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DESIGN OF AGING-RESISTA˜ MARTENSITIC STAINLESS STEELS FOR PRESSURIZED WATER REACTORS

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With the exception of AISI 403 or 410 grades, the use of high strength martensitic stainless steels in PWR is poorly developped because these materials, like ferritic stainless steels, become embrittled by the precipitation of a b.c.c. chromium-rich phase during aging at the operating temperature(290 to 350°C).

The influence of alloying elements and microstructure on the aging behavior of forged low-carbon martensitic stainless steels containing 12 to 16% Cr, 0 to 2% Mo and 0 to 8% Ni was determined during accelerated aging at 450°C. Quantitative relationships were derived between the maximum increase in hardness, the maximum shift in CVN transition temperature and the chemical composition (Cr , Mo , C) and microtructure . These relationships are consistent with the mechanical properties of electroslag-remelted production heats aged between 300 and 450°C up to 10000 h and can be used to determine the composit·onal criteria to be satisfied by aging resistant martensitic stainless steels.

1. INTRODUCTION

The use of high strength stainless steels in PWR system appears promising because it could allow reductions in weight and cost of some components like pump shafts, pump casings, stainless bolting, which are now fabricated from forged or cast austenitic stainless steels. Low carbon martensitic stainless steels tempered near 600°C, showing yield strength values between 600 and 1200 MPa together with acceptable toughness and stress-corrosion resistance, can be considered for this purpose. Up to date, only two martensitic stainless steel grades are allowed by ASME Code Section III and French Code (RCC-M) for the fabrication of class 1 forged components. The use of these grades in PWR system is poorly developped because 1), the plain13% Cr steels (AISI 403 or 410 grades) have limited hardenability, toughness and corrosion resistance and 2), the precipitation-hardened 16% Cr steels (AISI 630 grade) become embrittled by aging at the operating temperature (about 290 to 350°C).

Considering all grades of forged martensitic stainless steels, AISI 403 or 410 excepted, the main drawback for PWR applications is the fact that these steels, like ferritic stainless steels, are embrittled by the precipitation of a b.c.c. chromium-rich phase (α') during aging below 520°C(1)(2). Thus, one necessary condition to be fullfilled before using some of these grades in PWR system is to determine the basic laws of α' precipitation embrittlement. This was done in two steps. Firstly, the influence of alloying elements and microstructure on the aging behavior of martensitic stainless steels was determined quantitatively on laboratory heats submitted to accelerated aging at 450°C. Secondly, five electroslag-remelted production heats were used to determine the influence of temperature between 300 and 450°C on aging kinetics and to check the quantitative relationships developped independently in the first part of this study. All these results, together with corrosion resistance considerations, allow to give the definition of the criteria to be satisfied by aging-resistant martensitic stainless steels for PWR system.

2. INFLUENCE OF COMPOSITION ON AGING BEHAVIOR OF MARTENSITIC STAINLESS STEELS AT 450°C

A full description of experimental details and microstructural examinations was given elsewhere (3). Only the main results concerning aging behavior, which are used as reference data in this paper, are detailed below.

Materials

A series of extra-low carbon laboratory heats containing from 12 to 16% chromium, 0 to 8% nickel and 0 to 2% molybdenum, were melted in a vacuum induction furnace, then forged into 70 x 15mm bars. Two precipitation hardening stainless steels with 3% copper and 1% aluminium respectively were also prepared. Table I gives the chemical composition of each heat.

Table I. Chemical compositions of the laboratory heats (analyses performed on bars - weight%) and δ-ferrite and austenite contents in the as-quenched condition(%)

[illegible]	C	Mn	[illegible]	[illegible]	[illegible]	Cr	Ni	Mo	Al	Cu	[illegible] ppm	δ ferrite	retained austenite
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
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[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]

Heat treatment consisted of austenitizing for 1h at 1010°C followed by oil quenching, then tempering for 4 h at 590°C.

The microstructures of these laboratory heats in the as-quenched and tempered condition were examined. All the materials presented a lath martensite structure with a prior austenite grain size of between 4 and 6 ASTM.

Austenite contents, as-measured by a magnetic method, and the other identified phases are given in Table II.

Table II. Austenite contents and identified phases in the as-quenched and tempered condition (laboratory heats)

Material Identification	Identified phases					Observations
	γ(%)	$M_{23}C_6$	M_2 (C,N)	Cu	NiAl	
Z14C13 Z10C13	0 0	\ -	\ -	- -	- -	no examination performed
13-4 15-4 16-4 16-5	4 5 6 13	X X X -	- - - -	- - - -	- - - -	no examination performed
13-8	34	X	-	-	-	
13-4-1 13-8-2	7 35	X X	- -	- -	- -	
15-4 PH	7	X	-	X	-	
13-8-2 PH	13	X	-	-	X	

Aging behavior

Figure 1 shows the rate of hardening as a function of holding time at 450°C. All compositions exhibit hardening during aging at 450°C, with the exception of straight 13% Cr steels which will be discussed later. To facilitate comparisons, the increase in hardness as a function of time is shown on figure 2.

As for ferritic stainless steels (4,5), the maximum hardening increases with the Cr content (fig.2a). Figures 2b and 2c show that the maximum hardening increases also with the Mo content of the steel.

Tensile properties and CHARPY V Notch transition curves were determined in the unaged condition and after 1000 h aging at 450°C (Table III). Increases of yield strength and tensile strength at 20°C were generally of the same order of magnitude except in the case of 13-8-2 PH where yield strength decreased and tensile strength increased. Aging at 450°C for 1000h caused slight softening in heat Z14C13. Elongation at fracture was similar for both unaged and aged condition with values from 20 to 25% (16 to 20% for 13-8-2 PH heat which had a much higher tensile strength than the other materials examined).

Aging had a strong effect on CVN impact properties with an increase of the transition temperature by between 50 and 200°C (Table III). In most cases upper shelf energy values were greatly reduced by aging (see figure 5). In straight 13% Cr heats (Z14C13 and Z10C13) aging for 1000h at 450°C caused a slight reduction in the transition temperature and no significant change in the upper shelf energy, which is consistent with the softening effect reported above.

After aging for 10000h at 450°C, a fine homogeneous precipitation was observed in the martensitic phase of the chromium-nickel steels (see e.g. fig. 3).

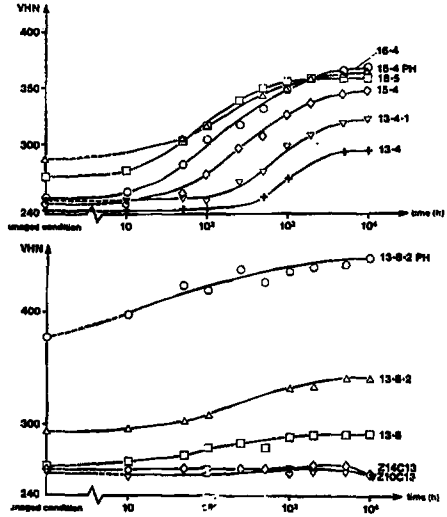


Figure 1 - Hardening rate of martensitic stainless steels during aging at 450°C(laboratory heats)

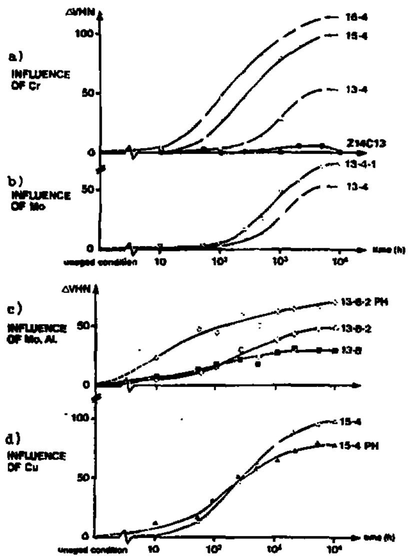


Figure 2 - Influence of alloying elements on the increase in hardness during aging at 450°C.

Table III. Tensile properties and CHARPY V Notch transition temperature in the unaged condition and after 1000h aging at 450°C (laboratory heats)

Material Identification	Yield Strength at [illegible] °C (MPa)			Tensile Strength at [illegible] (MPa)			[illegible] Temperature at [illegible]		
	unaged	aged	difference	unaged	aged	difference	[illegible]	[illegible]	difference
Z14C13	636	[illegible]	[illegible]	916	769	[illegible]	[illegible]	[illegible]	[illegible]
Z10C13	-	-	[illegible]	-	-	-	[illegible]	[illegible]	[illegible]
13-4	644	[illegible]	+ 19	710	762	[illegible]	[illegible]	[illegible]	[illegible]
15-4	[illegible]	[illegible]	[illegible]	[illegible]	932	[illegible]	[illegible]	[illegible]	[illegible]
16-4	[illegible]	[illegible]	[illegible]	[illegible]	1048	[illegible]	[illegible]	[illegible]	[illegible]
16-5	[illegible]	[illegible]	[illegible]	[illegible]	1057	[illegible]	[illegible]	[illegible]	[illegible]
13-8	[illegible]	[illegible]	[illegible]	[illegible]	851	[illegible]	[illegible]	[illegible]	[illegible]
13-4-1	[illegible]	[illegible]	[illegible]	738	849	+ 111	[illegible]	[illegible]	[illegible]
13-8-2	[illegible]	[illegible]	[illegible]	[illegible]	901	[illegible]	[illegible]	[illegible]	-
15-4 PH	[illegible]	[illegible]	[illegible]	[illegible]	1029	[illegible]	[illegible]	[illegible]	[illegible]
13-8-2 PH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

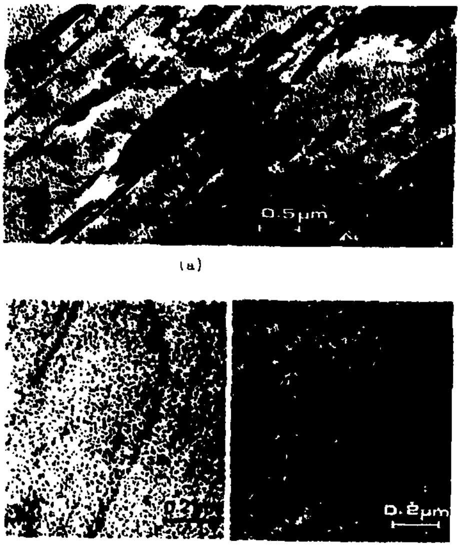


Figure 3 - Heat 13-4, as aged for 10000h at 450°C
Morphology and distribution of α' particles
(a) and (b) thin foils
(c) extraction replica

These particles were identified as α', a chromium-rich b.c.c. phase containing about 5 to 10% Fe (3) ; This result is consistent with previous work on aging of ferritic stainless steels (6)(7). The presence of α'-depleted zones adjacent to austenite in heats 13-4 (fig.3a) and 13-8 indicates that these compositions are close to the solubility limit of α' at 450°C.

The addition of molybdenum modified the composition of the α' phase which was found to have higher Fe and Mo contents : this leads to higher volume fractions of α' for a given Cr content. In heats 13-8-2 and 13-8-2 PH, plates, tentatively identified as σ phase (3), were observed in addition to the α' particles; these plates are too coarse to contribute to the hardening observed during aging.

The behavior of the precipitation-hardening martensitic stainless steels (13-8-2 PH and 15-4 PH) will be discussed in next section.

3. RELATIONSHIPS BETWEEN MECHANICAL PROPERTIES AND MICROSTRUCTURAL FEATURES

Hardening

Given the nature of the precipitates (chromium-rich α' phase), one may expect maximum hardening at 450°C to be a function of the chromium content in solid solution before aging. Extra hardening was also noted in molybdenum-containing steels, as observed by COURTNALL and PICKERING (8), and is probably related to the increase in volume fraction of α' in the presence of molybdenum.

An attempt was made to correlate maximum hardening at 450°C to Cr and Mo contents in solid solution prior to aging, using the following parameter :

$Cr^* = \%\,Cr + \%\,Mo - A(\%\,C)$, where $A \sim 16$ when the only carbides formed during tempering are $M_{23}C_6$, and $A \sim 12$ when $M_{23}C_6$ and $M_2(C,N)$ are present in approximatively equal proportions, as in the straight 13% Cr steels (see Table II).

Figure 4 shows that the maximum hardening at 450°C depends not only of the Cr^* parameter, but also on the quantity of austenite, a phase which does not harden during aging. A good representation of results shown in figure 4 was obtained by means of equation (1), where γ is the austenite content :

$$\Delta VHN_{max} = (22.1 - 0.313\,(\%\gamma))\ (Cr^* - 10.2) \qquad (1)$$

with 0.992 as correlation coefficient and 9.4 as standard deviation.

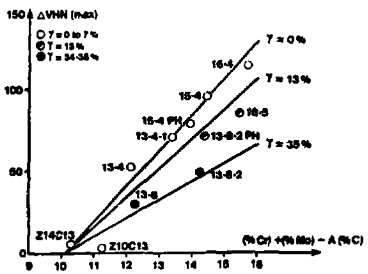


Figure 4 - Influence of chemical composition and austenite content on the maximum hardening observed during aging at 450°C. The straight lines are calculated from equation (1).

The α'-phase solubility limit at 450°C (Cr^*=10.2%), which corresponds to the minimum standard deviation when the results are adjusted by the least squares method using equation (1) above, agrees well with results reported in the literature (about 10% Cr at 450°C (6), about 11% Cr at 475°C (9)).

Figure 4 shows no clear difference in the maximum hardening of 15-4 PH and 13-8-2 PH, the precipitation hardening grades, and that of Cr-Ni or Cr-Ni-Mo grades. This point deserves some more explanations. The PH heats exhibit some hardening during the first few hours of holding at 450°C as can be seen on figures 2d and 2c; this is due to additional precipitation of the intermetallic compounds ε (Cu) and Ni Al respectively, owing to a decrease in solubility at 450°C as compared with the tempering temperature (590°C). This behavior has already been observed in 17-4 PH steel by ANTONY(1).

After 10000h at 450°C, the rate of hardening of 15-4 PH and 13-8-2 PH is nearly the same as that of a Cr-Ni or a Cr-Ni-Mo steel containing equal contents in Cr^* and austenite, as if hardening due to α' only was found. Electron microscopy clearly showed that ε and Ni Al particles coarsen during 10000h holding period at 450°C (3), suggesting that the softening due to the coalescence of ε or Ni Al particles is offset by the hardening caused by the increase in volume fraction of the same phases (due to the reduced solubility at 450°C).

Toughness

The effect of aging on the tensile properties of the materials considered (increase in yield and tensile strength, slight variation in elongation at fracture) is, for practical purposes negligible, but aging does have a considerable effect on impact energy transitions curves. Figures 5 and 6 summarize the results obtained, part of which were already presented in Table III.

Figure 5 shows that the upper shelf energy (of CHARPY V-Notch transition curves) decreases when hardness increases, irrespective of the austenite content and of the material condition, unaged or aged for 1000h at 450°C.

Whatever the austenite content, the shift in the CVN transition temperature (as measured at half upper shelf energy) due to aging is, on first approximation, proportional to the corresponding increase in hardness (figure 6). The following equation was obtained by the least squares method :

$$\Delta T\ (°C) = -12 + 2.17\ (\Delta VHN) \qquad (2)$$

A shift in the transition temperature has already been observed in ferritic stainless steels (5)(10) and is due to a shift to higher temperatures for the cleavage mode of fracture. However at the lower end of the transition range, fracture in Z14C13 heat appeared mainly intergranular. This was not the case for Z10C13 heat (containing 0.3% Mo), and in the other heats the proportion of intergranular fracture was low (< 20%) and do not appear to vary significantly after aging. No intergranular fracture was observed in grades containing 1 or 2% Mo, in agreement with published data on reversible temper embrittlement in martensitic stainless steels (11).

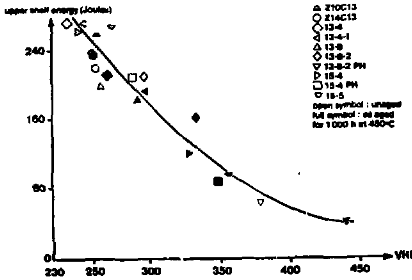


Figure 5 - Variations in upper shelf energy with hardness of aged or unaged materials (laboratory heats).

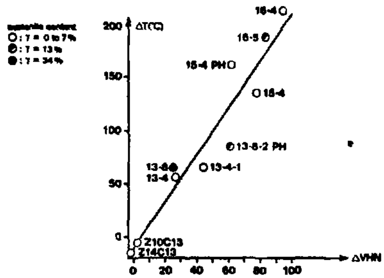


Figure 6 - Relationship between the shift in CHARPY V-Notch transition temperature and the increase in hardness due to aging (laboratory heats).

4. AGING OF PRODUCTION HEATS BETWEEN 300 AND 450°C

Materials

In the second part of this study, 5 production heats of about 2500 kg in weight were used. Steelmaking involved first fusion in a H.F. furnace, then electroslag remelting to get 400 x 400mm square section ingots. After heating near 1200°C, the ingots were forged into 130 x 60mm bars. Table IV gives the chemical composition of each heat.

Table IV. Chemical compositions of the production heats (analyses performed on bars - weight %)

Material identification	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Cr	[illegible]	[illegible]	[illegible]	[illegible]	Al
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.0282	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.17	0.0235	[illegible]

Heat treatment consisted of austenitizing for 1h at 985°C(1040°C for 17-4 PH heat) followed by oil-quenching, then by tempering for 4h at 600°C/air cooling. In the case of 16-4 heat, two tempering temperatures were chosen in order to promote the formation of different austenite contents. The detailed heat-treatment procedure is given below :

Material identification	Austenitizing	Tempering
13% Cr	985°C 1h/Oil Quenching	600°C 4h/Air Cooling
13-1	985°C 1h/Oil Quenching	600°C 4h/Air Cooling
13-4	985°C 1h/Oil Quenching	600°C 4h/Air Cooling
16-4	985°C 1h/Oil Quenching + 0°C 3h	550°C 4h/Air Cooling
	id.	620°C 4h/Air Cooling
17-4 PH	1040°C 1h/Oil Quenching + 0°C 3 h	600°C 4h/Air Cooling

In the as-quenched and tempered condition, all materials exhibited a lath martensite structure with a prior austenite grain size of about 4 ASTM. Austenite contents and the other identified phases are given in Table V.

Table V. Austenite contents and identified phases in the as-quenched and tempered condition (production heats)

Material identification	Tempering temperature	δ ferrite (%)	γ (%)	$M_{23}C_6$	Others
13% Cr	600°C	∿ 3	0	X	M_2 (C,N)
13-1	600°C **	0	0	X	M_2 (C,N)
13-4	600°C	0	11	X	-
16-4	550°C	0	5	X	-
	620°C	0	27	X	-
17-4 PH	600°C	0	10	X	ε (Cu)

<u>Aging treatments and tests performed</u>

The aging treatments were limited to the following :

300°C	10000 h	400°C	1000 h	450°C	1000 h
350°C	5000 h		5000 h		5000 h
	10000 h		10000 h		10000 h

In each condition, hardness and tensile properties were measured at room temperature. CHARPY V-Notch impact tests were also performed in order to determine the ductile to brittle transition curves.

<u>Aging behavior</u>

1) Hardening :

The variations in hardness as a function of time and temperature of aging are shown on figures 7 to 9; on these figures isochronal hardening curves were tentatively drawn.

All compositions exhibit age-hardening with the exception of 13% Cr and 13-1 heats which do not harden and show some softening after 10000 h aging at 450°C (Fig. 7 and 8).

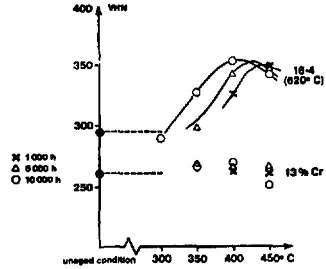


Figure 7 - Variations in hardness as a function of time and temperature of aging for 13% Cr and 16-4 (tempered at 620°C)steels.

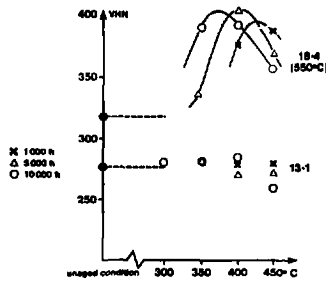


Figure 8 - Variations in hardness as a function of time and temperature of aging for 13-1 and 16-4 (tempered at 550°C) steels.

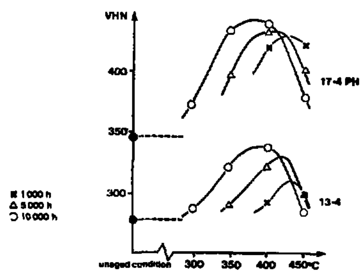
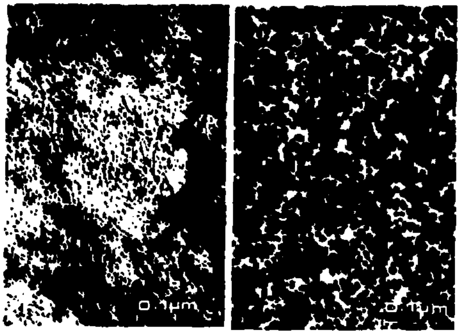


Figure 9 - Variations in hardness as a function of time and temperature of aging for 13-4 and 17-4 PH steels

The highest hardness values are obtained after aging for [illegible]h or 10000h at 400°C. At 450°C, maximum hardening occurs near 1000h, in contrast with the results obtained on laboratory heats where maximum hardening was observed between 2000h and 10000h; at this temperature hardening kinetics are faster and maximum hardening is lower in production heats than in laboratory heats.

T.E.M. examinations on aged production heats show that α' nucleation evolves from purely homogeneous at 400°C to partially dislocation-controlled at 450°C (see e.g. Fig. 10). On the contrary, α' nucleation is purely homogeneous in laboratory heats aged at 450°C (see e.g. Fig.3). This originates in differences in dislocation density within the martensite laths, the dislocation density after tempering being higher in production heats than in laboratory heats. The relevant microstructural examinations will be presented in another paper (12).



a) thin foil b) extraction replica

Figure 10 - 13-4 production heat, as-aged for 10000h at 400°C (a) and 5000h at 450°C (b) - Morphology and distribution of α'-particles

It can be noticed that in the unaged condition hardness is higher in production heats than in the homologous laboratory heats (figures 1,7,8,9). This is in agreement with the differences in dislocation density within the laths quoted above, because the other parameters controlling the yield strength (packet size and lath width (13)) are nearly the same in production and laboratory heats.

The previous considerations on α' nucleation explain why maximum hardening in production heats (obtained at 400°C) is consistent with the values calculated from equation (1), although equation (1) was established from 450°C aging data on laboratory heats (Fig. 11).

2) Embrittlement :

CHARPY V-Notch impact specimens (longitudinal direction) were used to determine the evolution of the impact energy transition curves as a function of time and temperature of aging. As an example, the results obtained for 13-4 steel are presented on Figure 12.

At all temperatures between 300 and 450°C, aging results in a decrease in the upper shelf energy and in an increase in the ductile to brittle transition temperature. Figure 13 gives for 13-4 steel the variation in upper shelf energy and CVN transition temperature (determined at half upper shelf level), as a function of time and temperature of aging. Compa-

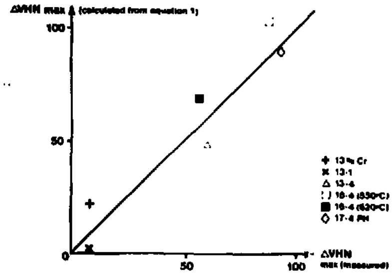


Figure 11 - Maximum increase in hardness due to aging (production heats) - Comparison of as-measured and as-calculated values

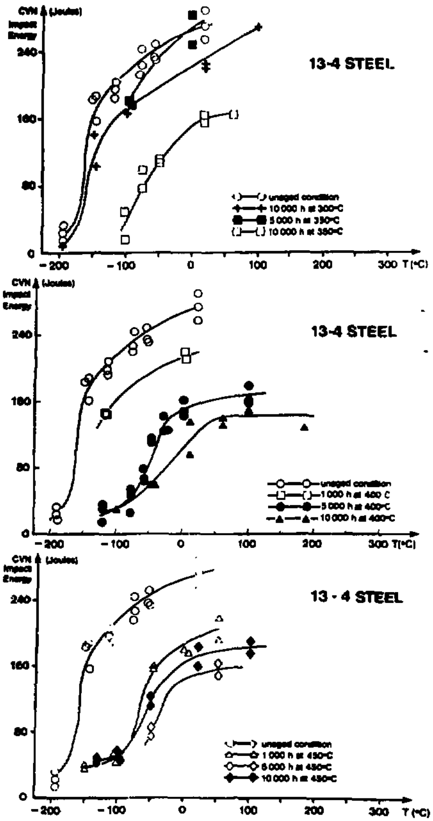


Figure 12 - 13-4 production heat - Influence of aging time and temperature on the CHARPY V-Notch impact energy transition curve.

ring figures 13 and 9, it can be seen that maximum hardening and maximum enbrittlement occur simultaneously. During the overaging process, although hardness and tensile properties may return to the unaged level, there is only partial recovery of upper shelf level and transition temperature.

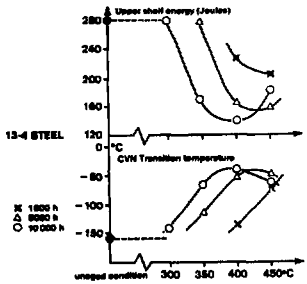


Figure 13 - Variations in upper shelf energy and CHARPY V-Notch transition temperature of 13-4 steel as a function of time and temperature of aging.

Figure 14 compares the measured values for the maximum shift in transition temperature due to aging and the values calculated from equation (2) for all production heats. A good agreement is observed between calculated and measured values, with the exception of 13-1 steel where the embrittlement due to aging is higher than the value calculated from α' hardening. S.E.M. examinations showed that the fracture morphology is predominantly intergranular in 13-1 steel as aged for 10000h at 400°C or 450°C. For this steel, where no hardening by α' occurs, aging results mainly in reversible temper embrittlement. Reversible temper embrittlement was also observed to some extent in 13% Cr and 17-4 PH steels which have the highest P and the lowest Mo contents of all productions heats (Table 3).

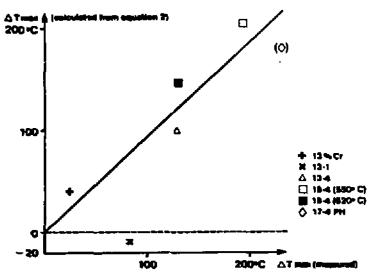


Figure 14 - Maximum shift in CVN transition temperature due to aging (production heats) Comparison of as-measured and as-calculated values.

The upper shelf energy value is mainly a function of hardness (or tensile strength) as it was the case for laboratory heats. Figure 15 shows that in the fully-aged condition (10000h at 400°C), the upper shelf energy values of production heats are close to the mean curve obtained on laboratory heats (fig.5). In the case of 16-4 steel tempered at 620°C, with a high austenite content, the upper shelf energy is significantly higher than the corresponding value on the mean curve.

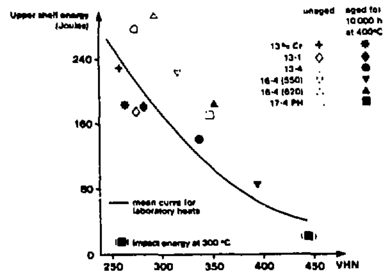


Figure 15 - Variations in upper shelf level with hardness for production heats in the unaged or fully-aged conditions. Comparison with the results obtained on laboratory heats.

3) Time-temperature relationship for aging:

The experimental results obtained on production heats show that maximum hardening and embrittlement occur near 10000h aging at 400°C. The question is now to know if these results can be extrapolated at the operating temperature of PWR which is near 300°C.

Studying the aging behavior of the cast martensitic stainless steel CA6NM, GYSEL and Colleagues (14) found that a time-temperature relationship exists when the evolutions of impact energy at 20°C or 300°C are considered. The value of the apparent activation energy given by these authors is about 100 kJ/mol.

Using the CVN transition curves obtained after 10000h aging at 350°C as reference condition*, the aging durations leading to nearly identical transition curves at 400 or 450°C were determined. The results presented in Table VI are consistent with the hypothesis of an apparent activation energy of 100 kJ/mol.

On this basis, aging for 10000h at 400°C is equivalent to 230000h at 300°C. As the anticipated service life at the operating temperature is 280000h (32 years), it appears that maximum hardening and embrittlement observed near 10000h at 400°C will be effective during the life of a component.

To give a full demonstration of this point, it is necessary to consider the evolution of α' precipita-

* This aging treatment induces a significant shift in transition temperature with values between 45 and 175°C according to the steel considered. (see e.g. fig. 13).

tion when aging temperature becomes lower. α' precipitation appears homogeneous at 350 and 400°C in the case of production heats (12); as maximum hardening observed at 400°C for production heats is the same as that obtained at 450°C for laboratory heats (where α' precipitation is homogeneous), it can be concluded that the solubility of Cr in low-carbon martensite, and thus α' volume fraction, does not vary significantly between 450°C and 400°C and thus below 400°C.

Table VI. Aging treatments giving identical CVN impact test transition curves (reference condition : as-aged for 10000h at 350°C).

Material	holding time at 400°C	holding time at 450°C
13-4	∿ 4000 h	n.d.
16-4 (550°C)	∿ 2000 h	n.d.
16-4 (620°C)	∿ 3000 h	∿ 1000 h
17-4 PH	∿ 3000 h	< 1000 h
calculated from Q=100kJ/mol	2400 h	690 h

n.d. = not determined because of differences in shape of the transition curves obtained after aging at 350°C and 450°C.

Previous considerations show that, as a first approximation, the maximum hardening and embrittlement due to α' precipitation are independent of aging temperature in the range 300-400°C. It can be concluded that equations (1) and (2) give a good approximation of the maximum hardening and embrittlement which will occur during the life of a component operating up to 32 years near 300°C.

5. DESIGN OF AGING-RESISTANT MARTENSITIC STAINLESS STEELS FOR PWR SYSTEM

All the results detailed in the previous sections can be used to give the design rules of aging-resistant martensitic stainless steels for PWR system. This design will be the result of a compromise because the alloying elements which improve corrosion resistance (Cr, Mo) increase the embrittlement due to aging at the operating temperature. The use of high austenite contents (20 to 30%) to reduce the embrittlement does not appear suitable because of the practical difficulty to control the austenite content through the tempering temperature and of the poor yield strength values associated with high austenite contents.

To have a good corrosion resistance in the primary coolant of a PWR, about 13% Cr are necessary when steels with extra low carbon content (∿ 0.05%) are considered. To increase the resistance to pitting corrosion and also suppress reversible temper embrittlement, an addition of about 1% Mo seems desirable.

With 0.05% C, 13% Cr and 1% Mo (Cr^* = 13.2%) and a nil austenite content, the maximum values for hardness increase and shift in CVN transition temperature during aging, calculated from equations (1) and (2), are:

$$\Delta VHN = 66$$

$$\Delta T = 130°C$$

To keep the transition temperature below 20°C during the whole life of a component, it is necessary to get a CVN transition temperature lower than -110°C in the unaged condition. This can be achieved with Ni additions of about 4% and carefully controlled steelmaking procedures. Using the experimental results obtained on 13-4 production heat (electroslag remelted and as tempered for 4h at 600°C), the following mechanical properties can be anticipated for a 0.05% C, 13% Cr, 4% Ni, 1% Mo steel :

Mechanical properties	Unaged condition	max. increase due to α' embrittlement (calculated)	Fully-aged condition
VHN	[illegible]	66	342
Yield Strength	[illegible] MPa	-	∿ 900 Mpa
Tensile Strength	[illegible] MPa	-	∿1000 MPa
Elongation at Fracture	[illegible]	-	∿ 20%
Reduction in Area	[illegible]	-	∿ 70%
Upper Shelf Energy	[illegible] J	-	∿ 110 J
CVN Transition Temperature (at 1/2 upper shelf energy)	[illegible] °C	+ 130°C	-35°C

The mechanical properties in the fully-aged condition are quite acceptable ; furthermore, the corrosion resistance of 13-4 steels, as tempered at 600°C or above, is known to be very high (2).

To get higher yield strength values (e.g. up to 1000 MPa, for some bolting applications) without increasing the carbon and chromium contents, it appears necessary to use precipitation-hardened steels, with higher nickel contents to keep very low CVN transition temperatures. The results obtained on laboratory heats (Table III) show that 13% Cr - 8% Ni steels, with at least 1% Mo and Al(or Cu)additions to promote precipitation hardening, present acceptable resistance to aging. These compositions allow to obtain a CVN transition temperature below 20°C in the aged condition but it seems necessary to try to increase the upper shelf energy in both unaged and aged conditions (fig. 7). Moreover the stress-corrosion cracking resistance of these grades in the primary coolant has to be checked.

These examples show that extra-low carbon 13% Cr steels with about 4% Ni and 1% Mo to obtain a medium strength level, with about 8% Ni, 1 or 2% Mo and Al(or Cu) additions to obtain a high strength level, appear suitable for use in PWR system. More work is needed to determine the acceptable limits in chemical composition and heat-treatment. A study of the corrosion and mechanical properties of commercial grades, which can be considered as acceptable candidates on the basis of the previous analysis, is now in progress.

6. CONCLUSIONS

This study of the aging behavior of low-carbon martensitic stainless steels in the temperature range 300-450°C (up to 10000h) leads to the following conclusions :

1) hardening is due to α' precipitation and increases with the Cr and Mo contents in solid solution before aging. A quantitative relationship between the chemical composition, austenite content and maximum increase in hardness was established.

2) embrittlement due to α' precipitation results in an increase in the CVN transition temperature and a decrease in the upper shelf energy. The shift of the transition temperature was quantitatively related to hardening. In the steels with high P and low Mo contents, reversible temper embrittlement increases the shift of the transition temperature.

3) the evolution of the CVN impact energy curves with time and temperature of aging is consistent with the time-temperature relationship proposed by GYSEL and Coll.(14), where the apparent activation energy is about 100 kJ/mol.

4) maximum hardening and embrittlement by α' precipitation will be effective during the life of a component operating up to 32 years near 300°C.

5) these results allow the prediction of the tensile and impact properties of martensitic stainless steels in fully-aged condition, and, as a consequence, give the design rules of martensitic stainless steels for use in PWR system. With carefully controlled steelmaking and heat-treatment procedures, commercial grades based on compositions such as 13% Cr - 4% Ni or 13% Cr - 8% Ni, with Mo additions and with or without additions promoting precipitation hardening, appear as acceptable candidates for use in PWR.

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