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Low carbon high nitrogen stainless steel

By

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Abstract:

Austenitic stainless steel is one of the most important stainless steels. This article aims to investigate the effect of partial and total replacement of nickel by nitrogen on both mechanical properties and phase of steel. The proposed stainless steels were produced in 10 kg induction furnace under nitrogen pressure. The produced stainless steels forged at high temperature. The investigated stainless steels heat treated at 1200 ^oC for 1 hour cooled in water, followed by tempering at 300 ^oC for1 hour. Nonmetallic inclusions such as nitrides were separated by electrolytic dissolution. Nitrogen as nitrides was determined and soluble nitrogen was calculated. XRD technique was used to investigate the types of nonmetallic inclusions. The microstructure of produced stainless steels was observed.

The tensile properties were determined of tempered stainless steels after quenching process. The base stainless steel has chemical composition 14.42%Ni, 0.0387%C,1.64%Si, 1.62%Mn, 20.24%Cr, 2.39%Mo and 0.008%N. It was found that it has yield and ultimate tensile strength 352.6 MPa and 550.2 MPa respectively. The developed stainless steel has the same chemical composition of the base one with 6.54%Ni and 0.232%N. It has yield and ultimate tensile strength 494.5 MPa and 714.9 MPa respectively. In addition to the free nickel stainless steel grade with 0.342%N- has yield and ultimate tensile strength 746.2 MPa and 886.0 MPa respectively. From experimental results, either partial or total replacement of nickel by nitrogen improves tensile properties, in addition to the microstructure will be not changed.

Keywords:
Austenitic Stainless Steel, High Nitrogen, Free Nickel Austenitic Stainless Steel

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1. Introduction:

Austenitic stainless steels have several applications in different fields. Conventional austenitic stainless steels must contain at least 8%Ni. Nickel is strategic alloying element; in addition it is expensive alloying element. Nickel acts as austenitic stabilizer in stainless steel.

Recently, there is a new trend in the world aims at the replacement of nickel by nitrogen as an austenitic stabilizer element [1-5]. Nitrogen is one of the strongest austenitic stabilizing elements among all the austenitic stabilizers i.e. C, N, Mn, Ni, Cu.

The partial replacement of nickel by nitrogen improves the mechanical properties, as well as the corrosion resistance.

This article aims at development of new grades of austenitic stainless steels through partial and total replacement of nickel with nitrogen. Also, investigation the influence of partial and total replacement of nickel by nitrogen on mechanical behavior.The main problem - faced by steel-making researchers - is how to introduce nitrogen into molten stainless steel and how keep it during solidification process.

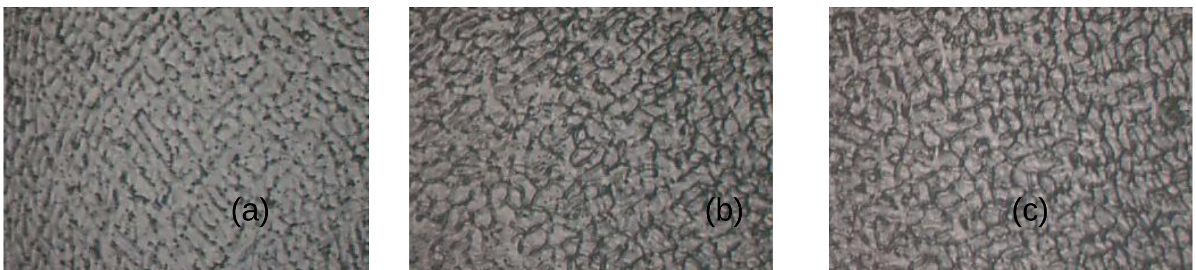
2. Experimental:

Two types of stainless steels with different contents from nickel and nitrogen were melted in 10 kg. induction furnace type IF-001 under different nitrogen pressure. The reference steel was melted in open air 10kg induction furnace. Molten metal was cast into refractory sand mould at 1600 ^oC, under nitrogen pressure. The produced ingots were recharged into reheating furnace. Ingots have square cross section area 60mm x 60mm. Stainless steels were heated up to 1150 ^oC and holded for 1 hour. The forging process starts at 1100 ^oC by using load of one ton free forging (dieing). The finishing temperature was 925 ^oC to produce rods of 30 mm^2 square. The kjeldahl apparatus was used to determine the total and insoluble nitrogen content in produced stainless steels. The chemical compositions of produced steels were determined by using spectroscopic analysis. The heat treatment processes of investigated stainless steels were carried out at 1100 ^oC, 1150 ^oC and 1200 ^oC, kept for one hour, followed by water quenching. The quenched stainless steels were tempered at 300 ^oC for 1 one hour. Hardness (HB) tests were carried out on polished quenched stainless steel samples. Tensile tests were carried out at room temperature for tempered stainless steels after heat treatment at 1200 ^oC. Microstructure examination of heat treated steels was carried out. Tempered stainless steels after solution treatment at 1200 ^oC were subjected to electrolytic dissolution for isolation of non-metallic inclusions. Non-metallic inclusions were examined by using D8 ADVANCE X-ray Diffractometer. Insoluble nitrogen was determined in investigated stainless steels.

3. Results.:

Produced stainless steels have nitrogen contents ranging from 0.008% up to 0.342 %, it associated with decreasing in nickel contents from 14.42 % down to 0.089%Ni. Table (1) shows the chemical composition of produced stainless steels. The microstructures of solution treated stainless steels at different temperatures were investigated as given in Figs.(1a, 1b, 1c). The hardness measurements after solution treatment at different temperatures (1100 ^{o}C, 1150 ^{o}C, and 1200 ^{o}C) for one hour were given at table (2). Yield strength, ultimate tensile, and elongation of tempered stainless steels after solution treatment at 1200 ^{o}C are listed in table (3).

The non-metallic inclusions of stainless steels containing nitrogen were isolated using electrolytic cell. Insoluble precipitates were collected and analyzed. The weights of precipitates of 50 gm dissolved steels were about 0.0, 0.13 and 0.265 gm of investigated stainless steels: 1 (reference steel), 2, 3 respectively. The contents of insoluble nitrogen were 0.023 and 0.051% of stainless steels 2 and 3. This values corresponding to about 10 % and 15% from total nitrogen respectively. The XRD structure analysis of isolated non-metallic inclusions of stainless steels 2 and 3 are given in Fig.2



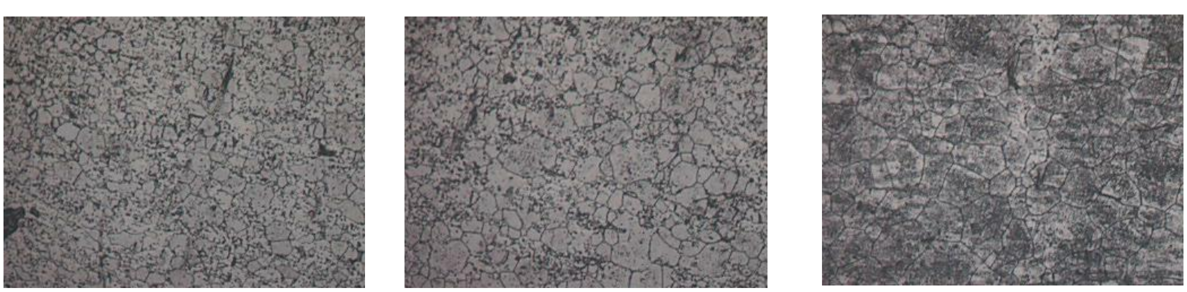
X100

Fig. 1a: Microstructure of reference steel after heat treatment at a-1100 ^{o}C, b-1150 ^{o}C & c- 1200 ^{o}C for 1 hour.

(a) (b) (c)

X300

Fig. 1b: Microstructure of steel 2 after heat treatment at a-1100 ^{o}C, b-1150 ^{o}C & c- 1200 ^{o}C for 1 hour.



(a) (b) (c)

X300

Fig. 1c : Microstructure of steel 3 after heat treatment at a-1100 °C, b-1150 °C & c- 1200 °C for 1 hour.

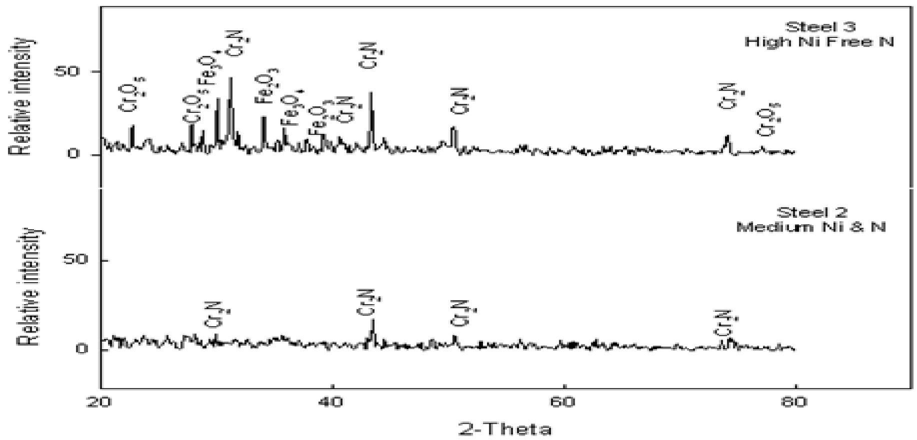


Fig.2: XRD of precipitates of steels 2 & 3 after quenched at 1200 oC, for 1 hour.

***Table (1)*: *Chemical composition of produced stainless steel*s**

No.	C	Si	Mn	P	S	Cr	Mo	Ni	N	Fe
1	0.039	1.64	1.62	0.021	0.0115	20.24	2.39	14.42	0.008	59.5
2	0.046	1.56	1.86	0.0199	0.0133	19.74	2.39	6.54	0.232	67.7
3	0.039	1.39	1.40	0.0204	0.0120	20.69	2.35	0.0893	0.342	73.9

Table (2): *Hardness of investigated stainless steels after heat treatment at different temperatures for one hour*.

Heat No.	Hardness(HB), of tempered stainless steels at 300 °C for 1 hour after solution treatment at		
	1100 °C	1150 °C	1200 °C
1	145.6	155.3	145.0
2	191.6	211.0	183.7
3	236.0	252.0	231.3

Table (3):*Yield, ultimate tensile strength, & elongation of tempered stainless steels after quenching from 1200 °C* **.**

Heat No.	Mechanical properties		
	Yield strength, MPa	Ultimate tensile strength, MPa	Elongation, %
1	352.6	550.2	51.8
2	494.5	714.9	55.7
3	746.2	886.0	19.0

4. Discussions:

The designed stainless steels must have a stable austenitic structure. Different ways to estimate the austenitic stability, the first way is to use the Schaeffler diagram [6]. Substitution of the contents of the alloying elements in given stainless steels by its nickel and chromium equivalents is given in equations (1&2) and Fig.3. [1], from these results, it can estimate the austenitic stability of steels 2 and 3 like reference steel. The estimated chromium and nickel equivalents of the investigated steels are given in table (4).

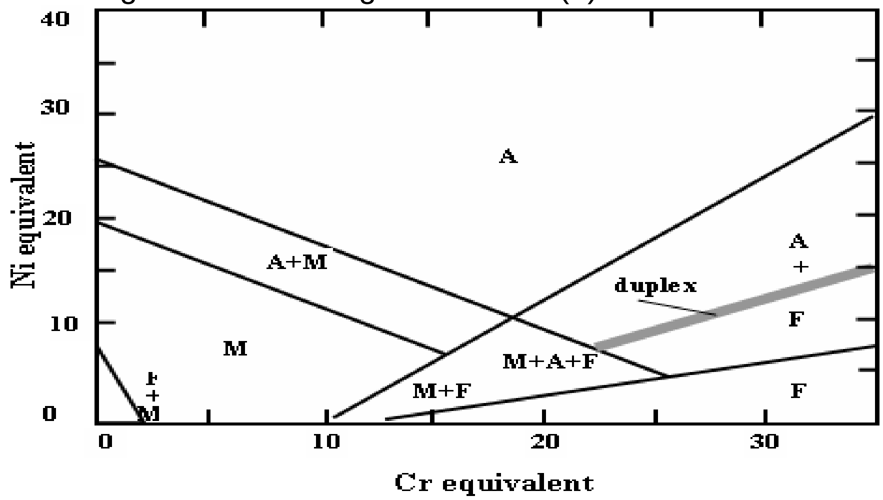


Fig.3: Schaeffler diagram[1], with (mass%), A= austenite, M= martensite, F= ferrite.

$$Cr_{eq} = Cr + 1.5Mo + 1.5W + 0.48Si + 2.3V + 1.7Nb + 2.5Al \qquad (1)$$

$$Ni_{eq} = Ni + Co + 0.1Mn - 0.01Mn^2 + 30N + 30\,C. \qquad (2)$$

Table (4): *Chromium and nickel equivalent for produced steels*

Steel number	1	2	3
Cr- Equivalent	28.6	24.1	24.0
Ni- Equivalent	15.8	15.0	12.5

As it was expected, all the designed steels have austenitic structure as it is clear from microscopic examination as shown in Fig. 1.

Non-Metallic Inclusions (NMI) were isolated, collected and analyzed. The XRD structure analysis of isolated (NMI) of stainless steels 2 & 3 as tempered after quenching from 1200 ^oC for one hour is illustrated in Fig.2. Results of XRD examination of NMI show that, non-metallic inclusions mainly consist of Cr_2N and some iron and chromium oxides. The peak of Cr_2N in steel 3 -free nickel high nitrogen steel - is higher than that of steel 2 (medium nickel and nitrogen).

There is no non-metallic inclusion separated from steel 1. This may be due to the steel sample has low carbon content (0.039%), very low nitrogen content (0.008%) and the rapid cooling may form very fine inclusions, So, it can not be isolated.

Fig. 4 shows that the influence of total nitrogen content on the hardness of treatable stainless steels at temperatures (1100 ^oC, 1150 ^oC, and 1200 ^oC). It is clear that the hardness of these stainless steels increases by increasing nitrogen content at different temperatures. Hardness of the same nitrogen content increases with rising the heating temperature in the range 1100 ^oC up to 1150 ^oC, Increasing of hardness can be due to more rapid cooling rate give more grain refining, which consequently has positive significant effect on hardness. By further

increase in temperature up to 1200 ^{o}C, hardness decrease due to the grain growth of the matrix as given in Figs.(1a, 1b, 1c). These results are in good agreement with previous work [7-9].
Examination the microstructures of quenched stainless steels from temperatures (1100 ^{o}C, 1150 ^{o}C, and 1200 ^{o}C) show that the grain size of investigated stainless steel number 3 (0.342% total nitrogen) is smaller than reference steel (0.008% total nitrogen) and stainless steel number 2 (0.232% total nitrogen). This attributed to the insoluble nitrogen content in steel 3 (0.051% insoluble nitrogen) is greater than of steel 2 (0.023% insoluble nitrogen) which have significant effect on grain size.

Fig.5 reveals that there is a strong positive correlation between total nitrogen content of stainless steels and both yield and ultimate tensile strength. The yield strength was observed to increase at an average rate of 1093 MPa /1mass % nitrogen – with regression factor (R) 0.88 - according to the equation (3) and the ultimate tensile strength increases at an average rate of 959 MPa /1mass % nitrogen – with regression factor (R) 0.96 - given by equation (4).

$$R_{0.2}(MPa) = 318 + 1093[N\%] \tag{3}$$

$$R_{m}(MPa) = 529.9 + 959[N\%] \tag{4}$$

The experimental results were in good agreement with the previous work [3, 10-12].
Figs.(6-7) show that the variation of yield & ultimate tensile strength with soluble and insoluble nitrogen content, respectively. It is clear that both soluble and insoluble nitrogen has significant effect on yield and ultimate tensile strength, but the insoluble nitrogen has more significant effect.

It is clear that there is a correlation between soluble nitrogen content of stainless steels and both yield and ultimate tensile strength. The yield strength was observed to increase at an average rate of 1260 MPa /1mass % nitrogen – with regression factor (R) 0.858 - according to equation (5) and the ultimate tensile strength increases at an average rate of 1112 MPa /1mass % nitrogen – with regression factor (R) 0.945 – as given in equation (6).

$$R_{0.2}(MPa) = 316.5 + 1260[N_{soluble}\%] \tag{5}$$

$$R_{m}(MPa) = 528 + 1112[N_{soluble}\%] \tag{6}$$

Also, there is a positive correlation between insoluble nitrogen content of steels and both yield and ultimate tensile strength. The yield strength was observed to increase at an average rate of 7771 MPa /1mass % nitrogen – with regression factor (R) 0.989 - and the ultimate tensile strength increases at an average rate of 6567 MPa /1mass % nitrogen – with regression factor (R) 0.998 – as given in equations (7&8) respectively.

$$R_{0.2}(MPa) = 339 + 7771[N_{insoluble}\%] \tag{7}$$

$$R_{m}(MPa) = 555 + 1112[N_{insoluble}\%] \tag{8}$$

However, soluble and insoluble nitrogen have different effects on the mechanical properties of nitrogen steels (steels 2 and 3) in quenched state. Increasing the soluble nitrogen content is accompanied with some losses in strengths. On the other hand, increasing the insoluble nitrogen content has a significant strength increment.

By increasing the soluble nitrogen, the solid solution hardening increases. However, this strength increment seems to be lower than the losses in precipitation strengthening (due to decrease of nitrides precipitates) with the result of decrease in both yield and ultimate tensile strengths as the soluble nitrogen increases.

Soluble nitrogen has positive effect on solid solution hardening. Solid solution hardening is due to atomic size misfit of the solute atoms and due to that the solute atoms being equivalent to regions which are elastically harder or softer than the matrix.
The increase in yield strength due to solid solution strengthening $\Delta R^{s}{}_{p}{}^{h}$ (MPa) could be expressed by the following equation (9) [7-9].

$$\Delta R^{s}{}_{p}{}^{h}=1.77*G_o*(X_N)^{0.5}*F_o^{1.5} \qquad (9)$$

Where:
G_o : is the shear modulus
X_N : is the concentration of nitrogen atom in solution
F_o : is a parameter to describe the interaction between dislocation and solute atoms.
X- Ray measurements given by many authors [11] give a value for F_o = 0.20 &G_o = 76 GPa at 0K.

Strength increment due to increase of insoluble (precipitated) nitrogen could be attributed to increase of precipitation hardening as a result of increasing the volume fraction of alloy nitrides precipitates. Increase of insoluble nitrogen would be accompanied by decreasing the soluble nitrogen with the result of decreasing the solid solution strengthening. However, it seems that the strength increment due to increase of precipitation hardening is higher than the strength decrement due to the losses in solid solution hardening resulting in net increases in yield and ultimate tensile strengths as the insoluble nitrogen content increases.
Insoluble nitrogen has positive significant effect on grain size. Grain size has a great effect on strength of steel. Grain size hardening depending on the nitrogen content, temperature and grain size, ΔRG (MPa), can be calculated by the equation (10)[13]:

$$\Delta RG=\{ 8+75*[1-(T/823)^{2/3}*CN\}*(1/[L]^{0.5}) \qquad (10)$$

Where: CN : Nitrogen concentration in mass %, L: Grain size in mm, T : Temperature in K
In contrast to the increase of yield and ultimate tensile strengths with increasing the precipitated nitrogen content (as nitrides), there is an increase in elongation by increasing nitrogen content up to 0.232, by further increasing, the elongation decrease as show in Fig. (8). The increasing in elongation by nitrogen (up to 0.232%N), most of nitrogen present in soluble form, while by further increase nitrogen (0.342%N) enhance the formation of nitrides. This has negative significant effect on elongation. This can be attributed to the restriction of austenite grain size due to the precipitation of nitride compounds in the austenite matrix

which in turn act as obstacles of grain growth. So, the decrease in grain size and increase of precipitation strengthening is accompanied by decreasing both elongations as it is clear in Fig. 9.

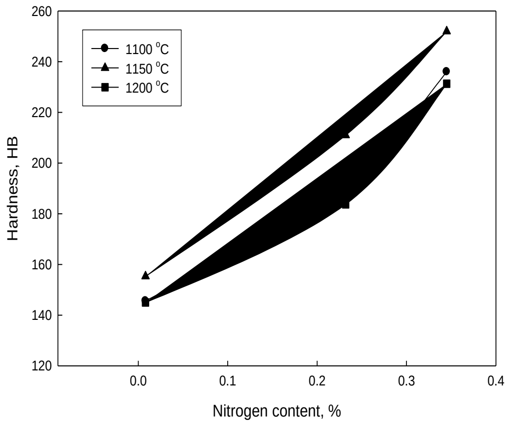


Fig. 4: The variation of hardness with nitrogen content at temperatures 1100 °C, 1150 °C, and 1200 °C.

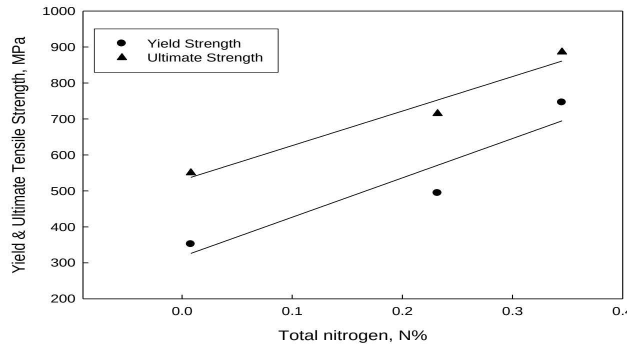


Fig.5: The variation of yield and ultimate tensile strength with total nitrogen content.

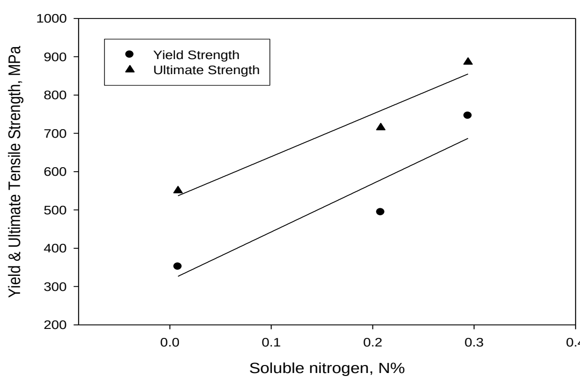


Fig.(6) Effect of soluble nitrogen on yiel(and tensile strength of investigated steels

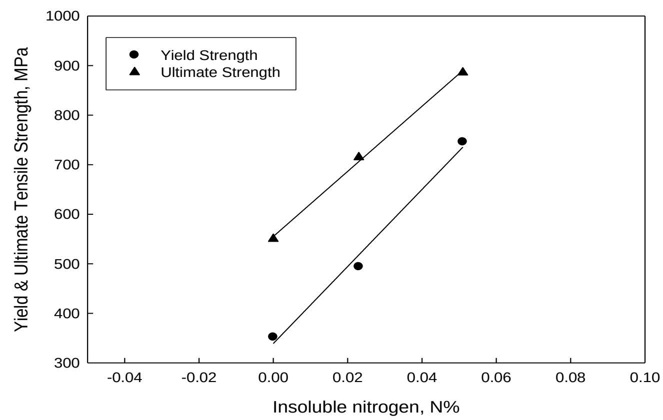


Fig.7 Effect of insoluble nitrogen on yield and tensile strength of investigated steels

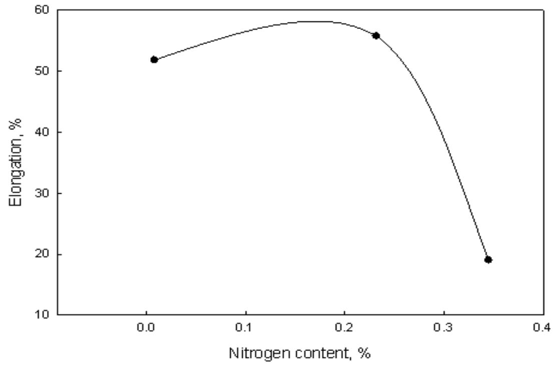


Fig.8: The variation of elongation with nitrogen content.

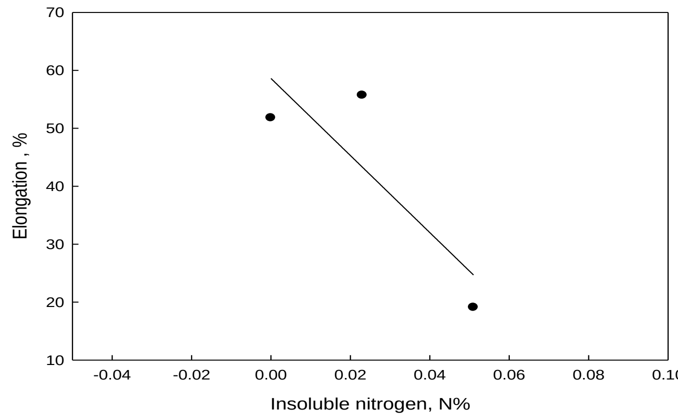


Fig.(9)Effect of insoluble nitrogen on elongation of investigated steels

5. Conclusions:

This article has been carried out to investigate the effect of partial and total replacement of nickel by nitrogen in austenitic stainless steel, on the mechanical properties and phase stability. From the results of this article, the following conclusions can be drawn

- The microstructures of the developed stainless steels mainly have austenitic phase
- The hardness - of heat treated stainless steels - increases by increasing nitrogen content at temperatures (1100 ^oC, 1150 ^oC, and 1200 ^oC)
- The precipitates mainly consist from Cr_2N
- Nitrogen, especially nitrides, has effect on grain refinement of austenitic stainless steels
- Partial replacement of nickel, by adding 0.232 % nitrogen, or total replacement of nickel, by higher nitrogen addition of 0.342%, improve mechanical properties
- Nitrogen content has a positive significant effect on grain size. As the nitrogen content increase as the grain size decreases.
- The actual factors which control the mechanical properties of nitrogen containing austenitic stainless steels may be summarized in the grain size, the solid solution strengthening and the precipitations hardening
- Yield and ultimate strength are improved by increasing total nitrogen content by rate 1093MPa/1massN% and 959MPa/1massN% respectively.
- Partial and total replacement of nickel by nitrogen improves yield and ultimate tensile strength.
- The partial replacement of nickel has little positive effect on elongation, in opposite side, the total replacement of nickel by nitrogen has negative significant effect on elongation.

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