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NITROGEN-CONTAINING STEELS

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NEW NITROGEN-BEARING AUSTENITIC STAINLESS STEELS WITH HIGH STRENGTH AND DUCTILITY

M. O. Speidel[1]

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The effect of nitrogen on the strength, ductility, and corrosion resistance of nitrogen-bearing austenitic stainless steels is studied. Fields of application of these steels are considered.

INTRODUCTION

In austenitic stainless steels nickel can be replaced by nitrogen. Articles produced from nitrogen-bearing steels are

– more environmentally friendly due to saving of resources;

– less expensive due to the low cost of nitrogen;

– much stronger (up to 3600 MPa);

– much more ductile than other steels with the same strength;

– more corrosion resistant (from the standpoint of localized corrosion resistance 1 wt.% nitrogen is equivalent to 20 wt.% chromium);

– more resistant to stress corrosion cracking;

– biocompatible due to the elimination of possible nickel allergy.

All these factors make austenitic stainless steels with high nitrogen content more promising materials for the future sustained technology and for production of articles that have longer service life and lower cost than other materials. The disadvantages of such steels are their limited weldability and the necessity for the personnel to have special knowledge. High-nitrogen austenitic steels have already occupied a specific niche, and some parts are produced from them at an industrial scale. We can expect that after the development of processes ensuring commercial-scale production such steels will be applied quite widely.

In the present work we will describe results of research aimed at creation of new nitrogen austenitic stainless steels with high strength and ductility.

NITROGEN IN SOLID SOLUTION

It can be seen from Fig. 1 that the most obvious and favorable effect of the introduction of nitrogen into iron solid solutions in steels bearing 23 wt.% Cr is stabilization of the fcc lattice. This effect is fully realized in high-nitrogen austenitic steels, but stabilization of the austenite phase at room temperature requires quenching. Consequently, the introduction of the requisite amount of nitrogen into the composition in the production of steel and retention of nitrogen in the solid solution in the heat treatment process require special knowledge from the steelmaker.

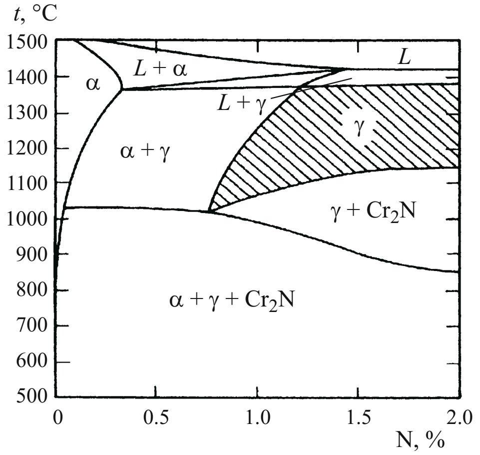

Fig. 1. Nitrogen in the solid solution widens the range of existence of stable phase with fcc lattice in iron-base alloys bearing 23 wt.% Cr. Without nitrogen such steels would never be austenitic but would always have a stable ferrite phase.

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[1] Swiss Academy of Materials Science, Birmenstorf, Swiss; Central Iron and Steel Research Institute (CISRI), Beijing, China.

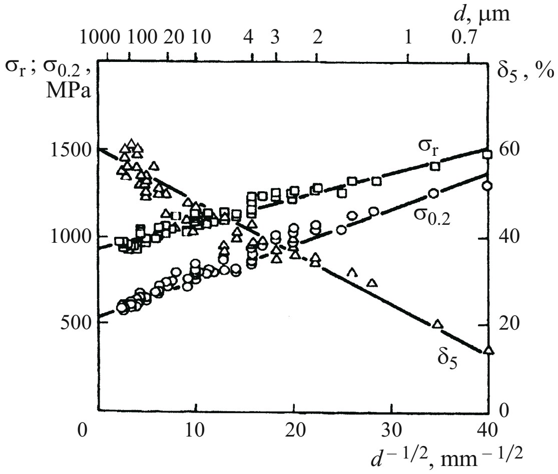

Fig. 2. Effect of the grain size (d) on the yield strength, ultimate rupture strength, and elongation of the metal of six heats of austenitic stainless steel CHSS (Fe –23% Cr – 16% Mn – 0.8% N): $\sigma^0_{0.2}$ = 530 MPa; σ^0_r = 930 MPa; δ^0_5 = 60%; $k\sigma_{0.2}$ = 21 MPa · mm$^{1/2}$; $k\sigma_r$ = 15 MPa · mm$^{1/2}$; $k\delta_5$ = – 1.2 % · mm$^{1/2}$.

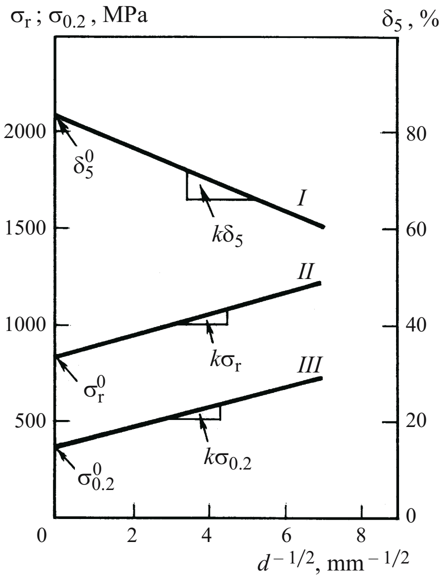

Fig. 3. Dependence of mechanical properties of austenitic stainless steels on the grain size: I) $\delta_5 = \delta^0_5 - k\delta_5 d^{-1/2}$; II) $\sigma_r = \sigma^0_r + k\sigma_r d^{-1/2}$; III) $\sigma_{0.2} = \sigma^0_{0.2} + k\sigma_{0.2} d^{-1/2}$.

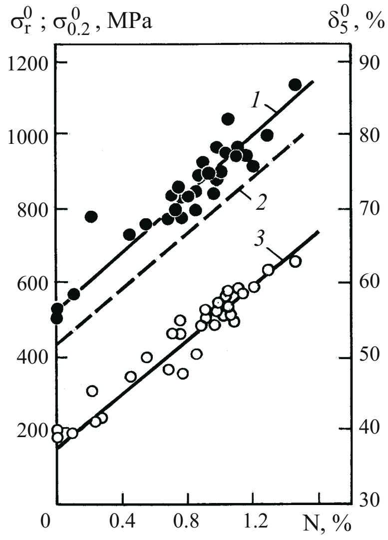

Fig. 4. Effect of the content of nitrogen on hardening of the solid solution of austenitic stainless steels: 1) $\sigma^0_r = 530 + 400$ [N]; 2) $\delta^0_5 = 52 + 20$ [N]; 3) $\sigma^0_{0.2} = 150 + 370$ [N].

STRENGTH AND DUCTILITY

The presence of nitrogen in the solid solution has a positive effect on at least four factors of hardening, i.e., hardening of the solid solution, hardening of grain boundaries, strain hardening, and strain aging [1 – 5]. Therefore, the effect of grain size should be allowed for in considering problems connected with the strength of high-nitrogen austenitic steels from the standpoint of both pure science and applications. An example of the effect of grain size is presented in Fig. 2. It can be seen that the yield strength in the steel grows from about 600 to over 1200 MPa with decrease in the grain size. The three equations presented in Fig. 3 are Hall-Petch equations for determining the yield strength $\sigma_{0.2}$, the ultimate tensile strength σ_r, and the elongation at fracture δ_5. The data presented in Fig. 4 reflect realization of the dream of metallurgists: nitrogen introduced into solid solution increases the strength and simultaneously the ductility.

It can be seen from Fig. 5 that strain aging is one of the most effective methods for raising the strength of austenitic steels with high nitrogen content; growth in the nitrogen concentration in the solid solution increases the strain aging coefficients. The respective degree of cold work hardening can ensure extremely high strength values. So far we have obtained $\sigma_{0.2}$ = 3600 MPa (Fig. 6) and there is no theoretical reason for this characteristic not to be pushed above 4000 MPa in the nearest future.

Strength is not the only characteristic taken into account in the development of structural materials. It is more desirable for a designer to consider the combination of strength and ductility (as it is shown in Fig. 7) or of strength and fracture toughness (as in Fig. 8). For example, the steels used in modern cars should have enough strength to enable the structure to be lightweight, and thus fuel efficient, for sustainable economy. These materials should also be ductile for two reasons, namely, on one hand, in order to absorb energy in a crash, i.e., to possess a high impact resistance, and on the other hand, in order to ensure high formability, for example, by high internal pressure. It follows from Fig. 7 that high-nitrogen austenitic steels are much superior to ferritic steels (with yield strength below 1000 MPa) used at present in the automotive industry, when compared with respect to the same value of strength and ductility.

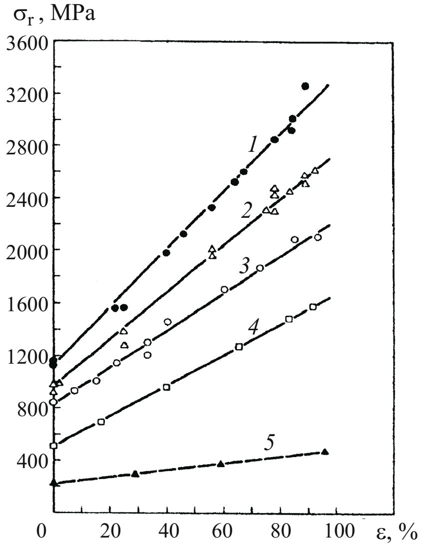

Fig. 5. Effect of degree of cold plastic deformation (ε is determined from the decrease in the cross section, %) on the ultimate rupture strength of austenitic stainless steels ($d_g = 30 – 60$ μm) with different contents of nitrogen and chromium: *1*) 1.2% N, 30% Cr; *2*) 0.8% N, 25% Cr; *3*) 0.4% N, 33% Cr; *4*) 0.077% N, 17% Cr; *5*) pure iron.

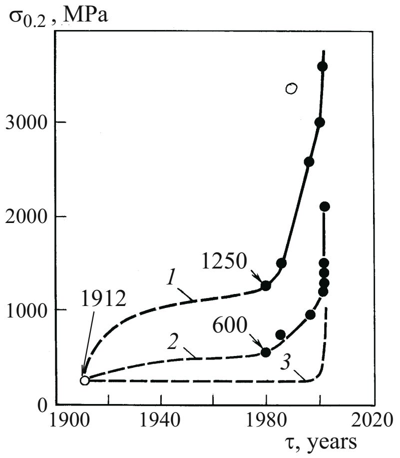

Fig. 6. Yield strength of different steels created in different years: ○) steels with stable austenite; ●) high-nitrogen steels fabricated traditionally without using superhigh pressure; *1*) after cold plastic deformation; *2*) after solution annealing; *3*) steel 316 ASTM.

A more thorough analysis of the data on strength and fracture toughness presented in Fig. 8 allows us to infer that high-nitrogen austenitic steels have the best combination of these characteristics not only as compared to any other steel but also as compared to other materials known in the world. Today no other known material has a better combination of strength and fracture toughness than high-nitrogen stainless steel!

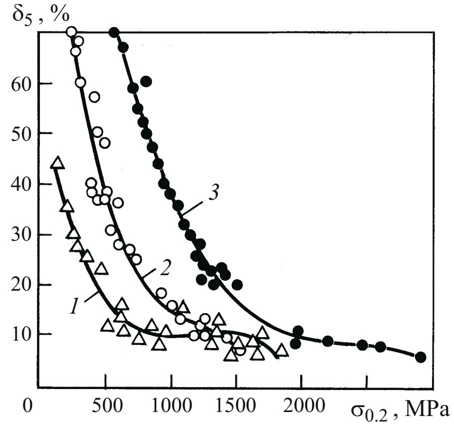

Fig. 7. Elongation at fracture as a function of the yield strength of steels: *1*) ferritic steels used in the car and armor industries; *2*) austenitic steels; *3*) high-nitrogen austenitic steels.

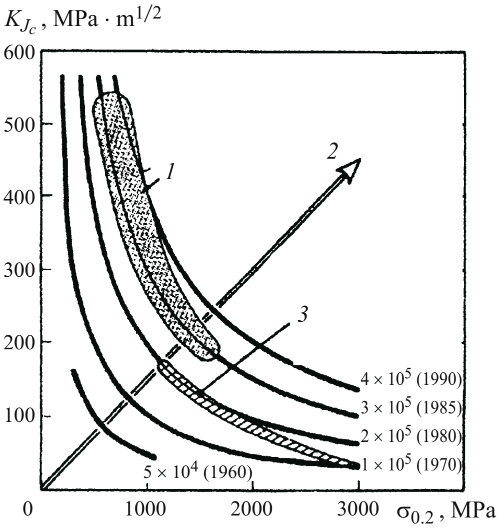

Fig. 8. Fracture toughness as a function of yield strength of various steels: *1*) nitrogen-bearing steels X5CrMnN1818; *2*) new steels; *3*) best maraging steels (2000); the values of $K_{J_c}\sigma_{0.2}$, MPa^2 · m$^{1/2}$ (the product of strength by toughness) double in every decade.

Applications often require materials with a high strength-to-density ratio. This parameter is decisive for light structures obtained with the use of sustainable technologies. This concerns not only cars but all moving (including trains, ships, airplanes, and rockets) and rotating articles. Figure 9 presents the ductility of presently used car sheet steels as a function of its strength-to-density ratio. We give comparative data for alternative materials (Al, Mg, Ti) and high-nitrogen austenitic steels. It is obvious that the latter are superior not only to the now used car sheet steels but also to Al-, Mg-, and even Ti-alloys!

Under triaxial stresses and impact loads corresponding to Charpy impact tests austenitic steels with very high nitrogen concentrations can fracture like brittle materials (as it is shown in Fig. 10). Fracture occurs over slip bands in planes (111) of the fcc lattice. This fracture mechanism limits the maximum useful concentration of nitrogen.

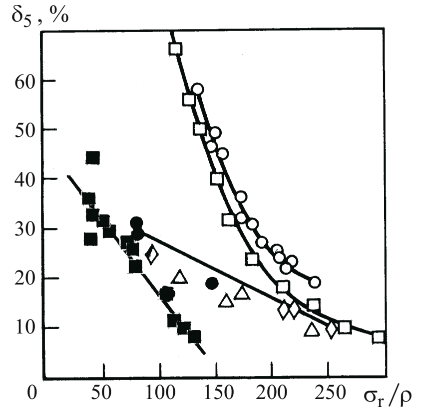

Fig. 9. Elongation at fracture as a function of the ratio of ultimate rupture strength to density for various materials: ■) car sheet steel; ●) Al-alloys; △) Mg-alloys; ◇) Ti-alloys; □) stable high-nitrogen austenitic steels; ○) metastable austenitic steels.

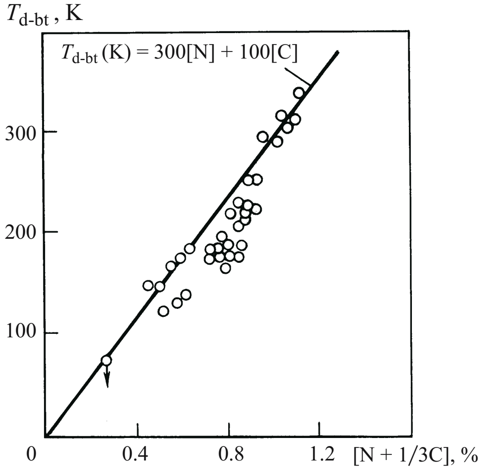

Fig. 10. Effect of nitrogen content in the solid solution on the ductile-brittle transition temperature $T_{d\text{-}bt}$.

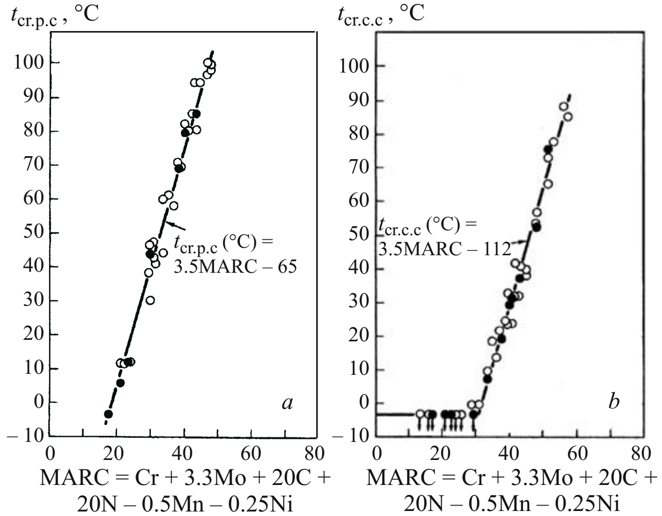

Fig. 11. Effect of chemical composition of commercial and experimental steels of the Fe – Cr – Ni – Mo – Mn – N system with fcc lattice on the critical temperature of pitting corrosion $t_{cr.p.c}$ (*a*) and critical temperature of crevice corrosion $t_{cr.c.c}$ (*b*) in accordance with the MARC correlation equation: *a*) tests in 20% solution of NaCl; *b*) tests in 6% solution of $FeCl_3$.

CORROSION RESISTANCE

Nitrogen present in the solid solution raises the resistance of austenitic steels to general corrosion, pitting corrosion, and crevice corrosion. The resistance to pitting and crevice corrosion depends on the composition of the alloy and obeys the following correlation equation:

$$\text{MARC} = \text{Cr} + 3.3\text{Mo} + 20\text{C} + 20\text{N} - 0.5\text{Mn} - 0.25\text{Ni},$$

where MARC is the measure of alloying for resistance to corrosion, and the figures at the chemical elements denote the weight percentage of the latter. It can be seen from the data presented in Figs. 9 and 10 that the correlation equation for MARC is applicable to both commercial and experimental austenitic stainless steels. Thus, it is important for choosing the composition of the alloy [1, 2]. The validity of MARC has not been confirmed fundamentally or explained by the present time. However, it is remarkable that it has been established for the whole of the studied group of austenitic stainless steels that 1 wt.% nitrogen is equivalent to 20 wt.% chromium where the corrosion resistance is concerned [6 – 8].

Stress corrosion cracking in hot concentrated chloride solutions is a well-known disadvantage of austenitic stainless steels. For example, it can be seen from Fig. 11 that austenitic stainless steels of type 304 and 316 undergo obvious stress corrosion cracking in 20% solution of NaCl at 105°C. On the contrary, the suggested high-nitrogen austenitic stainless steels resist this kind of cracking even after strain hardening ensuring a strength of 1400 MPa.

APPLICATIONS

Today high-nitrogen austenitic stainless steels are produced in industrial quantities but for very specific applications at high added value. Therefore, the production processes are quite expensive and often require the use of pressure metallurgy, for example, pressure electroslag remelting. However, the very high quality of the products allows us to expect further use and even expansion of the method. Quite recently, we developed a process for fabricating high-nitrogen steels with the use of available large-scale production equipment. Since improvements in this field are still desirable, it is clear that the time has come for mass production of high-nitrogen stainless steels or quantity production of steels of high quality.

The properties mentioned above and other advantages of high-nitrogen stainless steels not mentioned in the present paper for brevity considerations make such steels candidate materials for the transport industry (cars, railroads, ships), building industry (fixturing, rebars for reinforcing such corroding structures as bridges and tunnels), aerospace industry, ocean engineering, sports goods production, and even in the nuclear power industry and military applications.

The high strength, ductility, and corrosion resistance of high-nitrogen austenitic steels open up wider possibilities for designers, with lower consumption and longer service life of the materials. These properties are basic criteria for a sustainable technology.

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