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Development of high nitrogen, low nickel, 18%Cr austenitic stainless steels

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Two high nitrogen stainless steels are studied through metallographic, mechanical and corrosionistic tests and the results are compared with those shown by a standard AISI 304. These high nitrogen steels show a significantly higher mechanical strength than usual AISI 304 while their corrosion resistance lie among that of standard austenitic and that of standard ferritic stainless steels. *© 2000 Kluwer Academic Publishers*

1. Introduction

Austenitic stainless steels containing nickel have been indispensable for the progress of technology during the last 80 years. Due to the cost of nickel and to the prospected possibility of allergic reactions caused by this element, more and more laboratories and industries are trying to develop a new class of austenitic stainless steels without nickel [1–3].

To maintain the austenitic microstructure nickel reduction is balanced by nitrogen addition. Nitrogen alloyed austenitic stainless steels exhibit attractive properties as high strength and ductility, good corrosion resistance and reduced tendency to grain boundary sensitation [4]. Since nitrogen increases the stability of the austenite phase against the martensite formation [5], nitrogen alloyed austenitic stainless steels can be strengthened by cold working without formation of strain induced martensite. That results in higher mechanical properties and in a good balance between toughness and tensile properties. In this new class of stainless steels the presence of a high manganese content is required to attain the high nitrogen concentration in the melt avoiding the tendency to Cr_2N formation [6].

Specific potential applications of this new family of steels include automotive hose clamps, safety belt anchors, truck and bus frames, water supply and control structures, sewage treatment plant structures, bulk solids handling equipment, magnetic ore separator screens, coal buckets and hopper cars. Moreover, stainless steels have served successfully in many structural components in the transportation industry. In particular bus frames and bumpers can take advantage of the high strength of this new family of stainless steels.

Nitrogen alloyed steels have been known since many years [1–6]. However, the research reported in the scientific literature has been mainly focused on basic metallurgy aspects. Recently, we have reported the solidification behaviour of these materials showing the possibility of classical equations to predict the solidification mode of nitrogen alloyed steels as a function of their chemical composition [2]. In this paper, the mechanical properties and corrosion resistance of two high nitrogen, 18% chromium, austenitic stainless steels are reported. One of the steels studied is virtually nickel-free while the other has a low-nickel content. These alloys do not contain molybdenum and in this sense are similar to the standard AISI 304. Moreover, the high nitrogen content makes them good candidates for possible application as structural materials.

2. Effect of the alloying elements on the γ stability

In order to better design a new steel the effect of the alloying elements on the stability of the γ phase should be evaluated. This evaluation has been here performed using Thermo-Calc, a software and a thermodynamic database developed to predict the equilibrium in multicomponent systems [7]. The pseudo-binary phase diagram Fe-N for a hypothetical system containing 18.5% Cr, 10% Ni, 1.2% Mn at 1 bar is reported in Fig. 1. The chemical composition of a standard AISI 304 stainless steel is also indicated in the diagram by a dashed line for comparison purposes. Fig. 1 results show that N content cannot exceed 0.22% to avoid N_2 gas formation due to the sudden decrease in N solubility during steel solidification. Moreover, ferrite formation further decreases N solubility.

In order to compare the effects of Ni and N alloying the De Long diagram can be applied [8]. Following this approach the Ni equivalent of N is equal to 30; then, the addition of 0.22% of N is equivalent to 6.5% of Ni, resulting in a potential reduction of the Ni content from 10% to 3.5%.

Then, the next step is the analysis of the pseudo-binary phase diagram Fe-N for a system containing 18.5% Cr, 3.5% Ni, 1.2% Mn at 1 bar as reported in Fig. 2. The decrease in Ni content induces a marked

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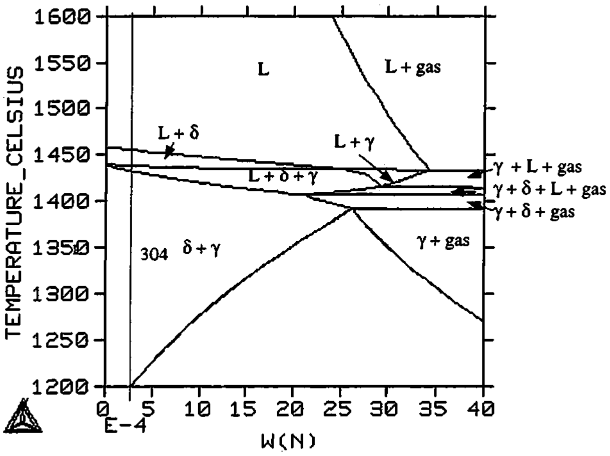

Figure 1 Thermo-Calc Fe-N pseudo-binary diagram for a system containing 18.5% Cr, 10% Ni, 1.2% Mn.

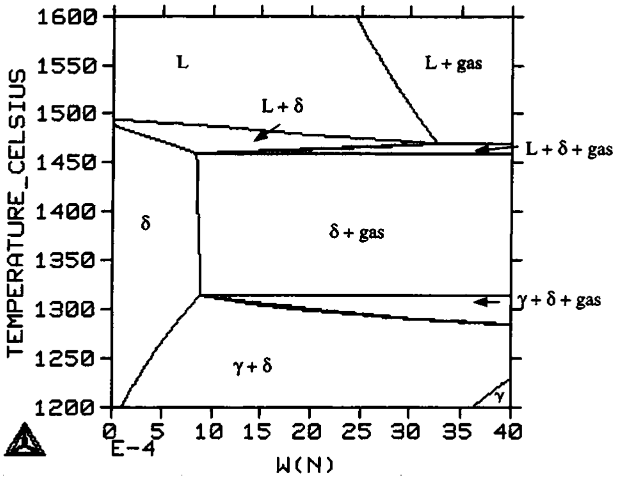

Figure 2 Thermo-Calc Fe-N pseudo-binary diagram for a system containing 18.5% Cr, 3.5% Ni, 1.2% Mn.

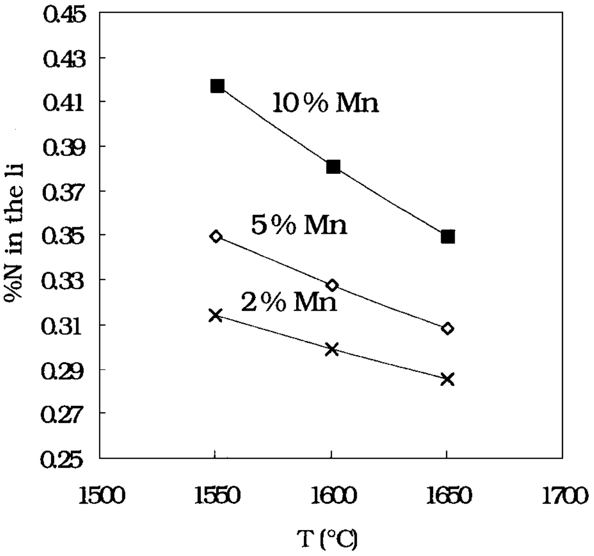

Figure 3 Solubility of N in Fe-18Cr-Mn alloy for different Mn additions.

decrease of N solubility during solidification due to the expansion of the single solidification region of the ferrite phase. However N solubility can be increased with the addition of other alloying elements. In fact, the effect of Mn in increasing the N solubility in the liquid is well known [9]. This effect is reported in Fig. 3 for temperatures ranging between 1550 °C and 1650 °C. The addition of 10% Mn increases the N solubility at 1550 °C up to 0.42%.

TABLE I Chemical compositions of the high nitrogen steels studied (mass %)

	C	Si	S	P	Mn	Cr	Ni	Mo	Cu	N
A	0.026	0.04	0.003	0.026	10.5	18.6	0.42	0.07	0.07	0.22
B	0.031	0.04	0.003	0.026	10.5	19.7	3.45	0.03	0.07	0.22

3. Materials and experimental procedure

Two high N and low Ni stainless steels were received as a plate of 25 mm of thickness. The chemical composition of the steels is shown in Table I.

The ferrite content of the as received plates was determined by automatic image analyser (AIA) after electrochemical etching in a solution containing 20 g NaOH in 100 ml H_2O. In order to study the stability of the γ - phase at the hot rolling temperature, 10 × 10 × 25 mm samples, drawn from the plates, were annealed in the temperature range 1100°C–1300 °C up to 10 min. The content of magnetic phase was measured by ferritescope. The plates were annealed at 1250 °C and hot rolled in laboratory down to 5 mm of thickness. The toughness of the hot rolled plates was measured using the Charpy test and compared with that of a standard AISI 304.

The hot rolled and annealed plates were cold rolled with reductions ranging from 20% down to 80%. Also in this case the content of magnetic phase (martensite and δ ferrite) in cold rolled sheets was measured by means of a ferritescope to analyse the work hardening behaviour.

The mechanical properties of the cold rolled steel were examined by tensile testing and hardness measurements.

The corrosion resistance of the high N steels was analysed by potentiodynamic polarisation tests and compared with that of standard stainless steels. The specimen surface was polished by using increasingly finer abrasive papers, starting from a 300 grit paper and finishing up to a 1000 grit paper. Measurements were made at 25°C with a conventional glass cell. Electrolyte was a deaerated 35 g/l NaCl solution. The potential of the working electrode was measured using a saturated calomel electrode (SCE) as reference. The counter electrode was a platinum foil. The scan rate was 2.4 V/h. Before starting, cathodic reduction of passive film was performed at −1 V/SCE for 90 s. The pitting potential values, E_p, were taken as the last value at which the current was as low as that of a completely passive specimen. Each steel was subjected to a minimum of three complete scans.

4. Results and discussion

The volumetric percentage of δ-ferrite measured in both as received steels A and B via AIA are reported in Table II. Although the results of ferrite content are affected by the highest degree of dishomogeneity of A, it is evident that this steel has a significative higher ferrite content than material B. The highest ferrite content in A is related to the lowest content in nickel, unbalanced by an adequate modification of the concentration of austenite and ferrite forming elements.

In order to analyse the behaviour of the materials under hot rolling, the effects of the thermal treatment of the steels have been studied in terms of the percentage of δ-ferrite as a function of the reheating temperature. The results of this study are reported in Fig. 4 for both materials studied. Above 1150°C, δ-ferrite content increases as a consequence of the reheating in the dual phase δ-γ region.

Edge cracking did not occur during hot rolling although the ferrite content at $T = 1250\,^\circ$C (12%) was at the limit of the tolerated ferrite content for this family of steels [10]. Toughness was measured on the hot rolled B steel and compared to that of a standard AISI 304. Results are shown in Fig. 5. The high nitrogen austenitic stainless steel shows a higher critical temperature than the standard AISI 304 stainless steel. However, its toughness is higher than that of standard AISI 304 for $T > -100^\circ$C. Regarding possible applications as a structural material it can be concluded that the service temperature range for this material should be kept above -100°C.

Both A and B steels were then cold rolled at different reduction rates. The magnetic phase content (ferrite $+ \alpha'$-martensite) was determined via ferritoscope and compared to the magnetic phase present in a standard AISI 304. The results are shown in Fig. 6. Both low nickel steels show a lower content of magnetic phase with respect to the conventional AISI 304 steel: that means that the austenite phase in the low Ni steels is more stable than in standard AISI 304 against the martensite formation.

M_d30, defined as the temperature at which, with a 30% deformation the material shows 50% magnetic

TABLE II Volumetric percentage of δ-ferrite in steels A and B. (Number of fields: 30, magnification: 200×)

	Ferrite %	Max %	Min %	SD
A	3.93	6.42	1.10	1.42
B	1.12	1.86	0.53	0.37

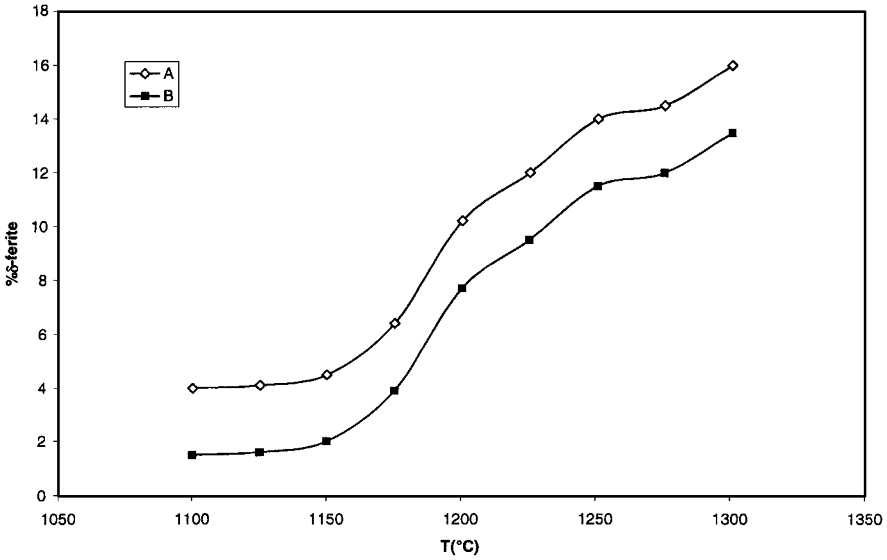

Figure 4 δ-ferrite content in rehated plates of A and B steels. Holding time: 10 min.

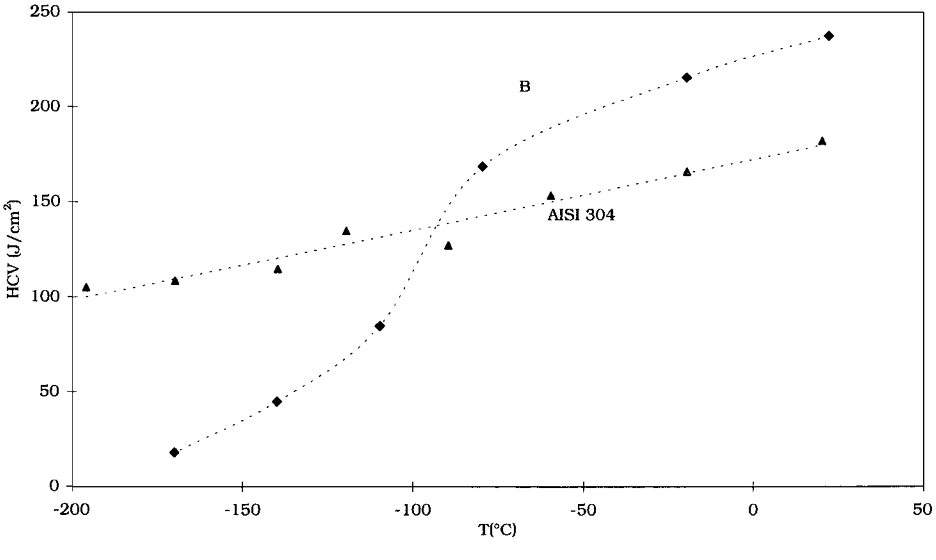

Figure 5 Toughness of the B steel and, as comparison, of a standard AISI 304.

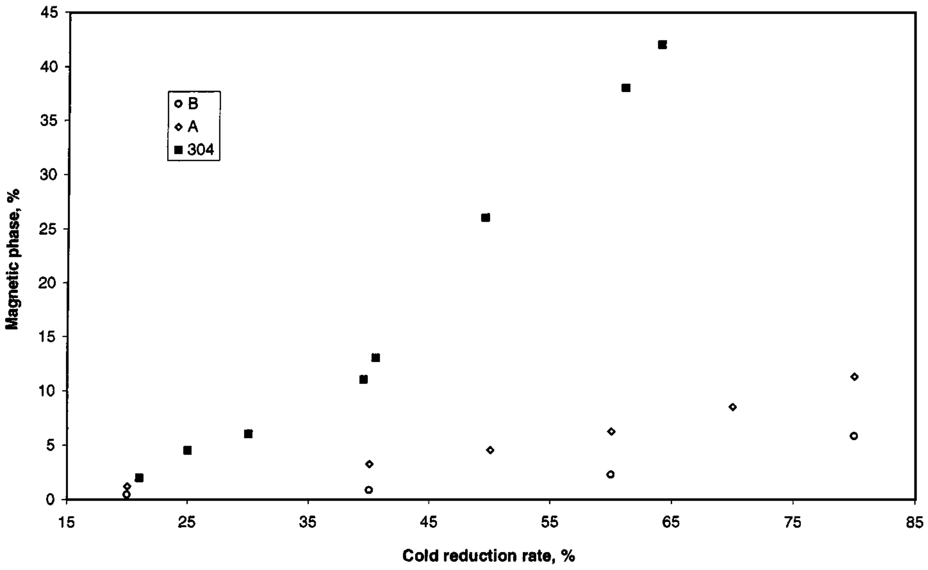

Figure 6 Magnetic phase in cold rolled A and B steels, and, as comparison, in a standard AISI 304.

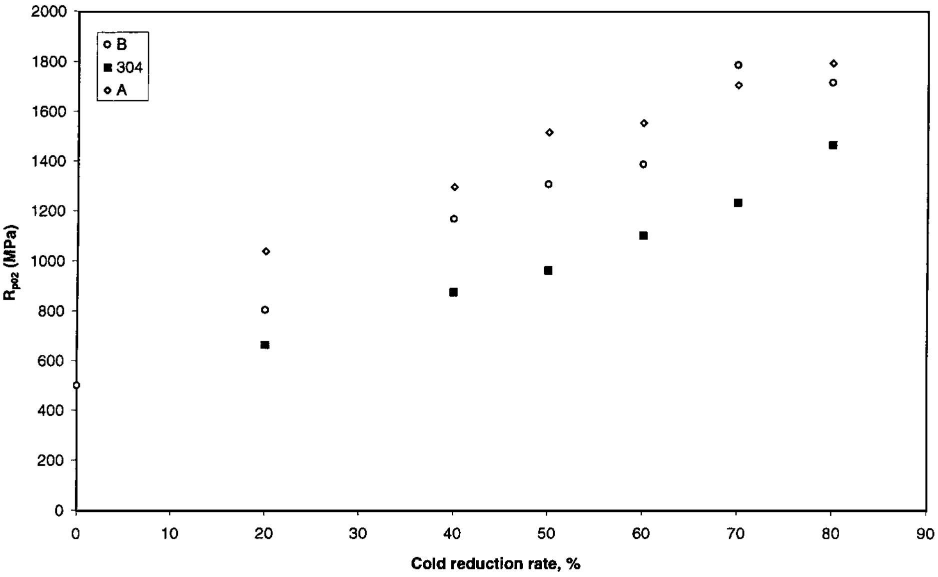

Figure 7 Yield stress of cold rolled A and B steels compared with the one of a standard AISI 304.

TABLE III M_d30 values calculated according to Angel (Equation 1) in steels A, B and AISI 304

Steel	A	B	AISI 304
M_d30 (°C)	−44	−91	106

phase content was calculated according to the following formula due to Angel:

$$M_d30(^\circ C) = 413–462(C + N)\text{-}9.2Si\text{-}8.1Mn \text{-}13.7Cr\text{-}9.5Ni\text{-}18.5Mo \quad (1)$$

The different values of M_d30, reported in Table III, confirmed the magnetic measurement results. From the definition of M_d30 it results that the higher the M_d30 value the higher the martensite content, in agreement with the experimental results.

The work hardening behaviour of the cold rolled A and B steels was studied as a function of cold reduction by tensile tests and hardness measurements and compared to that of a standard AISI 304 (Figs 7–9). Both low nickel steels have higher mechanical resistance with respect to the AISI 304 because of the higher nitrogen content. Cold working may attain yield strength of more than 1500 MPa. It is worth of note that the ratio R_m/Rp_{02} is sufficiently high to guarantee good ductility even at these high strength levels.

Samples of cold rolled A, B (cold reduction = 70%) have then been annealed for $t = 90$ s in the temperature range 1000–1200 °C. The values of the hardness in such samples are shown in Fig. 10 in comparison with typical values of standard stainless steels. These results indicate that a temperature of $T = 1200$°C is sufficient to guarantee an efficient annealing for both steels. The values of the mechanical properties corresponding to these conditions, as obtained by tensile test, are shown in Table IV and compared to those of standard stainless steels.

The mechanical properties reported in this research make high nitrogen steel a good candidate for those

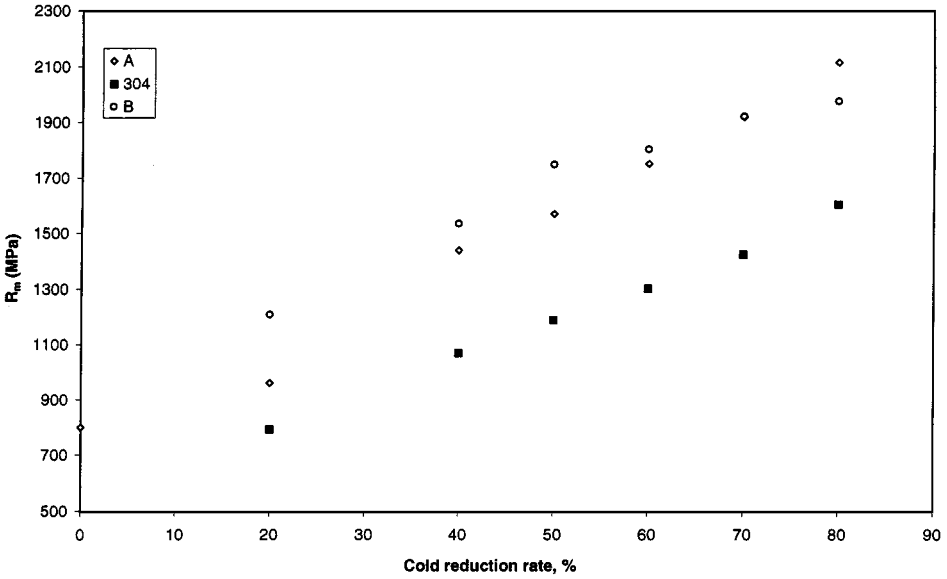

Figure 8 Tensile strength of cold rolled A and B.

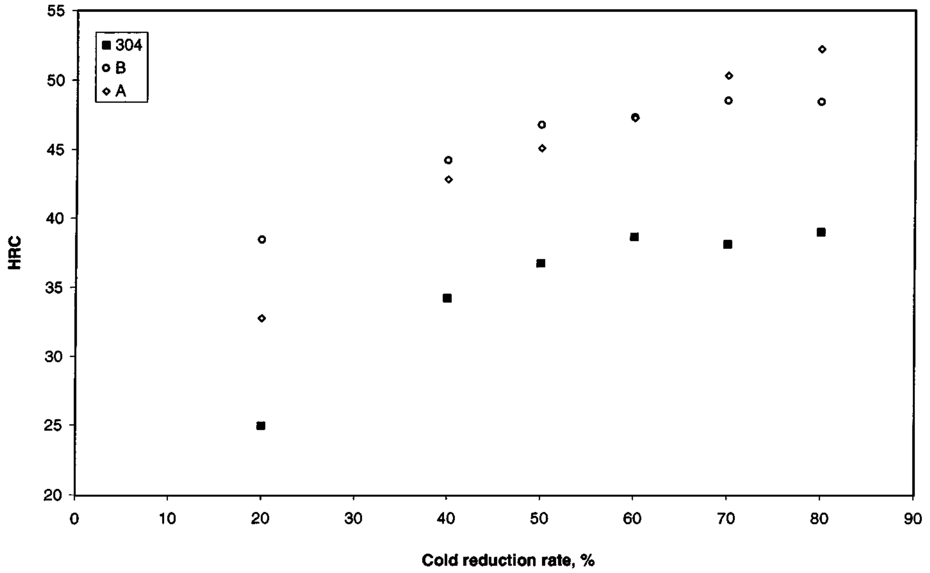

Figure 9 Hardness of cold rolled A and B steels compared with that of a standard AISI 304.

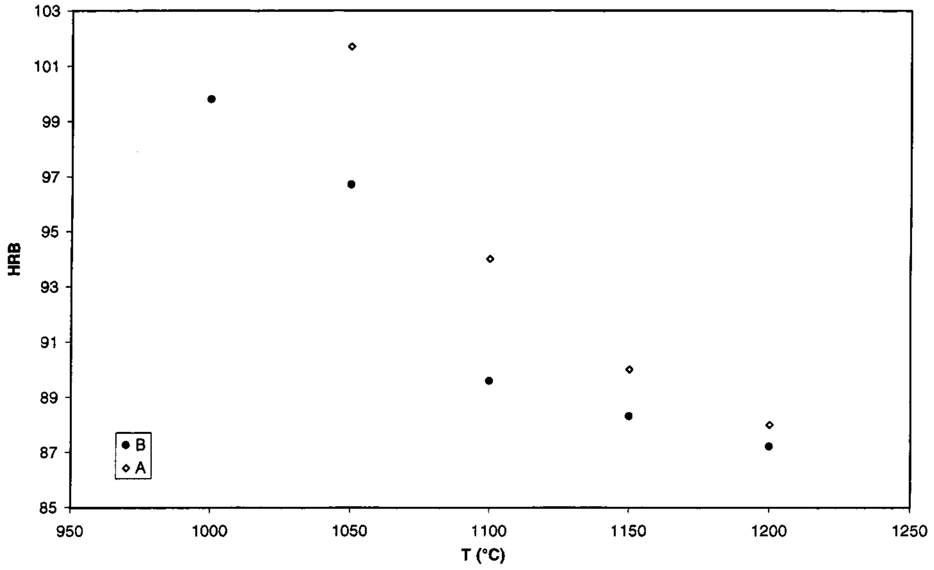

Figure 10 Hardness of A and B steels as a function of the annealing temperature.

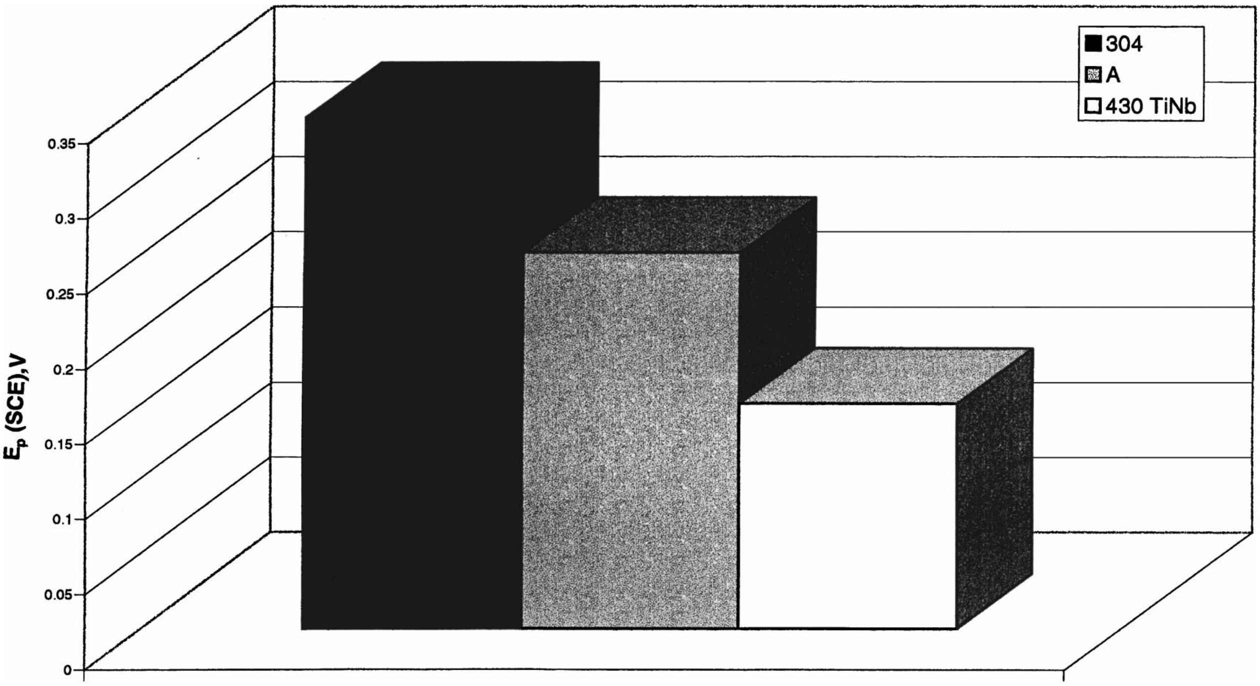

Figure 11 Pitting potential of A steel and, for comparison, of a standard AISI 304 and of a AISI 430 TiNb.

TABLE IV Mechanical properties in cold rolled and annealed steels A and B and, as a comparison, in standard stainless steels

Steel	R_{p02} (MPa)	R_m (MPa)	ε_{max} %
A	475	815	47
B	494	832	47
AISI 304	270	620	55
AISI 430	300	470	30

applications in which high energy absorption is required such as anti-crash, anti-intrusion bars in vehicles.

Pitting corrosion resistance has been evaluated on polished samples of steel A through a potentiodynamic test in a solution containing 35 g/l of NaCl. The value of the pitting potential, E_p, of the studied steels and, for comparison, of the standard AISI 304 and AISI 430 TiNb are shown in Fig. 11. The pitting potential of the high nitrogen steel is slightly lower than that of type 304, but sufficiently high to guarantee a good environmental resistance in structural applications.

5. Conclusions

Two low Ni austenitic stainless steels have been studied showing significantly higher mechanical properties than standard austenitic stainless steels. They show, in annealed conditions, a higher toughness than the standard AISI 304 in the temperature range $T > -100°C$. Moreover, they may be strengthened by cold working keeping ductility high.

The mechanical and corrosion properties may be improved by increasing the nitrogen content. However, Thermo-Calc results show that a further increase in the nitrogen content needs to be accompanied by a change in the chemical composition so to favour N solubilisation and to avoid porosity.

Regarding to possible applications of these new stainless steels as structural materials it can be concluded that their strength, toughness and ductility make these materials suitable for a wide range of uses in annealed conditions. Localised corrosion resistance is adequate to the proposed structural use of the new steel, being not far from the performance typical of type 304 steel.

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