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THE RELATION BETWEEN THE GRAIN SIZE AND THE TENDENCY OF AUSTENITIC CORROSION RESISTANT STEELS TO INTERCRYSTALLINE CORROSION

by

Vladimir Cihal

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ABSTRACT: On the basis of collected knowledge about intercrystalline corrosion of austenitic stainless steels a suggestion of evaluating the influence of grain size upon intercrystalline corrosion, both of unstabilized and stabilized steels, is discussed.

According to well-known and adapted formulas which express the influence of nickel, chromium and molybdenum, niobium and - above all carbon, A ~~the following~~ relation was stated, which includes the influence of grain size and evaluates the resistance of steels, type Cr18Ni19, to intercrystalline corrosion.

$$0{,}005\sqrt{2^{N-1}}\,.\,(Cr-17)+f\,.\,\frac{Ti-3{,}43(\%\,N-0{,}021)}{4}-0{,}002\,.\,(Ni-10)-C\geq 0.$$

The ~~This~~ relation is represented by a nomograph on logarithmic scale with the aim, to evaluate intercrystalline corrosion of stainless steels with different granularity and different composition, in a simple way.

In the conclusion, practical applicability of the suggested method is demonstrated.

English translation: 10 pages.

THE RELATION BETWEEN THE GRAIN SIZE AND THE TENDENCY OF AUSTENITIC CORROSION RESISTANT STEELS TO INTERCRYSTALLINE CORROSION

Vladimir Cihal*

HOW GRAIN SIZE IS RELATED TO INTERCRYSTALLINE CORROSION OF AUSTENITIC STAINLESS STEELS

On the basis of collected knowledge about intercrystalline corrosion of austenitic stainless steels a suggestion of evaluating the influence of grain size upon intercrystalline corrosion, both of unstabilized and stabilized steels, is discussed.

According to well-known and adapted formulas which express the influence of nickel, chromium and molybdenum, niobium and — above all carbon, the following relation was stated, which includes the influence of grain size and evaluates the resistance of steels, type Cr18Ni9, to intercrystalline corrosion:

$$0{,}005\sqrt{2^{N-1}}\,.\,(Cr'-17)+f\,.\,\frac{Ti-3{,}43\,(\%\,N-0{,}001)}{4}-0{,}002\,.\,(Ni-10)-C'\geqq 0.$$

This relation is represented by a nomograph on logarithmic scale with the aim, to evaluate intercrystalline corrosion of stainless steels with different granularity and different composition, in a simple way.

In the conclusion, practical applicability of the suggested method is demonstrated.

Along with the development of corrosion resistant steels resistant to intercrystalline corrosion a great deal of attention was given recently to the limiting content of carbon — also called the minimum — at which value and below the steel no longer has a tendency toward intercrystalline corrosion. Associated with this is not only the problem of development and introduction into production of low carbon content stainless steels but the determination of the minimum carbon content also has a considerable significance in stabilized steels and in steels alloyed with molybdenum.

On the basis of the currently generally recognized theory of intercrystalline corrosion — depletion of grain boundaries of chromium created by the deposition of complex carbides of chromium (Cr, Fe, Mo)$_{23}$C$_6$ — almost all factors governing the tendency of stainless steel toward intercrystalline corrosion are known. Among these factors belong primarily the carbon content of steel, then the amount of chromium, nickel, molybdenum and also manganese, the grain size, the content of stabilizing elements and their effectiveness, thermal treatment, the content of nitrogen and often also the manner of molding. The number of factors and the interconnection of their effects indicate the relatively large difficulty of solution which cannot be accomplished without a statistical interpretation of a large number of tests.

Current knowledge of properties of austenitic corrosion resistant steels allows one, with the help of available data, to determine with certainty the influence of some factors. The scope of this work is primarily the study of one of the important factors, that is, the size of the grain which is also important in corrosion problems occurring in welding. We encounter in practice in a number of cases, for example, in the welding of thick-walled vessels or on repeated heating of the steel in the zones of critical temperature a tendency toward intercrystalline corrosion in nonstabilized as well as in stabilized steels. In the latter steels the cause of intercrystalline corrosion that appears after in the critical temperature regions preceding overheating of steels is the dissolution of stable carbides and the growth of the steel grain.

As the steel grain enlarges the surface of grain boundaries decreases, so that the concentration of chromium carbides increases on the boundaries at the same content of carbon in steel. This is confirmed by morphology and by the distribution of chromium carbides on the grain boundaries determined by the electron microscope. It is also generally known and recently proved by spot microanalysis that the penetration of intercrystalline corrosion occurs only at a certain concentration of the precipitate which creates a continuous depletion of grain boundaries of chromium. It can thus be said that the fine-grained steels, due to their enlarged surface of grain boundaries, are much more resistant to intercrystalline corrosion than coarse-grained steels because the continuous network of carbides, and thus the depletion of grain boundaries of chromium, are formed more readily in coarse-grained steels. The amount of carbides per unit of the grain surface at a given content of carbon will differ depending on the grain size. According to some references [1] the amount of carbon corresponding to the chromium carbides formed per unit surface of grain increases approximately 1.41 times when the grain dimension changes by a unit of grain size which is essentially the same by our [2] and by the foreign standards [3, 4].

INTERCRYSTALLINE CORROSION OF STEELS Cr18Ni9

The statistical study of F. Bogin [5] and the experimentally found scattering of results of tests for intercrystalline corrosion of corrosion resistant steels can be exploited in further areas of this field. In practice we also often find steels which have a different susceptibility to intercrystalline corrosion although they have the same chemical composition. The cause of this diversity was often found to be due to the difference of their grain sizes and this serves as a proof at the same time that the factor of the grain size cannot be ignored [6].

Since nickel if present in high amounts in steel enhances the effect of carbon from the point of view of sensitivity toward intercrystalline corrosion then the so-called effective content of carbon C', expressed by the relation

$$C' = C + 0{,}002\,(Ni - 10), \qquad (1)$$

is used for the evaluation, where C is the content of carbon in steel in weight percent, Ni is the content of nickel in weight percent from which it follows that, when Ni is less than 10, the modified content of carbon in steel is lower than the actual.

For the purpose of study of the effect of grain size on the tendency toward intercrystalline corrosion which is especially important in steels whose composition lies on the border line of resistance we can, in agreement with the work of G.L. Svarcova [1], write a general dependence of the content of chromium on the minimum content of carbon in steel which assures the resistance toward intercrystalline corrosion at a given grain size

$$f(N).(Cr - Cr_0) + C_r \geq C', \qquad (2)$$

in which $f(N)$ is the function expressing the grain size, Cr denotes the content of chromium at which the susceptibility toward intercrystalline corrosion is no longer dependent on the grain size, Cr_0 is a constant indicating the chromium content at which the tendency to intercrystalline corrosion is a function of grain size, C_r is the amount of carbon dissolved in austenite, C' is the effective carbon content in steel according to Eq. (1).

For the expression of the function $f(N)$ we utilize the data of routine measurements of grain size. According to the definition of grain size (N) the number of grains (n) per unit area is expressed by the relation $n = k \cdot 2^{N-1}$. Let us suppose further that the grain has a hexagonal shape remembering that two grains are divided by one border. A general expression for the length of grain boundaries in a unit area of a metallographic ground section (in mm^2 or in the studied 10 cm^2 at 100× magnification) is $O = K' \sqrt{2^{N-1}}$. According to this the function $f(N)$ in Eq. (2) can then be expressed by the relation

$$f(N) = K . \sqrt{2^{N-1}}. \qquad (3)$$

By substituting into Eq. (2) we get with the value of grain size N the relation

$$K . \sqrt{2^{N-1}} . (Cr - Cr_0) \geq C' \qquad (4)$$

The constants in this equation have to be determined experimentally. Gobin employs for their determination the already mentioned statistical measurements and he arrives at the values $K = 0.005$ and $Cr_0 = 17$. Svarcova determines these constants from the calculation of the amount of carbides of chromium deposited on the unit circumference in several steel kinds stabilized with titanium and she arrives at values that are on the whole in agreement with his, $K = 0.00625$, $Cr_0 = 16.7$. Considering the statistical character of Gobin's test we used his values, however more rounded. The

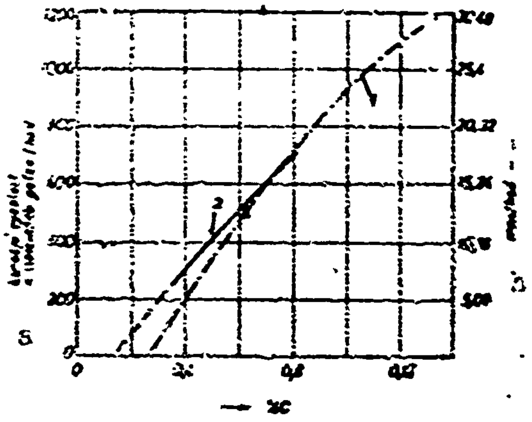

Fig. 1. The dependence of the rate of intercrystalline corrosion (mm/hours) on the carbon content. 1) According to Bain, Rutherford, Aborn; 2) corrected curve according to Heger and Hamilton [7]. a) Rate of corrosion in thousandths of inches/hour; 2) mm/hour.

value of the constant $C_0 = 0.015$ differs from the data obtained from mathematical statistical analysis of Bain, Rutherford and Aborn's diagram (Fig. 1) according to whom the minimum rate of intercrystalline corrosion is reached only at a carbon content below 0.01% and which has a much larger effect on the distortion of results compared with the constant Cr_0. We have therefore decided not to include it in the relation Eq. (1). The symbol C' denotes a total free (not bound) carbon modified with regard to the nickel content in the steel.

On the basis of the above-mentioned fact we have selected the following relation determining the resistance of corrosion resistant steels of the type Cr18Ni9 toward intercrystalline corrosion

$$0{,}005 \cdot \sqrt{2^{N-1}} \cdot (Cr - 17) - C' \geq 0 \qquad (5)$$

which we have expressed nomographically in a diagram in Fig. 2. The application of this diagram can be demonstrated with a simple example. If we have a steel containing 20% chromium and 10% nickel, of grain size $N = 5$, then, when carbon content is 0.06% (and lower) the steel will still be resistant toward intercrystalline corrosion. On the other hand for a given content of chromium and carbon we can read from the graph the grain size which still ensures the resistance of steel to intercrystalline corrosion. As was mentioned above the relation of the grain size and intercrystalline corrosion is important even in steels alloyed with molybdenum and in stabilized steels. We shall, therefore, attempt to rearrange the obtained relation so that we could apply the given nomogram even to the latter types of corrosion resistant steels.

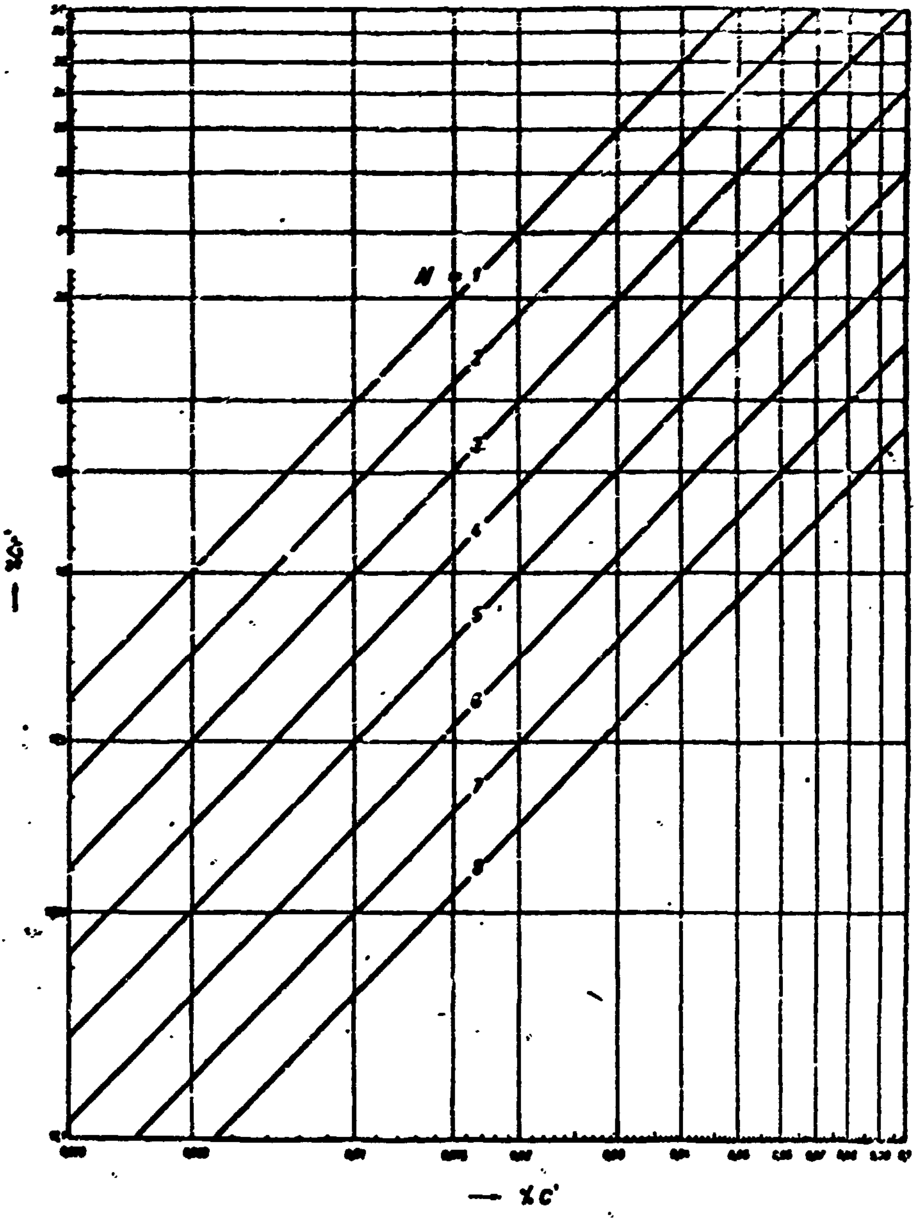

Fig. 2. The influence of grain size on the susceptibility of corrosion resistant steels to intercrystalline corrosion.

$$Cr' = Cr + b\,.\,Mo;\ C' = C + 0{,}002\,.\,(Ni - 10) - f\,.\,\frac{Ti - 3{,}43\,.\,(\%\,N - 0{,}001)}{4}\ \overset{A}{\text{resp.}}$$

$$C'_1 = C + 0{,}002\,.\,(Ni - 10) - f_1\,.\,\frac{Ti}{4};\ C'_2 = C + 0{,}002\,.\,(Ni - 10) - f_2\,.\,\frac{Ti\ v\ izolátu}{5};\ B$$

$$C'_3 = C + 0{,}003\,.\,(Ni - 10) - \frac{Ti\ v\ TiC}{4}\ C$$

A) Cr; B) Ti in isolated material; C) Ti in TiC.

THE EFFECT OF MOLYBDENUM ON THE RESISTANCE TO INTERCRYSTALLINE CORROSION

The admixture of molybdenum into corrosion resistant steels has a favorable effect on the steels by improving their overall corrosion resistance and by increasing the value of carbon content at which the steel is still resistant to intercrystalline corrosion. Thus in the presence of molybdenum the value for the chromium content in Eq. (5) increases and it can be expressed by the relation

$$Cr' = Cr + b . Mo, \qquad (6)$$

in which Cr is the percentage of chromium in steel, Mo is the percentage of molybdenum in steel, b is the coefficient of equivalency considered by Gobin to be equal to 1, Cr' is the effective content of chromium as plotted in the graph.

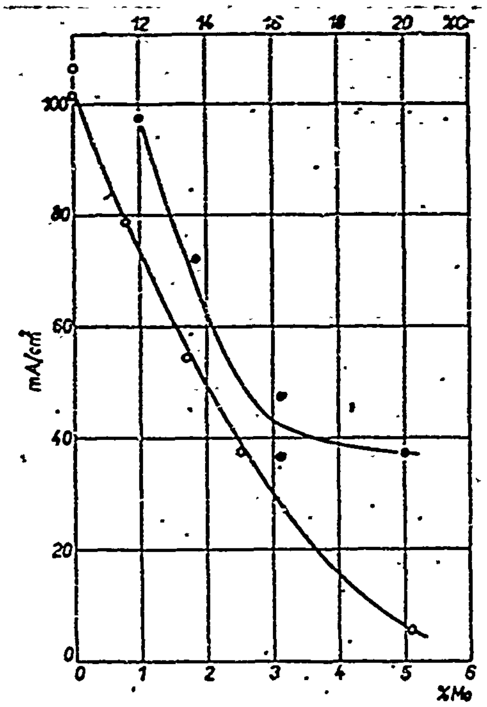

Fig. 3. The effect of molybdenum (O) and chromium (●) on the critical passivation current density j of the steel type Cr18Ni12Mo2 in the solution 1M – HCl + 0.01% KCNS at 20°C.

We believe that there is not as yet sufficient justification for the value of coefficient b and for the present we must be satisfied that b = 1 and to ascertain its value in the future.

Basically it is correct to consider its additive effect with chromium since in the standard austenitic corrosion resistant steels it is deposited as complex carbides with chromium and not as a special carbide; in a solid solution it improves the ability of passivation much more distinctly than chromium (Fig. 3).

We lack the exact data of the percent distribution of molybdenum in a complex carbide, but considering its effect in the solid solution it seems probable, that the value of coefficient b is higher than 1. This would also be born out by the fact [8] that the percentage Ti = 4. (°C) roughly suffices for the stabilization of steel Cr18Ni10Mo2Ti so that molybdenum actually behaves indirectly as a stabilizer although not as an effective one as titanium, because the complex carbides containing molybdenum dissolve in austenite already at 1100°C.

STABILIZED CORROSION RESISTANT STEELS

The problem of the effect of grain size on the tendency toward intercrystalline corrosion is much more complicated in stabilized steels. An admixture of a stabilizing element in suitable quantities imparts to stainless steels a resistance to intercrystalline corrosion. In practice various formulae for the minimum contents of stabilizing elements are used that relate to the carbon content in the steel and that ensure its resistance to intercrystalline corrosion. Most of them are for steels stabilized with titanium and these are mostly used also in this country. It was found, however, that the addition of a stabilizing element in relation to the carbon content, especially if it approaches the theoretical value, is quite insufficient if the stabilized steels are subjected to unfavorable heat loads, for example, in welding. The carbon bond to the stabilizing element is disrupted at the overheated sites, and the carbon is capable again of binding chromium in the critical temperature region and of developing a tendency of stabilized steels toward intercrystalline corrosion. Exactly in these steels the grain size is an important factor which determines secondarily whether a steel is suitable from the point of view of intercrystalline corrosion. Once the relation expressing the effect of the nitrogen content in steel, and the effect of the grain size are established more precisely it will be possible in many instances to find the resistance of such steels only on the basis of chemical and metalographical analysis by calculation, or from a diagram, without the need to carry out the tests for intercrystalline corrosion.

The relations derived for nonstabilized steels may be used to an advantage also for stabilized steels with such a modification that for the calculation of the free carbon content we apply the data for the distribution of the stabilizing element in steel, that is, for carbon, nitrogen and solid solution. Since the value of the stabilizing element in a solid solution is a function of temperature, time of heating and its amount in the steel, and since we do not have as yet a sufficient foundation for its mathematical expression it will be advantageous, also considering future statistical analysis of the studied relations, to substitute this value with the so-called coefficient of effectiveness γ, which we can assume to be equal to 1 for steels stabilized by annealing.

Substituting the relation thus obtained for free carbon content in Eq. (5) we arrive at an expression

$$0{,}005 . \sqrt{2^{N-1}} . (\mathrm{Cr}' - 17) + f . \frac{\mathrm{Ti} - 3{,}43 . (\%\,\mathrm{N} - 0{,}001)}{4} - 0{,}002 . (\mathrm{Ni} - 10) - \mathrm{C}' \geq 0., \qquad (7)$$

for steel stabilized by titanium which determines its resistance toward intercrystalline corrosion, in which is also denoted Ti as the total content of titanium in steel, $\%$N as the amount of nitrogen in steel in percent weight, f as the coefficient of effectiveness of the stabilizing element.

Similar relation may be written also for steels stabilized with niobium. The above expression presupposes an analysis of nitrogen in the calculation of the free carbon content. If we do not know its content we can simplify the appropriate portion of Eq. (7), for example, to the form f_1 Ti/4; at the same time, however, the coefficient f has a considerable effect on the accuracy of the results. If, on the contrary, we know either the percentage of titanium in the isolated residue or outright the amount of titanium bound to carbon and nitrogen, besides knowing the chemical composition of the steel, the value of the free carbon can be expressed more accurately, for example in the second case, without the use of the coefficient of effectiveness. Isolation of carbides and their analysis, however, is very demanding and is not routinely carried out in all laboratories. For this reason we are giving several methods of evaluation of free carbon in steel so that laboratories with less equipment can evaluate the stabilized corrosion resistant steels from the above relations.

CONCLUSION

The decisive significance of this solution of the grain size effect on the tendency of corrosion resistant steels toward intercrystalline corrosion is in the fact that it allows one to evaluate steels with medium carbon content which would often be classified as unsuitable and rejected but which can be quite suitable provided they are fine-grained. Similarly the stabilized steels which would not be suitable by the usual criteria, or vice versa, can be evaluated more accurately by the given process and many fine-grained steels can be kept in production or improved as far as intercrystalline corrosion is concerned by heat processing (stabilizing annealing). The application of this method is not less significant in the evaluation of welded corrosion resistant steels especially in the region of the weld in which the grain size changes due to the temperature effect (for example, the growth of the grain in the close proximity to the molten metal). Steel that has in the original state a perfect resistance toward intercrystalline corrosion here becomes often susceptible as the grain grows and the effectiveness of the stabilizing element decreases. Exactly these phenomena of intercrystalline corrosion, associated also with "knife" corrosion, can be detected with the usual tests only with great difficulty.

It is apparent that this method cannot completely substitute other ways of control, that is, tests for intercrystalline corrosion. It will be necessary to check thoroughly the reliability of the calculated and nomographically expressed data and mainly to check the precision of the constants in the relations on the basis of a larger number of statistically evaluated results. We have, therefore, applied to some of our laboratories which deal with corrosion resistant steels to help us obtain as much additional data as possible.

In the evaluation it is necessary to heed the subjective views in the determining of various quantities, also to consider local changes in the composition of steel, changes in steel structure, etc.

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