steels that possess higher resistance to hot cracking. The present investigation evaluates the hot crack susceptibility of 304L type austenitic stainless steels to the chemical composition of the alloying material with the implementation of Response Surface Methodology. The propensity for hot cracking is determined primarily by the hot cracking susceptibility factor.

## 2.1 Alloy Design

Two principles are normally applied to develop new cracking resistant stainless steels:

1. To use additional alloying elements to obtain desirable properties to resist hot cracking, and
2. To maintain a high level of purity in the steel by reducing impurity contents (*i.e.*, carbon, sulphur and phosphorus) to achieve the enhanced resistance to hot cracking.

In this case, the new high-purity 304L austenitic stainless steels were developed based mainly on the second principle. In addition, the possible reduction of delta ferrite is also a concern. Therefore, the object of this research was to develop new Grade 304 L austenitic stainless steels encountering hot cracking during welding resistance. The methodologies used to solve these problems were based on adjusting alloying elements and/or reducing impurity levels. Since 1988 a program had been instituted called “alloy shaving” that uses the minimum alloying elements to prevent cracking [8]. During this research, the solution of a simultaneous optimization problem were accomplished with variation of Nickel, Chromium, Sulphur and Phosphorous while keeping molybdenum, manganese, silicon and carbon constant.

## 2.2 Influence of the number of alloying elements

In this problem, the percentages of the following 8 alloying elements were taken as independent variables; Mn, P, S, Si, Cr, Ni, Mo and P. Chromium, Nickel, Phosphorous and Sulphur had been selected as critical independent compositional variables, which were identified based on their significant effect on hot cracking to carry out the experiments. Noticeable differences has been found if we were introducing rest four alloying elements, while additional noise was introduced in the data set Composition of standard 304L austenitic stainless steel is given in Table 1.

**Table 1; Composition of Standard 304L Austenitic Stainless Steels**

Composition (wt %)								
C	Mn	P	S	Si	Cr	Ni	Mo	Fe
0.03	2.0	0.031-0.045	0.022-0.03	1	18-22	8-13	0.0213	Balance

## 2.3 Role of Alloying Elements

Carbon is an interstitial alloying element. As a result it can diffuse rapidly through the structure and concentrate on the grain boundaries. It precipitates with chromium and forms of chromium carbide, which depletes the grain boundaries of chromium, thus destroying the corrosion resistance. Chromium is added is to provide corrosion protection to the steel but also a key ingredient in the formation of intermetallic compounds as  $\alpha$  (alpha prime) which

causes embrittlement in 304L steel [9]. Addition of nickel to a Fe<sub>20</sub>Cr alloy, in an aggressive chlorine containing environment, a decrease in stress corrosion cracking resistance occurs. Fe-Cr-Ni (Mo) alloys system in nickel austenite steels, exhibit a wide range of mechanical properties that are unparalleled by any other alloy system today [10].

Sulphur as undesirable impurity is strongly rejected into the liquid during solidification of austenite, rapidly lowering the melting point of the interdendritic liquid [11]. In alloys rich in austenite stabilizers as 304 L, heats with excessive sulphur content may experience hot cracking or may affect the amount of hot cracking as opposed to its quality of weld puddle control or penetration [12]. Like sulphur, phosphorus also forms low-melting eutectics with iron, chromium and nickel. The cracking tendencies of P and S tend to be combined and are assumed additive as shown in figure 1. It particularly harmful in 304L since it has a strong tendency to spread as liquid films [13]. Low diffusivity of P in austenite and ferrite phases even at high temperatures virtually precludes homogenization [14].

The original purpose of manganese addition was the prevention of solidification cracking associated with the formation manganese sulfide as manganese combines more readily with sulphur, than does iron [15]. It has powerful deoxidation capacity, in 304 type austenitic stainless steels; it appears to have little effect in promoting austenite versus ferrite [16].

In 304L steel, silicon segregates during solidification particularly in combination with nickel, resulting in formation of low melting eutectic constituents. For the above reason, silicon is held below 1 wt%. Silicon forms a number of silicides (FeSi, Fe<sub>2</sub>Si, Fe<sub>3</sub>Si, Fe<sub>5</sub>Si<sub>3</sub>) and a Cr<sub>3</sub>Si intermetallic element, all of which tend to embrittle the structure [17]. Austenitic grade 304L steel can be quite sluggish in the molten state during solidification and the addition of silicon in the weld filler metal can improve their fluidity [15]. The beneficial effects of nitrogen to a refinement in the dendritic structure [14]. Nitrogen is a strong solid solution strengthening agent and even small additions of N can increase dramatically the strength of austenitic alloys and that is why their content levels should be controlled carefully in order to achieve the desired microstructure balance [18].

### 3 Experimental Procedures

The experiments were conducted as per the design matrix at random to avoid effect of systematic errors creeping into the system and HCS was calculated. The High purity 304L steels were produced by melting the high purity raw materials with a low level of C, S, P and Si content via the vacuum induction furnace. The plates were subsequently solution heat-treated at 1050°C for half an hour, followed by water quenching. Sensitization treatment was carried out at 650°C for an hour, followed by air cooling. To determine the effect of these elements, 304L Grade steel with several compositions were produced as given in Table 2.

#### 4.1 Quantification of hot cracking susceptibility factor

Since hot cracking was the major concern, HCS factor was quantified to examine the hot cracking sensitivity of the developed metal for different combinations. The calculated values of the Hot Crack Sensitivity for given specifications, is given in Table 2. Here results reveal that HCS for the typical 304L is found least for composition taken in experiment no. 8 and maximum for composition taken in experiment no. 10. Hot cracking susceptibility increases markedly as the P and S contents exceeds. Lowest value 0.053 is observed for P and S contents, which directly illustrates emphasis of P+ S effect on HCS. As with the increased value of P+S, HCS increases. Effect of phosphorous and sulphur is given in the figure 1, which indicates susceptibility to hot cracking, somewhat susceptibility and non susceptible cracking zone with respect to Cr/ Ni equivalents.

**Table 2; Compositions of the 304L Austenitic Stainless Steels (wt-%)**

S.NO.	Carbon	Nickel	Chromium	Silicon	Phosphorus	Molybdenum	Sulphur	Manganese	HCS
1	0.3	13.0	22.0	1.0	0.045	0.0213	0.030	2.0	8.68394
2	0.3	8.0	22.0	1.0	0.045	0.0213	0.022	2.0	6.62815
3	0.3	8.0	18.0	1.0	0.031	0.0213	0.022	2.0	7.14492
4	0.3	13.0	18.0	1.0	0.031	0.0213	0.030	2.0	9.54033
5	0.3	8.0	18.0	1.0	0.045	0.0213	0.030	2.0	8.05353
6	0.3	13.0	18.0	1.0	0.045	0.0213	0.022	2.0	9.78813
7	0.3	13.0	22.0	1.0	0.031	0.0213	0.022	2.0	7.90416
8	0.3	8.0	22.0	1.0	0.031	0.0213	0.030	2.0	6.41548
9	0.3	8.0	22.0	1.0	0.045	0.0213	0.030	2.0	6.91171
10	0.3	13.0	18.0	1.0	0.045	0.0213	0.030	2.0	10.1185
11	0.3	8.0	18.0	1.0	0.045	0.0213	0.022	2.0	7.72312
12	0.3	8.0	18.0	1.0	0.031	0.0213	0.030	2.0	7.47532
13	0.3	8.0	22.0	1.0	0.031	0.0213	0.022	2.0	6.13193
14	0.3	13.0	18.0	1.0	0.031	0.0213	0.022	2.0	9.20993
15	0.3	13.0	22.0	1.0	0.045	0.0213	0.022	2.0	8.40038
16	0.3	13.0	22.0	1.0	0.031	0.0213	0.030	2.0	8.18772

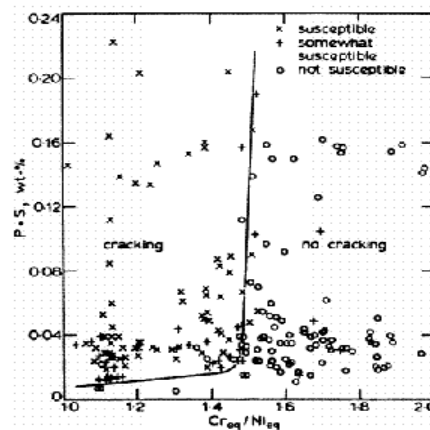


Fig. 1, Cracking susceptibility of 300 series stainless steel based on Cr/Ni equivalent.[19]

#### 4.2 Weldability Tests

The propensity for encountering weld solidification cracking decreases dramatically at  $Cr_{eq}/Ni_{eq}$  ratios slightly less than 1.5 for equivalence determined from WRC-1992 calculations, as shown in Figure 2 [20]. The difference between the "critical"  $Ni_{eq}/Cr_{eq}$  ratios for the WRC-1992 and H&S is due to different coefficients attached to the various elements. This effect can clearly be seen by applying the H&S and WRC-1992 calculations to a typical heat of Type 304L SS listed in Table 1. The difference between the two calculations is a few percent. To evaluate the possible solidification morphologies allowed by the specification ASME SA 240 types 304L, the appropriate composition ranges listed in Table 1 were used at the extreme values for Ni and Cr and the  $Cr_{eq}$  and  $Ni_{eq}$  were calculated using the formula from the WRC-1992 equivalence equations [7].

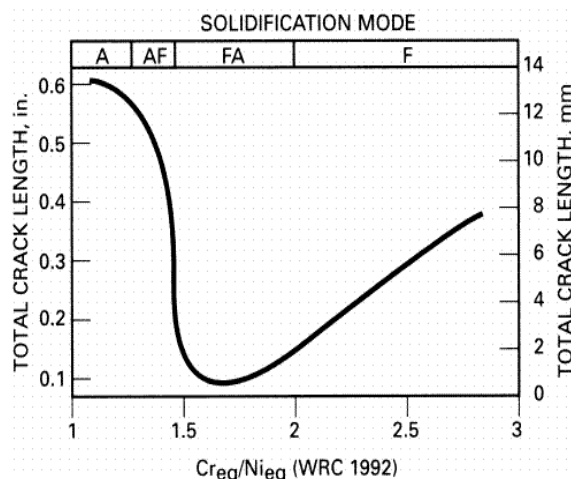


Fig.2: Cracking susceptibility based on WRC-1992 Cr and Ni equivalence [20]

## 5 Conclusion:

The estimated value of the coefficient of the model indicates as to what extent the important process variables affect the responses quantitatively. The result as given in table 4 shows that nickel and chromium has the significant parameters that affect hot cracking susceptibility while phosphorous and sulphur has little effect on weld bead. The value of F-ratio for a desired level of confidence (95%) was achieved that indicated model may be considered adequate within the confidence limit. A review of hot cracking in all experimental steel welds shows that the problem is more prevalent in experiment no. 10. The propensity for hot cracking is determined primarily by detailed effects of impurity elements S, P and Si and alloying elements Cr, Ni, Mn and Mo for various compositions of 304L. The result presented here reveals HCS for the experiment no 8 and 13 is found. Hence filler metals should overalloyed with Cr, Mo, Si, Ni, C, N and Mn in most cases for controlling formation of delta ferrite. Variations within the composition limits of these alloys can affect both the mechanical properties and welding characteristics of the alloy.

Table 3 Results of ANOVA on composite desirability

S.No.	Parameters	Sum of squares	DOF	F - value	Significance	Standard deviation	% of contribution
1	Ni	14.724	1	3.06	0.80	0.7376	43.00%
2	Cr	5.99	1	2.13	0.04	1.081	17.49%
3	P	1.15	1	0.76	0.397	1.23	3.36%
4	S	0.38	1	0.24	0.632	1.253	1.11%
5	Error	12					35.04%
	Total	34.244					100.00%

## References:

- [1]. John C. Tverberg, The Role of Alloying Elements on the Fabricability of Austenitic Stainless Steel, P.E. Metals and Materials Consulting Engineers Mukwonago, Wisconsin
- [2]. N.R. Baddoo, B.A. Burgan, A Fire Engineering Approach to a Stainless Steel Structural Systems, The Steel Construction Institute, UK
- [3]. <http://www.autokumpo.com>, weldability of austenite steels.
- [4]. David S.A., J.M. Vitek and D.J. Alexander "Embrittlement of Austenitic Stainless Steel Welds"

- 
- [5]. Shankar V. et.al., Solidification cracking in austenitic stainless steel welds, *S<sup>-</sup>adhan<sup>-</sup>a*, Vol. 28, Parts 3 & 4, India, pp. 359–382, 2003.
- [6]. Baldev Raj, et al., Development of fuels and structural materials for fast breeder reactors, *S<sup>-</sup>adhan<sup>-</sup>a* Vol. 27, Part 5, October 2002, pp. 527–558. © Printed in India
- [7]. Korinko P. S., Malene S. H., Considerations for the weldability of types 304L and 316L stainless steels, Department of energy, U.S., 2001.
- [8]. Tverberg J. C., The role of alloying elements on the fabricability of austenitic stainless steel, P.E. metals and materials consulting
- [9]. Borland J. C., Younger R. N. (1960), Some aspects of cracking in welded Cr–Ni austenitic steels. *Br. Weld. J.* 7, pp 22–59.
- [10]. Copson H. R., Physical Metallurgy of Stress-Corrosion Fracture, Interscience, New York, 1959.
- [11]. Cunat P. J., Alloying Elements in Stainless Steel and Other Chromium-Containing Alloys, International Chromium Development Association, Paris, 2004.
- [12]. Lundin C. D., Chou C. P. D., Sullivan D. J., Hot cracking resistance of austenitic stainless steel weld metals, *Weld. J.* 59: pp. 226s–232s, 1980.
- [13]. Brooks, J. A., and J. C. Lippold, Selection of Wrought Austenitic Stainless Steels, *Metals Handbook*, Vol. 6, 1993.
- [14]. Folkhard E., *Welding metallurgy of stainless steels* (New York: Springer Verlag) Springer-Verlag, Wien- New York. X 279 S., 115 Abb., 25 Tab., 487 Lit. Hardcover: DM 98,-, ISBN 3-211-82043-4, 1988.
- [15]. Cunat P. J. Alloying Elements in Stainless Steel and Other Chromium-Containing Alloys, International Chromium Development Association, Paris, 2004.
- [16]. Lippold J. C., Damian, Kotecki J., *Welding Metallurgy and Weldability of Stainless Steels*, John Wiley & Sons Inc, 2005.
- [17]. Kyriakongonas A. P., 3D Numerical Modeling of Austenitic Stainless Steel 316L Multi-pass Butt Welding and comparison with Experimental Results, National technical university of Athens school of Naval Architecture and Marine Engineering.
- [18]. Stevens S. M., Forms of nitrogen in weld metal, *WRC Bull.* (369), pp 1–2, 1989.
- [19]. Li L., Messler R.W., The Effect of Phosphorous and Sulfur on the Susceptibility to Weld Hot Cracking in Austenitic Stainless Steels", *Welding Journal*, 71, pp. 171s-179s, 1999.
- [20]. Anon, *Welding Handbook*, Eighth Edition, Volume 4., Materials and Applications Part 2., AWS, Miami, FL. 1998.
- [21]. Takalo, T., Suutala, N., and T. Moisio, "Austenitic Solidification Mode in Austenitic Stainless Steel Welds", *Met. Trans. A*, Vol. 10A, pp. 1173-1181, Aug. 1979.