EFFECTS OF RECRYSTALLIZATION/STABILIZING ANNEALING ON COLD FORMED PIPES OF W1.4435 STEEL

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The alloying elements which have been further added to Cr-Ni austenitic stainless steel enhance their thermodynamic instability and generate the possibility of hardening by precipitating of fine and disperse carbides and/or intermediary phases [1].

The paper, by using the non-compositional programming method, aimed to resolve a complex and significant issue - to make explicit the interdependencies between the resistance characteristics of W1.4435 austenitic stainless steel pipes and the degree of cold forming applied to their walls and namely the thermal and temporal parameters of recrystallizaton/stabilizing annealing applied after cold forming.

Keywords: W1.4435 steel, cold forming, recrystallization/stabilizing annealing, non-compositional programming method

1. Introduction

The austenitic stainless steels play an important role in the global production of stainless steels due to their large and various usages [1-4]. The W1.4435 steel is a component of this steel class, its low carbon content below 0.03% and molybdenum content between 2.5%...3% cause its main hardening phases to be the intermetallic phases; the intergranular corrosion susceptibility of this steel is mainly due to possible separation of phase σ [Fe(Cr,Mo)] on grain boundaries.

According to Bain et al. [5], the Cr - Ni stainless steels are not susceptible to intergranular corrosion at carbon content equal or below 0.02%; this level is currently considered as being the carbon concentration limit under which no intergranular corrosion occurs for this steel class.

However, Heger and Hamilton [6] claim that absolute intergranular corrosion resistance of Cr-Ni stainless steels is attained independently of sensitization regime parameters for carbon content < 0,009%; this level represents the carbon solubility limit in austenite at the lowest sensitization temperature where the carbides separation is still possible.

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Experimental results confirming these affirmations have been obtained also by Roha [7], which conclude that for not stabilized steels which have been sensitised long holding times at low temperatures, the ranges where the intergranular corrosion susceptibility occur are shifting to low carbon concentrations (Fig. 1).

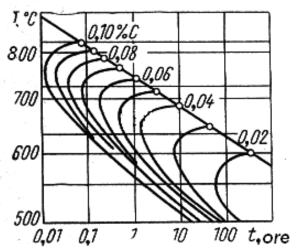

Fig.1 Shifting of the ranges where the intergranular corrosion susceptibility occur in Cr-Ni stainless steels depending on concentration of carbon dissolved in the solid solution [7, 8]

It was observed that the limit carbon concentration ensuring protection against intergranular corrosion of Cr-Ni stainless steels cannot be set [9] because the susceptibility to the intergranular corrosion is determined not only by the steel carbon concentration but also by the presence and proportion of certain alloying elements.

Three intermetallic phases are often found in Cr-Ni austenitic steels that contain few molybdenum percentages (Fig. 2): phase σ (the most studied but also undesirable), phase χ - $Fe_{36}Cr_{12}Mo_{10}$ [10] and phase Laves η - Fe_2Mo [3, 4, and 11].

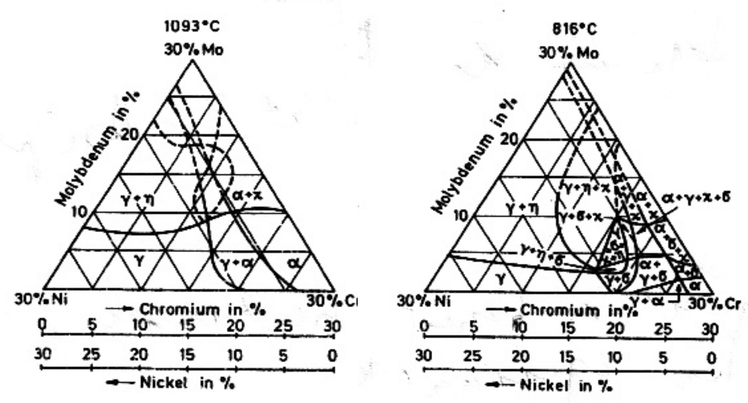

Fig.2 Isothermal sections in the ternary systems: Fe-Cr-Ni-Mo (%Fe=ct=70 at%), at 1093°C and 816°C [11]; α-ferite;γ -austenite; σ-phase σ; χ -phase (χ); η – phase Laves (η)

Recent researches have been shown that the phase χ appears previously to phase σ and transforms into it following to long time ageing [12-14]; the carbon is soluble in phase (χ) and thus this can be assimilated to $M_{18}C$ type carbide [15]. $M_{23}C_6$ is a carbide which is probable to occur in Cr-Ni steels such as AISI 316 and has been identified with the approximate formula $(Cr_{16}Fe_5Mo_2)C_6$ [10]; the presence of nitrogen in steel impede the carbide precipitation for W 1.4435 steel.

Particular significance on the stabilizing annealing of cold formed austenitic stainless steels and implicitly on their maximum performance (high mechanical characteristics and low intergranular corrosion susceptibility) is attained by rigurous correlation of the stabilizing annealing parameters with the cold processing conditions [2, 16, 17, 18, 19].

Studies of Aborn & Rutherford and Vialle & Van den Bosh [20] concluded that the strain hardening caused by cold processing can contribute to the increase of intergranular corrosion resistance of Cr-Ni stainless steels when subsequent stabilizing annealing at temperatures in the range 650^{o}C÷800^{o}C is applied (Fig. 3); heating in this temperatures range lead to the precipitating of carbides and intermetallic compunds and also at recrystallization of phases.

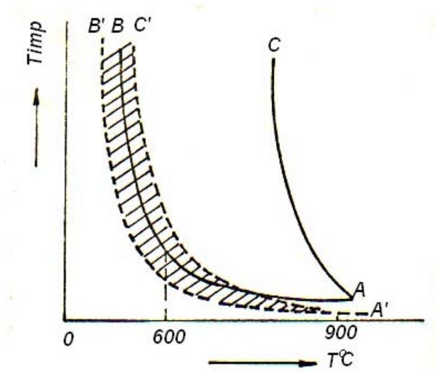

Fig.3 Time-temperature plane of the ternary diagram: intergranular corrosion susceptibility - time - temperature corresponding to the Cr-Ni stainless steel [20]: zone ABC – range where the steel is not strain hardened and is susceptible to intergranular corrosion; zone A'B'C'- range where the steel is strain hardened and is susceptible to intergranular corrosion;

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Precipitation of these phases ocurrs preferentially on sliding planes, consequently their capacity of chemical homogeneizing is more rapid [21].

In the case of stainless steels which have as main hardening phases - intermetallic phases, the correlation of the degree of cold forming - stabilizing annealing parameters - mechanical characteristics level - intergranular corrosion susceptilibility is complex and represents the object of the current paper.

2. Experimental

The experimental researches aimed to make explicit the interdependencies between the strength characteristics of W1.4435 austenitic stainless steel pipes and the degree of cold forming applied to their walls and namely the thermal and temporal parameters of recristallizaton/stabilizing annealing applied after cold forming, in order to enhance the mechanical resistance characteristics and thus to avoid the intergranular corrosion. These become possible through the non-compositional programming method (Table 1) and performing of the experimental cycle in accordance with the conditions set by the programme: central orthogonal compositional programming of II - order [22]. The independent variables and the range of values where these have been varied are mentioned in Table 1.

Table 1

Correspondence between the levels of factors expressed in coded units (Xi) and natural units (Zi)

Factors	Independent variables, Zi/Xi			Dependent variables,Yi		
	Cold forming degree, ε Z_1	Annealing temperature, T^oC, Z_2	Isothermal maintaing time,h Z_3	Rm, MPa Y_1	Rp $_{0,2}$, MPa Y_2	A_5, % Y_3
Code	X_1	X_2	X_3			
Base level,X_{i0}/Z_{i0}	0/50	0/800	0/8	-	-	-
Variation range, Δxi/ΔZi	$\lvert 1 \rvert$/20	100	2	-	-	-
Superior level, $X_{i0}+\Delta X_i/(Z_{i0}+\Delta Z_i)$	+1/70	+1/900	+1/10	-	-	-
Inferior level $X_{i0}-\Delta X_i/(Z_{i0}-\Delta Z_i)$	-1/30	-1/700	-1/6	-	-	-

Note. Yi-represent the dependent variable expressed in natural units

The complete chemical analysis has confirmed the steel chemical composition according to that prescribed by SR EN10088/3-98: 0.025%C, 0,09%Si, 0.04%P, 0.025%S, 1.8%Mn,18.2%Cr, 13.4%Ni, 2.8%Mo, 0.10%N.

Samples have been taken from steel pipes having the degree of cold forming required by programme and have been annealed in hydrogen atmosphere in furnaces having automat temperature control systems; after heat treatment, the samples have been tested (mechanically, for intergranular corrosion) and have been analyzed metalographically. The tensile strength test has been made on EDZ 40 type universal machine (acc. to SR EN ISO 6892-1/2010 Annex E, max load of 400 KN,); R_m, Rp_{02} and A_5 have been determined. The intergranular corrosion tests have been made by means of Strauss test (boiling in a mixture of $CuSO_4*H_2SO_4$, acc. to ISO 3651-2/1998), after a previous sensitization of samples by heating at 675^oC/1h; the claim resistant/not resistant to intergranular corrosion has been given after examination of the zone bend on bolt at 180^o.

The highlighting of presence of δ ferrite and the determination of its proportion in steel have been made with Feritscop FMP30 (acc. to DIN EN ISO 17655 - ISO 17655/2003). The metallographic analysis has been performed on Epytip microscope; the samples have been electrolitically etched in 10% oxalic acide solution (the austenitic grain size number has been determined according to ASTM E 112-96-2004 at magnification of 100:1).The X-Ray analysis has been performed in order to identify the hardening phases which can precipitate following to the stabilizing annealing realized in different conditions after cold forming; the DRON UM-1 diffractometer (Cu Kα filtered radiation) has been used. The electron microscopy performed with Cambridge M-9 electron probe microanalyser has revealed the composition namely the profiles of main elements – chromium, nickel and molybdenum in the above-mentioned steel.

3. Results & interpretations

The real conditions of experiments, imposed by the adopted non-compositional programming method adopted and the results obtained after the development of experimental cycle are mentioned in Table 2.

Table 2

Matrix of the central compositional orthogonal programming of second order and the results of the experimental researches

N0. exp.	X_0	X_1/Z_1	X_2/Z_2	X_3/Z_3	X_1'	X_2'	X_3'	***R_m, MPa***	***Rp $_{0,2}$, MPa***	***A_5, %***
1	+1	-1/30%	-1/700°C	+1/10h	+0,27	+0,27	+0,27	***696***	***315***	***30,9***
2	+1	+1/70%	-1/700°C	-1/6h	+0,27	+0,27	+0,27	***692***	***346***	***42,1***
3	+1	-1/30%	+1/900°C	-1/6h	+0,27	+0,27	+0,27	***596***	***245***	***45,2***
4	+1	+1/70%	+1/900°C	+1/10h	+0,27	+0,27	+0,27	***609***	***250***	***49,5***
5	+1	-1/30%	-1/700°C	-1/6h	+0,27	+0,27	+0,27	***689***	***296***	***34,1***
6	+1	+1/70%	-1/700°C	+1/10h	+0,27	+0,27	+0,27	***714***	***333***	***35***
7	+1	-1/30%	+1/900°C	+1/10h	+0,27	+0,27	+0,27	***618***	***309***	***54,5***
8	+1	+1/70%	+1/900°C	-1/6h	+0,27	+0,27	+0,27	***650***	***266***	***46,9***
9	+1	+α/74,3%	0/800°C	0/8h	+0,746	-0,73	-0,73	***743***	***340***	***20,6***
10	+1	-α/25,7%	0/800°C	0/8h	+0,746	-0,73	-0,73	***673***	***336***	***40***
11	+1	0/50%	+α/921,5°C	0/8h	-0,73	+0,746	-0,73	***625***	***264***	***46,7***
12	+1	0/50%	-α/678,5°C	0/8h	-0,73	+0,746	-0,73	***748***	***541***	***26,3***
13	+1	0/50%	0/800°C	+α/10,43h	-0,73	-0,73	+0,746	***625***	***266***	***40,9***
14	+1	0/50%	0/800°C	-α/5,57h	-0,73	-0,73	+0,746	***653***	***270***	***43,6***
15	+1	0/50%	0/800°C	0/8h	-0,73	-0,73	-0,73	***688***	***410***	***27,8***

In the case of central orthogonal compositional programming of second order, α=1.215 (see table 2) for the case of existence of three independent factors and

$$x_i' = x_i^2 - \frac{\sum_{u=1}^{N} x_{i_u}^2}{N} = x_i^2 - \overline{x_i^2}$$

The statistical processing of experimental results as well as the verification of the compatibility of the programming method have been led to the following particular forms of the interdependencies taken into analysis:

- in coded form:

$$Y_1 = R_m = 695.3 - 37.5X_3^2 + 15X_1 - 46.7X_2 \quad (1)$$

$$Y_2 = R_{p_{0.2}} = 390.5 - 31.4X_1^2 + 12.3X_2^2 - 78.7X_3^2 - 55.6X_2 - 13X_1X_2 - 14X_1X_3 \quad (2)$$

$$Y_3 = A_5 = 29.55 + 4.48X_2^2 + 8.38X_3^2 - 1.48X_1 + 7.88X_2 - 1.92X_1X_2 - $$
$$- 1.32X_1X_3 + 2.77X_2X_3 \quad (3)$$

where: X_1, X_2, X_3 represent the independent variables and have the significance mentioned in table 1.

- in decoded form:

$$R_m = 431.4 + 0.75 \bullet \varepsilon - 4.67 \bullet 10^{-1} \bullet T - 9.4 \bullet t^2 + 150 \bullet t \quad (4)$$

$$R_{p_{0.2}} = 10^{-2}\varepsilon(1585 - 7.85 \bullet \varepsilon - 0.65 \bullet T - 35 \bullet t) - 10^{-2}T(219.9 - 0.123T) - $$
$$- t(19.675 \bullet t - 323.3) - 232.95 \quad (5)$$

$$A_5 = 428.53 + 10 - 4 \bullet T(4.48 \bullet T - 9.6 \bullet \varepsilon + 138.5 \bullet t - 7014) + $$
$$+ t(2.,095 \bullet t - 0.033 \bullet \varepsilon - 42.95) + 0.958 \bullet \varepsilon \quad (6)$$

where: ε,T, t represent the degree of cold forming (%), temperature of recrystallization /stabilizing annealing (^{o}C) and holding time at annealing temperature (hours), each in natural values, in the limits established by the experimental programme adopted.

The experimental error of the calculated results (determined by means of the mathematical expressions of the interdependencies (rel.1-6)), in relation to those determined experimentally is in the limits +/-5%. The graphical expressions of the calculated mathematical models (Fig. 4), for a particular case (isothermal holding time = ct = 8h at stabilizing temperature) together with the optic micrographs (Fig. 5), have outlined aspects revealed also by the mathematical models in their coded (eq.1÷3), or decoded (eq.4÷6) expressions:

- the interdependencies are complex and the conclusions drawn have to be corroborated with the information given by the investigations realized (optic metallography, X ray diffraction, other);

- independently of mechanical-thermal processing (cold forming followed by stabilizing annealing), the mechanical characteristics are superior to those prescribed in standard for this steel in solution quenched state ($Rm \in [500 \div 700]$MPa;Rp_{02}=min200MPa;A_5=min 40% [23]); thus, the mechanical resistances are in the upper range, or even somewhat higher, the yield point is mostly two times higher than the minimum required value and the elongation is frequently higher than minimum imposed value (fig.4, table2);

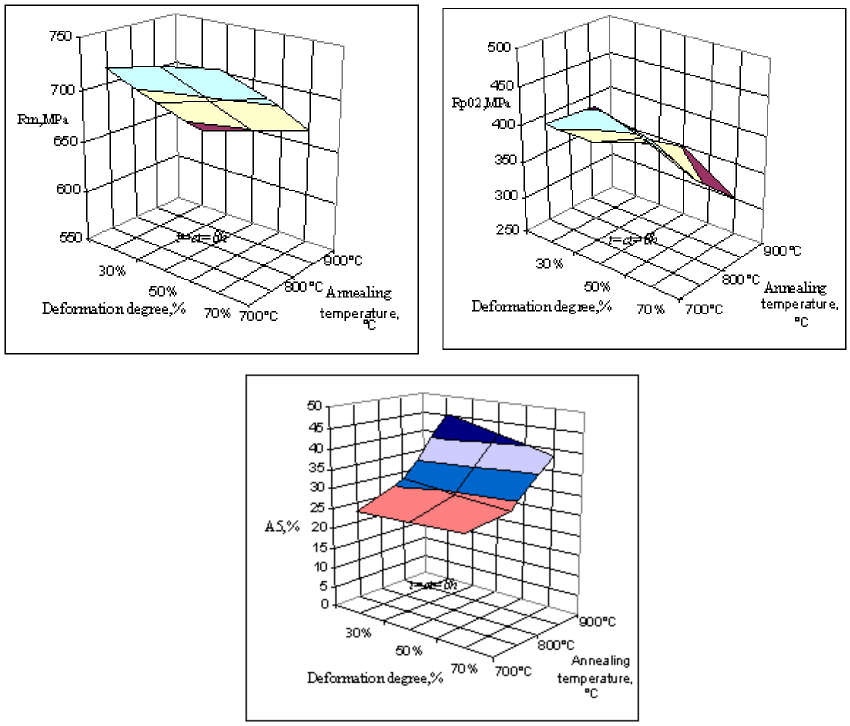
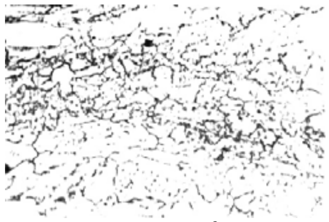


Fig.4 The response surfaces of the calculated mathematical models, corresponding to the interdependencies between the mechanical characteristics of steel W1.4435, the degree of cold forming and the temperature of stabilizing annealing (holding time = ct= 8 h)

- the increase of cold forming degree over 50% requires the increase of annealing temperature over 800°C (for holding time of 8 hours), or, as alternately, the increase of holding time over 8 hours (if temperatures higher than 800°C can not be ensured) considering the phases recrystallization need; it was observed that for a degree of cold forming of 50% (Fig. 5), a complete phases recrystallization is ensured by holding at 800°C for more than 10 hours (according to the steps imposed by the programming method adopted).

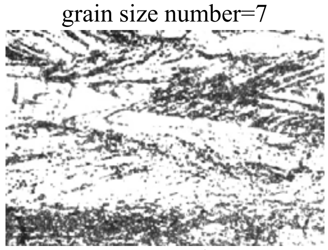
The stabilizing annealing parameters, applied after cold forming have to be thus correlated such as the grain size numbers to vary in close limits, 5-6, preferably mostly 6. The increase of the cold forming degree implies an enhance of the stabilizing annealing parameters in order to ensure complete phases recrystallization and obtaining of a grain size number in the limits of 5-6.

This grain size number correlated with the effective concentration of chromium in steel, value which takes into consideration also the concentration of the molybdenum in steel, dissolved in the solid solution (%Cr_{ef}=%Cr+%Mo), reduces at minimum the susceptibility to intergranular corrosion of steel for carbon effective concentrations below 0.1%.

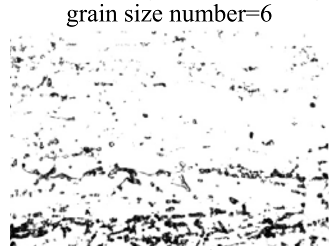


a) ε=30%;$T_{annealing}$=700^{o}C;$t_{annealing}$=6h
grain size number=7

b)ε=30%; $T_{annealing}$ =900^{o}C; $t_{annealing}$ =6h
grain size number=6

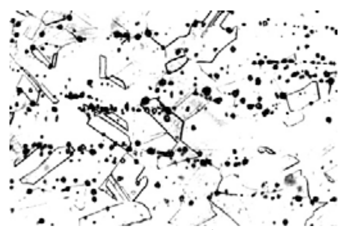


c)ε=50%; $T_{annealing}$ =800^{o}C;t $t_{annealing}$ =8h,
strain hardened



d)ε=50%; $T_{annealing}$ =800^{o}C; $t_{annealing}$ =10h
grain size number=6

e) ε=70%; $T_{annealing}$ =700^{o}C;$t_{annealing}$=6h
grain size number=6-7; partial strain hardened

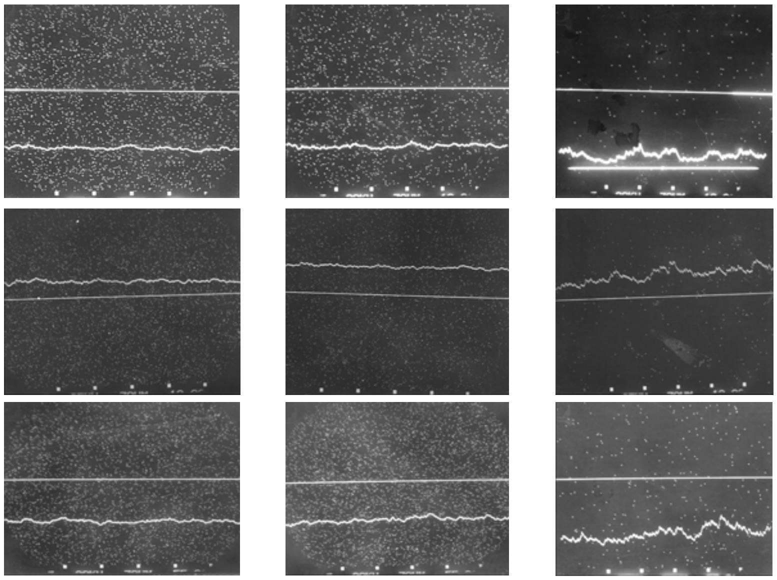


f) ε=70%; $T_{annealing}$ =900^{o}C;t $t_{annealing}$ =10h
grain size number=5

Fig.5 Micrographs of W1.4435 steel cold formed and annealed in different time-temperature regimes. Etching reagent: oxalic acid 10% - electrolytic attack, 500:1

Precipitating hardening phases during stabilizing annealing after cold forming has been occurred on directions which correspond to the creep direction of material during cold forming, on sliding planes, dislocations, other, except for low cold forming degrees,~30%, as seen in Fig. 5. The separation of the hardening phases in rows can apparently influence the corrosion resistance level: the investigations performed with the electron probe microanalyser (Fig. 6) have not highlighted nor notable changes of the chemical composition in different microvolumes, neither concentrations on the grain boundaries, phenomenon determined by the fine precipitation. An exception to the rule is observed in the case of molybdenum distribution, which being available in low concentrations (~

2,8%) is mainly found in Cr, Fe, $Mo)_{23}C_6$ type carbides or in σ phase (observed by X ray diffraction) and thus depleting the solid solution



T_{anneal}=700°C
t_{anneal}=6 h

T_{anneal}=900°C
t_{anneal}=6 h

T_{anneal}=900°C
t_{anneal}=10 h

Fig.6 X ray diffraction images corresponding to the distribution of chromium (a), nickel (b) and molybdenum (c) in samples of W 1.4435 steel, cold formed at (ε=70%) and annealed in different time-temperature regimes (magnification 500:1).

The X ray diffraction analysis have outlined the presence of all phases mentioned in the literature for this steel [σ, χ, η, Cr, Fe, $Mo)_{23}C_6$], in relatively low proportions but high enough as to ensure the increase of steel resistance characteristics. As it was assumed, the δ ferrite has not appeared in the case of processing of this steel (characterized by with chromium concentration higher than 18% and nickel concentration higher than 12%) [22] for every heat treatment variant taken into analysis.

4. Conclusions

The stabilizing annealing applied after cold forming can represent a technological variant which is very attractive for the mechanical characteristics increase without affecting the corrosion resistance of the W1.4435 austenitic stainless steel products. The estimation of stabilizing annealing technological parameters in order to lead to steel products of W 1.4435 which are resistant to intergranular corrosion resistance (for long time at low or high temperature) and which possess certain mechanical characteristics can be ensured by the interdependency relations determined by the adopted programme.

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