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Research paper

Attainment of Nitrogen Solubility, Characteristic Study and its Effects on Martensitic Stainless Steel using Conventional Method of Melting in as Cast Condition

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Abstract

Steels ruled the world for the past two century owing to the carbon as an interstitial element, due to corrosion and less toughness on hard phases like martensite, was in a need to develop the corrosion resistive with more hardness without compromising toughness is in martensitic steel using nitrogen as interstitial in spite of carbon. Though the many technologies available to produces nitrogen-alloyed steel, due to cost effectiveness and process complication conventional method is chosen. Through conventional melting achieved nitrogen solubility in melts M1, M3, M5, M9, M10, M11 as 0.510 to 0.992 in volume fraction. This result has validated with theoretical nitrogen solubility using Sievert's law. Nitrogen solubility got above 1.02 to 1.35 of volume fractions in few melts, found porosity/ gas holes as confirmed by Simmons (1996). The hardness test and microstructure also reveals that the performance of the nitrogen solubility in hardness as-cast condition. The hardness is 341 to 472 HV, in this M10 is the highest of 472 HV hardness in as-cast condition concerning the nitrogen solubility of 0.973 M3 shows 341 is due to low Cr The microstructure also influence the hardness in decreases is due to higher percentage content of ferrite and also hardness increases is due to the attributed network of ferrite and alloy carbides.

1. Introduction

All steels contain some amount of dissolve gases of O_2 H_2 and N, in this nitrogen is effective in improving the mechanical and corrosion properties of martensitic stainless steels in solid solution or precipitates as very fine and coherent nitrides compounds with ferrous or alloying elements. Normally prime alloying elements for Martensitic Stainless Steel (MSS) are 12-18% Cr 4-6% Ni, but to reduce the cost of Ni also to avoid the skin allergic, Nitrogen is replacing its place in martensitic stainless steel is the major fraction. Mn also added to compensate Ni in the form of nitride, it influences the mechanical properties in MSS. Nitrogen is replacing carbon as an interstitial element and Ni in improving mechanical properties. One may, therefore, expect that nitrides should be more coherent with the matrix than carbides and that the interfacial energies Γ should, therefore, obey this inequality, { Γ carbide/matrix > Γ nitride/matrix}. Hence, Foct [1] discussed that the driving force for the growth of nitrides is comparatively less than that of carbides. Because of nitrogen, the MSS increases its hardness without compromising toughness also increases the corrosion resistance and wear resistance due to its coherent precipitates.

As reported by [2] alloying is the easiest way of enhancing the nitrogen solubility. Apart from an elevated pressure, the solubility of nitrogen in the steel may be raised by introducing alloying elements into the melt. Alloying elements like Ti, Zr, V, Nb, Cr, Mn and Mo are added to enhance nitrogen solubility, while in the order of W, Mo, Mn, Cr, Nb, V, Zr and Ti nitrogen is increasingly attracted to the melt

2. Solubility of Nitrogen

Computation of theoretical nitrogen solubility Using Sievert's law. Gavriljuk V.G

The equilibrium content of nitrogen in steel depends on three variables: temperature T, nitrogen pressure p_{N2} and alloy concentration of the steel 'X' as solved by [3,4]. . Due to interatomic spacing the N-solubility is lowest in ferrite as compared to austenite. In a nitrogen atmosphere, the dissolution of nitrogen in steel is governed by the reaction.

$$\frac{1}{2}N_2 = [N]_{(\text{Dissolved in liquid Fe})} \quad (1.1)$$

The value of K equilibrium constant derived from the value of standard Gibbs free energy for this reaction log K= -ΔG°/RT at 1600°C.

$$K = \frac{a_N}{\sqrt{p_{N_2}}} = \frac{f_N.\%N}{\sqrt{p_{N_2}}} = 0.045 \quad (1.2)$$

K is the ratio of the nitrogen activity in solution aN and the partial pressure of nitrogen. The Henrian activity coefficient fN relates the chemical activity of dissolved nitrogen to its concentration [N] in mass%. This implies the validity of Sievert's law $[N] \sim \sqrt{p_{N_2}}$. In a dilute solution of nitrogen in pure iron, fN reaches until by adding an alloying element 'X' the concentration of dissolved nitrogen is changed and the activity coefficient is adjusted accordingly.

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$$f_N^X = \frac{[N]_{Fe}}{[N]_{Fe-X}} \quad (1.3)$$

the influence of dissolved [X] in mass% on aN was interpreted by Wagner. A Taylor series expansion leads to first order (e_N^X) and second order (r_N^X) interaction parameters (Gavriljuk and Berns 1999).

Table 1: Theoretical Nitrogen solubility and Actual nitrogen solubility fractions after solidification

Alloys	Theoretical N Solubility	Actual Wt.% of Nitrogen	N solubility fractions	Interstitial gap occupied by N in %
M1	0.0974	0.050	0.510	51.00
M2	0.1430	0.120	0.840	84.00
M3	0.1279	0.090	0.700	70.00
M4	0.1210	0.110	0.900	90.00
M5	0.1235	0.161	1.300	130.0
M6	0.1210	0.125	1.030	100.3
M7	0.1200	0.095	1.350	135.0
M8	0.1160	0.119	1.025	102.5
M9	0.1023	0.085	0.837	83.07
M10	0.1120	0.109	0.973	97.32
M11	0.1260	0.1250	0.992	99.20

The first and second order parameters are reported to have a significant influence on the solubility prediction of stainless steels. Based on the experimental chemical composition, the theoretical nitrogen solubility at 1600°C in stainless steel was calculated using equations (1.4) and (1.5) and the computed values for 11 melts were listed in Table. 1.

$$\log f_N^X = e_N^{Cr} \cdot (\%Cr) + r_N^{Cr} \cdot (\%Cr)^2 + e_N^{Mn} \cdot (\%Mn) + r_N^{Mn} \cdot (\%Mn)^2 + \quad (1.4)$$

$$\%N = K / f_N^X \quad (1.5)$$

Experimental work

To attain the nitrogen solubility, conventional melting was carried out in a high-frequency acid lined induction furnace (1200 Hz). The capacity of the furnace is 100kg with a power rating of 125 kW. The various raw materials used for melting are CA15 (410) scrap, pure iron, LCFe-Cr, Nitrogenated Fe-Cr, LCFe-Mn, Pure Nickel, LCFe-Mo.

The chemical composition of various charging raw materials is given in Table 2. Raw materials requirement is selected based on the theoretical nitrogen solubility calculation using an equation 1.4 and 1.5. To attain the nitrogen solubility, charge calculations made to achieve the desired chemical composition for 60 kg computed using an equation 1.6 and attainment of chemical composition for melt M3 shown in Table 2. The raw materials are charged into the furnace, melted and deoxidized with the suitable alloying elements as listed in Table 3.

$$Wt\%\ of\ materials = \frac{X\ materials\ contain\ in\ raw\ material\ X\ Require\ wt\ \%}{100}$$

….1.6 Selection of raw material and scrap materials is based on the requirement of basic chemical composition of the melt.

Table 2: Raw charge materials and its contents

Raw Materials	%C	% Si	%Mn	% Cr	%Mo	%N	% Ni
CA15	0.09	1	0.8	12.5	0.1	-	0.7
Pure Fe	0.02	-	-	-	-	-	-
LCFeCr	0.10	2	-	60	-	-	-
LCFeMn	0.10	-	62	-	-	-	-
NFeCr	0.03	-	-	58	-	0.06	-
Pure Ni	0.02	-	-	-	-	-	99.9
LCFeMo	0.15	-	-	-	59	-	-

Table 3: Charge compositions are in wt % for melt M3

Charge Materials	C	Si	Mn	Cr	Mo	N	Ni	Fe
CA 15	0.054	0.6	0.33	7.5	-	-	-	Bal
Pure Iron	0.0032	-	-	-	-	-	-	Bal
LCFeCr	0.0123	0.24	-	7.385	-	-	-	Bal
LCFeMn	0.0037	-	0.217	-	-	-	-	Bal
LCFeMo	0.0003	-	-	-	0.0338	-	-	Bal
NFeCr	0.0052	-	-	1.015	-	0.105	-	Bal
Pure Ni	0.0004	-	-	-	-	-	0.19	Bal
Shell	0.02*	-	-	-	-	-	-	Bal
Total	0.09	0.84	0.547	15.90	0.0338	0.105	0.19	Bal

Pouring Temperature = 1600°C,

*Coconut shell is will give 80%C to obtain required carbon 25g added.

Charged materials were melted at 1600°C using high-frequency induction furnace to avoid the turbulence of molten steel so that there is no refining stage and erosion of refractory from the furnace. Because of restricted stirring slag covers can be maintained. Deoxidization process was carried out after pouring 1/3rd of liquid metal in ladle and deoxidizers additions in the order of Ca-Si, Fe-Si-Zr, Fe-Ti, and Se. The deoxidizing elements are given in Table-4. After completion of these processes, the final chemical composition is taken by using Spectro analysis.

Table 4: Deoxidizers addition in the ladle.

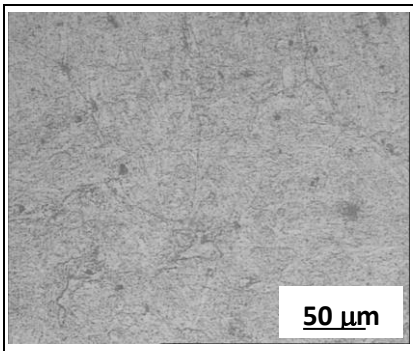
Charge	%wt.	%Ca	%Si	%Ti	%Zr	%Se	%C	%Al
CaSi	0.5	32	61	-	-	-	0.05	
FeTi	0.5	-	-	35	-	-	0.1	
FeSiZr	0.5	-	18	-	35	-		0.05
Se	0.03	-	-	-	-	99		
Al	0.02	-	-	-	-	-		94.4

Table 5: Obtained chemical composition (wt%) of Nitrogen Alloyed Martensitic Stainless Steel (NAMSS) by conventional melting

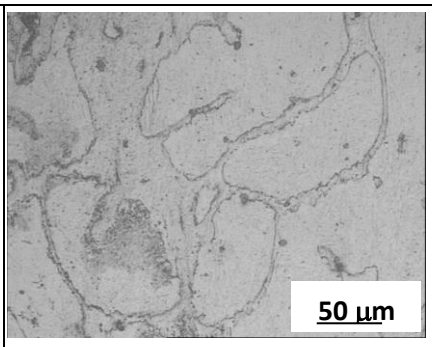
Melts	C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	W	Ti	Al	Nb	N	Fe
M1	0.096	0.360	0.020	0.020	0.470	0.130	8.22	1.080	0.220	0.030	-	-	-	-	0.05	Bal
M2	0.030	0.770	0.010	0.025	0.570	0.150	20.26	0.480	0.030	0.090	-	-	-		0.12	Bal
M3	0.090	0.810	0.008	0.025	0.540	0.190	10.84	0.020	0.080	0.010	-	-	-	-	0.09	Bal
M4	0.090	0.800	0.008	0.010	0.510	1.830	15.51	0.020	0.080	0.010	-	-	-	-	0.11	Bal
M5	0.100	0.700	0.014	0.024	0.470	0.190	15.43	0.005	0.060	0.043	0.038	0.034	0.015	0.004	0.161	Bal
M6	0.130	0.670	0.014	0.027	0.730	0.154	15.29	0.003	0.060	0.009	0.038	0.020	0.015	0.004	0.125	Bal
M7	0.130	0.650	0.016	0.030	0.620	1.400	15.00	0.007	0.060	0.023	0.039	0.023	0.025	0.012	0.095	Bal
M8	0.130	0.650	0.016	0.027	0.620	1.400	14.90	0.007	0.060	0.023	0.039	0.023	0.025	0.012	0.119	Bal
M9	0.220	1.030	0.20	0.030	0.890	0.630	16.80	0.250	0.015	0.019	0.032	0.049	0.070	0.0017	0.085	Bal
M10	0.200	1.098	0.018	0.030	0.830	0.620	17.20	0.250	0.015	0.020	0.030	0.052	0.099	0.0014	0.109	Bal
M11	0.320	1.160	0.018	0.032	0.786	0.613	17.96	0.240	0.014	0.019	0.030	0.044	0.077	0.0015	0.125	Bal

Micro Examination

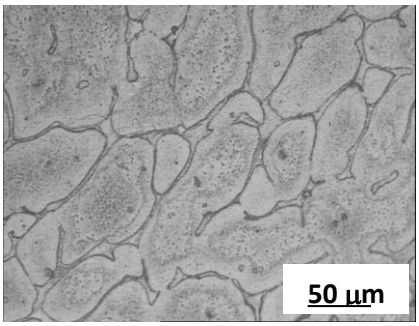
The as-cast microstructure of the selected six melts M1, M3, M4, M9, M10, and M11 are shown in Figures 2 a to f.



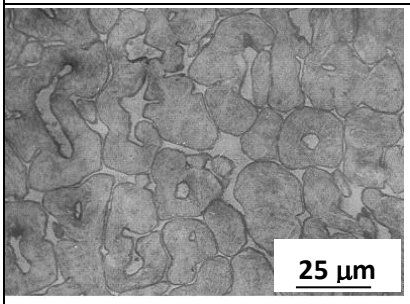
a). As-cast optical microstructure of M1



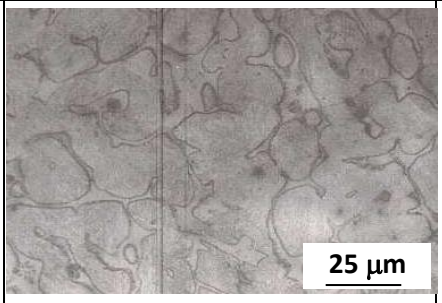
b). As-cast optical microstructure of M3



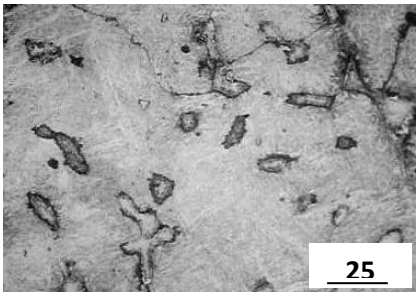
c). As-cast optical microstructure of M4



d). As-cast optical microstructure of M9



e). As-cast optical microstructure of M10



f). As-cast optical microstructure of M11

3. Results and Discussions

Nitrogen Solubility in Melting.

To attain the nitrogen solubility referred the Sieverts law. Alloying elements were added based on the theoretical nitrogen solubility, for the melts from M1 to Melt 11. Compared the theoretical nitrogen solubility and experimental nitrogen solubility. The theoretical nitrogen solubility is higher than the experimental nitrogen solubility, some of the melts are lower than some other melts. The volume fractions of nitrogen in a solid solution of the melt are listed in Table-1. It shows its effectiveness of stay in the melt interstitial gap as solid solution strengthener. Were the volume fractions of nitrogen solubility not exceeds one and above are shown defect free in visual inspection, other melts shows the nitrogen solubility is higher than one and above are defected.

To confirm the attainment and not attainment of nitrogen solubility are revealed in the samples of melts M4 and M5 are shown in Figure-1. Melt M4 shows the sufficient interstitial gapes are occupied by nitrogen so that the M4 and M1, M3, M9, M10, M11 are defecting free melts. The theoretical nitrogen solubility is less in almost all melts except for melts M5, M6, M7, and M8 found porosities/ gas defects were obtained in the cast metal after solidification is due to an excess of volume fractions of the interstitial gap in the melts as stated by [4] and [5] have reported that the excess of nitrogen forms Fe and Cr carbo-nitrides, while still higher nitrogen content forms porosity and its solubility fractions are more than one in the austenite phase. Also support of these melts Simmons [6] reported that during solidification, the liquid metal can become supersaturated with nitrogen, resulting in foaming of the melt.

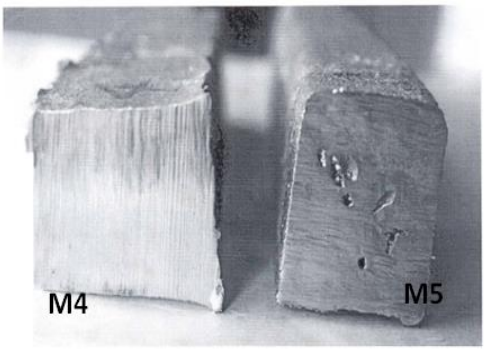


Fig. 1: Defect-free (Melt 4) and with a defect (Melt 5) of NAMSS

Out of eleven melts, six melts M1, M3, M4, M9, M10, and M11 were taken for further study of as cast hardness test to find the effect of sufficient nitrogen content in the melts.

High Nitrogen Stainless Steel.

[6,7] viewed that Solubility of N is increased by the addition of alloying elements such as Cr, Mn, Mo, since these elements decrease the chemical potential of N. The larger the stability of nitrides of the transition metals, the smaller is the' electron density. Alloying of Ti, V, Cr, Zr, Nb, Mo nitrides are much more stable than Mn, Fe nitrides Ni and Cu nitrides are unstable. In contrast, with carbides, there is often a structural compatibility between the crystallographic lattices of solid solutions and nitrides which often are Hagg's compounds.

4. Characterization of As-Cast NAMSS Samples

Hardness measurement

The hardness were found in as cast condition to find the character of the Nitrogen Alloyed Martenetistic Stainless Steel (NAMSS) of six melts M1, M3, M4, M9, M10, and M11 are given in Table (6)

Table 6: Variations of Hardness in NAMSS as-cast condition**.**

Melts	M1	M3	M 4	M9	M10	M11
Hardness (HV) @ 10 kg load	402	341	472	427	436	389

The hardness of melts ranges from 341 to 472 HV. The lowest hardness values of 341 HV is for melt M3 might be due to lower Cr and lower nitrogen and M1 is little is higher hardness than M3 is due to the influence of Mo. In addition to that, decrease in the solubility of nitrogen during the solidification of the steel, due to the formation of δ ferrite [2].

The hardness values of melts M1, M9, M10, and M11 though seem to be higher 389 to 436 HV; it is line with the various literatures. The hardness value of melt M4 is high and the same may be due to higher nitrogen content.

According to [2] the hardness variations in as-cast NAMSS can be due to the atomic concentration of carbon and nitrogen, and consequently, the number of occupied interstitial atomic positions may be lower than the atomic concentration of carbon. In addition, the nitrogen atomic radius is slightly smaller than carbon, which would cause less lattice deformation in the martensitic reaction.

Micro Examination

The as-cast microstructure of the selected six melts M1, M3, M4, M9, M10, and M11 are shown in Figures-2 a to f.

The microstructure is not uniform in the as cast condition due to the uneven rate of solidification of the melts.

The microstructure of as-cast sample of melt M1 reveals martensitic matrix as shown in Figure 2a. The microstructures of melts M3, M4, M9, M10, and M11 reveal martensitic matrix with considerable amount of ferrite and alloy carbides as shown in Figures-2 b to f.

The percentages of ferrite, alloy carbides have a direct relation with the hardness. In M3 the as-cast hardness is lower due to higher percentage of ferrite.

The higher hardness of melt M4 can be attributed to the network of ferrite and alloy carbides as seen in Figure-2c. Kaluba et al (1999) have reported that, in the as-cast condition, all Fe alloys show ferrite structure.

5. Conclusion

1. Nitrogen alloyed martensitic stainless steel can be successfully produced using conventional induction furnace.
2. Nitrogen alloyed martensitic stainless steel with nitrogen up to 0.125% can be produced in the conventional induction furnace.
3. The theoretical nitrogen solubility estimated by thermodynamic relationship could be achieved using the conventional induction furnace.
4. Micro porosities were observed in the test castings when actual nitrogen content exceeds the theoretical nitrogen content.
5. Hardness up to 472 HV can be obtained with melts containing 0.11wt% nitrogen in the as-cast condition.
6. The hardness decreases is due to higher percentage content of ferrite and also hardness increases is due to the attributed network of ferrite and alloy carbides.

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