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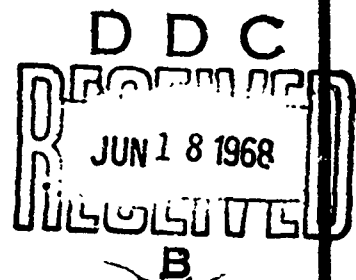
FOREIGN TECHNOLOGY DIVISION



THE RELATION OF THE PRECIPITATION PROCESSES TO THE PROPERTIES
OF CORROSION-RESISTANT STEELS

by

Vladimir Ciha and Oldrich Vanicek



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ABSTRACT : The authors trace the structural changes in stabilized stainless steels with respect to selective types of corrosion. Main consideration is given to delta ferrite and its decomposition in 1Cr18Ni9Ti steel. The electron microscope was used to advantage in the study of changes taking place in ferrite. Apart from the carbide precipitation, which initiates the ferrite decomposition, two phases, sigma and austenite, form from delta ferrite. The sigma phase in stabilized steels starts with the formation of lamellae at the grain boundaries between austenite and ferrite and spreads gradually inside the delta ferrite grains. The local change in chemical composition during ferrite decomposition is one of the main causes of increased attack in the given type of steel in the transpassive state. The selective attack on welded joints in these steels (at the weld junction) is closely associated with these structural changes and shows up especially well during treatment with hot concentrated nitric acid. English Translation: 14 pages.

THE RELATION OF THE PRECIPITATION PROCESSES TO THE PROPERTIES OF CORROSION-RESISTANT STEELS

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Structural changes which bring about the sensitivity to a selective corrosion in corrosion resistant steels are associated, primarily, with the interaction between chromium, in the case of stabilized steels, also with titanium or niobium, and the carbon or the nitrogen of these steels. Regardless of the various opinions on the mechanism of the classical intercrystalline corrosion of stainless steels it can now be affirmed with certainty that it is associated with the precipitation of mixed carbides $Me_{23}C_6$, high in chromium, on the grain boundaries, even though these are not the only types of carbides found in corrosion resistant steels. It must be added that the shape, size and distribution of precipitates has an immediate relation to the phenomenon of intercrystalline corrosion that can occur when a continuous network depleted of chromium is formed on the boundaries of austenitic grains [1, 2, 3].

THE ANALYSIS OF THE PROBLEMS OF THE PRECIPITATION PROCESSES

It has been proved experimentally that the precipitation of carbides in thermally treated steels over a wide range of temperatures 450-950°C, their shape and their size are largely dependent on the time and the temperature, in a like manner as is the sensitivity to inter-

crystalline corrosion. Recently, also, the technique of transmission electron microscopy confirmed the results obtained by the study of extraction impressions, X-ray and electron diffraction and the chemical analysis of isolates [4,5].

The character of carbides depends on the nature of the boundary and they can be divided into three groups on the basis of the occurrence of intercrystalline corrosion:

a) two-dimensional flat particles - submicroscopic, very thin, and forming a continuous network on the boundaries of grains; typical for lower precipitation temperatures.

b) dendritic particles - in the initial stage as thin flakes expanding into geometrically developed forms; these are characteristic for the median precipitation temperatures.

c) individual crystallographically developed particles - they can be observed at all temperatures and all times of sensitization, they grow in number and size with the time and temperature of the precipitative heating.

An extreme sensitivity to intercrystalline corrosion occurs at relatively low temperatures and this is associated with the depletion of grain boundaries as a result of the precipitation of two-dimensional thin particles (Fig. 1). Similarly, the formation of martensite is associated with the maximum of depletion and that even at normal temperatures due to the shift of temperature of martensite conversion with decreasing content of chromium.

The tendency of corrosion resistant steels toward intercrystalline corrosion can be substantially reduced by stabilizing them with carbide-forming substances, titanium, or niobium. Carbides and nitrides of these elements are almost insoluble at conventional temperatures of solution annealing. It is sufficient for many purposes if their content

not sufficient for suppressing the selective attack in the immediate proximity of the weld in nitric acid. There are still other factors involved here which have not been fully explained and to which we have been lately paying much attention.

One of these factors is the reactions that take place during the decomposition of the metastable ferrite delta. Following superheating to very high temperatures the stabilized steels contain relatively different amounts of ferrite depending on their composition. And the steels with excessive amounts of titanium by which we are reducing the sensitivity to intercrystalline corrosion of the "carbide type," have a high content of ferrite (30-40%) after overheating. It has been gen-



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Fig. 1. Part of a ferrite delta grain and gamma boundary showing deposited carbides $Me_{23}C_6$ - 1250°C/1 hour/water + 550°C/72 hours/air - steel susceptible to intercrystalline corrosion in a standard solution.

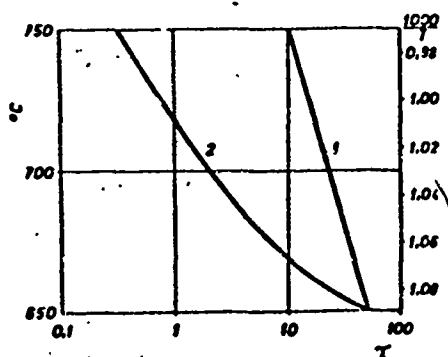
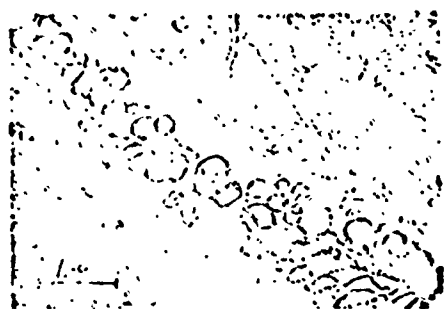


Fig. 2. Incubation period for the beginning of the formation of phase sigma in alloys Fe + 44.7% Cr (curve 1) and steel containing 20.2% Cr, 1.96% Mo, 6.38% Ni, 0.08% C (curve 2) [4].

erally known, and recently proved by microanalysis, that the composition of austenite and ferrite at equilibrium greatly differs [11], in which ferrite decomposes in the critical temperature region with a simultaneous formation of phase sigma, secondary austenite and, of course, with the precipitation of carbides from the overheated solution [12]. These phases also differ fundamentally in their composition from the original ferrite. With regard to the corrosion behavior of steel in nitric acid at high concentrations and temperatures (generally in the transpassive state), the high content of chromium in phase sigma is of particular interest. It has been reliably determined that phases high in chromium are strongly corroded in the transpassive state, that is, in environments with high oxidation-reduction potential, and phase sigma, in particular, has a low resistance [13] compared with, for example, ferrite with equal amount of chromium. It can be speculated, therefore, that its presence in steel will lower the corrosion resistance under these conditions and, in case of its unfavorable distribution in the structure, it can be the cause of a selective attack.

In order to apply these facts to the corrosion damage of welded joints in nitric acid, we must know the conditions for the decomposition of phase sigma. If phase sigma should apply in the above-mentioned increase of corrosion rate in nitric acid, its formation (primarily the initial stages) must take place in very short time intervals and its distribution must correspond to the character of corrosion damage. Corrosion in a zone adjacent to the welded metal in nitric acid, namely, has an intercrystalline course which is somewhat different from the intercrystalline corrosion of the "carbide type," for example, after the test in standard solution. Typical for it is the broad track on the boundaries of grains.

On the basis of the study of the influence of the quenching rate



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Fig. 3. The boundary ferrite-austenite showing a deposited phase - 1250° C/1 hour/water + 650°C/30 min/air.



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Fig. 4. Ferrite delta showing deposited carbides Me_{23}C_6 and TiC - 1250° C/1 hour/water + 650°C/5 min/air.

and the duration of tempering of iron alloys containing chromium or nickel the formation of phase sigma can actually be expected in the regions of metastable ferrite if there is a sufficient amount of nuclei for it. This is also confirmed by the finding [14] that an alloy containing 44.7% chromium, which lies by its composition in the region of stability of phase sigma according to an equilibrium diagram, must be quenched much slower (0.03°C/min for the decomposition of 3/4 of the total ferrite content) from the temperature regions of ferrite stability in order to obtain phase sigma, than a two-phase steel containing 25.21% chromium, 1.96% manganese, 5.38% nickel, 0.08% carbon (90% of ferrite is converted at a rate 0.12°C/min). The incubation period of the beginning of the conversion of ferrite during annealing is also much shorter for the above steel than for an alloy with a higher content of chromium (Fig. 2) and is shortened considerably as the temperature is

raised. When studying these alloys, there were to a certain degree initial "equilibrium" conditions of the routine solution annealing (1050° C/30 min/water) while in the environment of the welded metal we must consider the conditions to be strongly unequilibrated. If we add to it the fact that the incubation time of the precipitation of carbides is decreased with decreased time of superheating of the stabilized steels we can contemplate also the decomposition of ferrite already after short times or in a slow quenching from a high temperature, especially in heavy-walled welded joints.

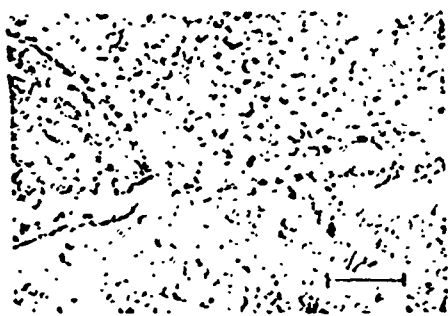
From these points of view, we have considered also the changes in the steel 08Cr18Ni10Ti studied by us, which is highly stabilized, shows a slight intercrystalline corrosion of the "carbide type" after overheating in only a narrow range of critical temperatures around 550°C, which shows, however, an increased corrosion rate in boiling nitric acid. Hence it follows that the sensitivity to intercrystalline corrosion brought about by annealing around 550°C is caused by the chromium depletion of the boundaries of grains during the precipitation of chromium carbides $Me_{23}C_6$, while the attack in nitric acid indicates a presence of a phase sensitive to rapid dissolving even after annealing at higher temperatures. Since these are properties found for the phase sigma [13] we analyzed the decomposition of ferrite delta with the intention to determine this phase.

THE STUDY OF THE DECOMPOSITION OF FERRITE δ IN THE STEEL Cr18Ni9Ti

The steel of the composition 0.08% C; 1.18% Mn; 0.88% S 18.24% Cr; 9.25% Ni; 0.21% Mo; 0.80% Ti was employed in the study. In order to enable the proof of the thermal conditions of welded structures, all samples of this steel were first subjected to solution annealing, 1250° C/1 hour/water, followed by thermal processing at various temperatures in the range 550-850°C and for various times. In addition, some samples

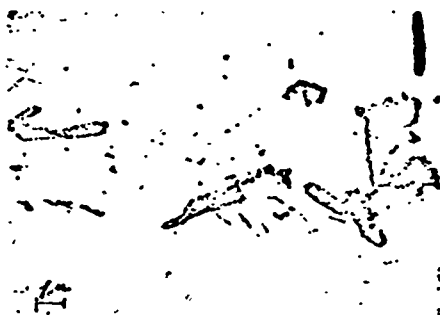
were annealed at 1400°C/10 min in vacuum/argon.

For the study of structural changes of this steel, electron microscopy and local electron diffraction in addition to light microscopy were found suitable. The technique of extraction replicas proved to be an important factor in the separation and identification of carbide particles. For electron microscopic observations were employed colloidal-carbon replicas shadowed by platinum, and carbon replicas. The etching



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Fig. 5. A portion of a boundary connecting some grains of ferrite delta - 1250°C hour/water + 650°C/5 min/air.



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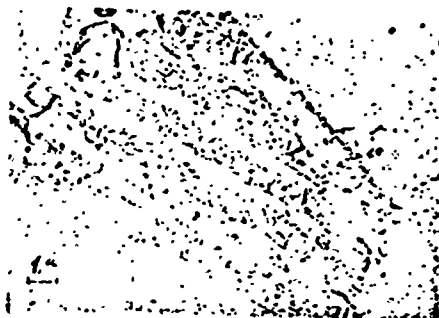
Fig. 6. Lamellar particles developing on the alpha-gamma boundary after quenching from high temperatures 1400°C/10 min/stream of argon.

was done potentiostatically in a solution of 5% H_2SO_4 at -0.15 to +1.5 V against a saturated calomel electrode or by a HCl/HNO_3 solution in glycerine. The ground sections for the extraction carbon replicas were successively etched by HCl/HNO_3 in glycerine, Br solution in meth-



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Fig. 7. Decomposition of ferrite delta on the alpha-gamma boundary - 1250°C/1 hour/water + 650°C/30 min/air.



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Fig. 8. Continuing decomposition of ferrite delta - 1250°C/1 hour/water + 650°C/72 hours/air.

anol and a 10% alcoholic solution of HCl.

Preliminary tests demonstrated that the decomposition of ferrite δ is a complex process in the region of the above temperatures in which the carbides of chromium in lamellar and globular form and the carbides of titanium mostly as fine needles are precipitating. The conversion of ferrite in the critical temperature region occurs only after a certain incubation period that depends on the composition, temperature of the precipitation, the conditions in previous processing, etc. In chromium-nickel steels, with a relatively low content of ferrite, can be observed that the incubation time is shorter than in alloys with a high chromium content. In the temperature zone 650°C a phase was observed to form at first on the ferrite-austenite boundary, which could not be

extracted and which was very strongly etched in the region of the transpassive state [15, 16]. (Fig. 3, etched at $+1.5 V_{SCE}$.)

Since the selective etching of the presumed phase σ could be carried out only by anodic etching in the transpassive state (in some cases even at a potential $-0.15 V$), it can be concluded that, whatever phase it may be, it has an increased content of chromium and by its properties it corresponds to phase σ . The presence of phase σ in steels annealed for a longer time was well demonstrable microscopically by a color reaction but this is not so for the initial stages of its formation.

This phase is formed on the boundaries of austenite-ferrite grains already after five minutes of heating to $650^{\circ}C$, and as the time of annealing is increased it grows through the grain of ferrite δ . It was not coincidental to observe the connection of the precipitation on the



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Fig. 9. Concentration of carbides TiC in a grain of ferrite delta - $1250^{\circ}C/1$ hour/water + $650^{\circ}C/32$ hours/air.

boundaries of austenitic grains between individual grains of ferrite; no unambiguous conclusion, however, can be drawn concerning it (Fig. 4, 5). At annealing temperatures around $550^{\circ}C$ these boundaries are strongly etched and, from the results of tests in a standard solution, it can be concluded that in this case we have chromium carbides $Me_{23}C_6$ with a corresponding depletion (Fig. 1). In each case, and thus also on the austenite-ferrite boundary, the formation of phase σ is preceded



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Fig. 10. Differentiation in the chemical composition of a grain of ferrite in the initial stages of decomposition - 1250°C/1 hour/water + 650°C/5 min/air.

by a precipitation of lamellar carbides depositing already at a relatively rapid cooling from high temperatures of overheating (Fig. 6). In the initial stages of precipitation we cannot exclude the preferential deposition of carbides Me_7C_3 since the electron diffraction of some lamellae showed a hexagonal configuration of the lattice. This finding agrees with the thermodynamic analysis of the stability of carbides depending on temperature. In agreement with previous investigations [2, 17] the effect of temperature and time on the deposition of carbides was confirmed.

With regard to it that the etching of the structures was oriented toward the proof of phase σ it cannot be concluded with certainty whether its formation is preceded by a diffusionless conversion of ferrite to austenite [17]. This does not refer to the zone close to the austenite-ferrite boundary in which besides the phase σ a secondary austenite and carbides Me_{23}C_6 were observed, which, in some cases, caused consid-

erable difficulties in the elucidating of the structure of ferrite (Fig. 7, 8).

The concentration of the precipitation of titanium carbides in ferrite grains, with the exception of the initial zone of their decomposition, is remarkable, that is, their penetration into the grains. This confirms that the observed phase is evidently the phase σ high in chromium and dissolving only a small amount of titanium and carbon (Fig. 9). A short heating time already causes changes in the composition of ferrite, manifest by a different etching ability in the marginal regions (Fig. 10).

COLLECTED RESULTS

The structural changes occurring at various temperatures in stabilized corrosion resistant steels are concerned not only with the precipitation of carbides and the conversion of austenite to martensite but also with the formation of intermetallic compounds, in particular, of the phase σ . Besides their effect on the mechanical properties, their influence on the corrosion resistance of these steels has to be considered. Phases high in chromium dissolve in solutions of high redox potentials much faster than phases low in chromium and higher in nickel; the rate of their formation is, therefore, of interest to us. The rate of conversion is associated primarily with the diffusion processes, for out of one phase - ferrite - two phases must be formed - sigma and austenite - disregarding the precipitation of carbides. An exception is the diffusionless beginning of the conversion of ferrite with the detection of occasional forms of secondary austenite. The primary process during the decomposition of ferrite cannot be as yet stated with certainty and from the above findings it is possible to consider also carbides as nuclei. The fact that phase sigma is formed rapidly just in those steels in which carbon is perfectly balanced can be confirmed by

the low solubility of carbon in phase sigma. It will be found, therefore, in sites low in carbon, that is, for example, in the environment of deposited carbides. On the other hand, one can expect, during the formation of phase sigma, the formation of carbides in the direct proximity, if higher solubility of carbon in the adjacent solid solution is not possible, as was also found in the study of the decomposition of ferrite.

Lamellae of phase sigma formed preferentially on the boundaries of grains spread gradually into the ferritic grains during a slow quenching or longer heating. Since the formation of phase sigma is associated with contraction, a disintegration of the connected lamellae takes place as a result of the formation of multiple-axis tensile stresses.

In conclusion, we can state that, regardless of what the observed phase is, it seems to be the cause of an increased attack of the mentioned steels in the environment of nitric acid at higher concentrations and temperatures, or generally in the transpassive state.

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