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Physical metallurgy of BATMAN II Ti-bearing martensitic steels [1]

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Abstract

Seven laboratory experimental casts of 7–9% Cr Ti-bearing martensitic steels were obtained via VIM process. Plates of 25 mm thickness were produced by hot rolling. On each cast CCT diagrams and critical temperatures were determined. Several austenitizing treatments were performed to study the grain size evolution. The effect of microstructure on impact properties were finally investigated. This paper discusses the role of chemical composition on microstructural and physical properties and shows the beneficial effect either of low-temperature austenitizing or double-austenitizing steps on impact properties.

1. Introduction

Suitability of ferritic/martensitic steels for structural applications in an MFR machine is strongly linked to the temperature's window foreseen for the operative condition of the Tokamak Reactor [1]. Thermal stability and, moreover, embrittling phenomena occurring at low irradiation temperatures could limit their use in the environment of a Fusion machine. Nevertheless 7–9% Cr, 2 W steels exhibit so encouraging behaviours [2–5] that several Associations endeavour to optimise chemical composition and thermal treatments for reducing detrimental effects of irradiation on mechanical properties.

Although recent results show that some 7–9% CrWVTa martensitic alloys exhibit a moderate shift of DBTT at low irradiation temperature [6], it is not so clear if irradiation embrittlement will get a saturation level under a 14 MeV neutron irradiation.

Experiments carried out in a mixed spectrum on Ni-doped martensitic alloys [7], irradiated to produce a He/dpa ratio comparable to that evaluated in a Fusion environment, seem to indicate the absence of this saturation phenomenon, while dual ion-beam experiments show no particular effects on hardening [8]. Moreover, manganese increase due to iron transmutations, could in any case, contribute to delay a saturation of the DBTT shift [9,10]. These evidences imply that Transition Temperature's shift not only must be rather limited after a relevant fast neutron dose, but it would be the lowest possible in the unirradiated condition.

To investigate the role of some alloying elements on a 7–8.5% Cr, 1.5% W, V matrix, seven small experimental casts were conceived and realised. In this paper, we report their effects on after heat treatments' morphologies and impact properties.

2. Experimentals

BATMAN II steels were produced using a VIM process. Chemical compositions of as cast alloys are reported in Table 1.

All ingots were chemically homogenised at 1200°C for 10 h in air then hot rolled up to ≈25 mm thick

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Table 1
Chemical composition of BATMAN II steels

Cast No	C (%)	Cr (%)	W (%)	Ti (%)	V (%)	Mn (%)	B (ppm)	Si (ppm)	N (ppm)	S (ppm)	P (ppm)	Ni (ppm)
1951	0.12	8.45	1.45	0.12	0.17	1.34	70	330	70	12	50	260
1952	0.134	8.67	1.42	0.12	0.20	0.48	62	500	41	<20	50	340
1953	0.13	7.55	1.41	0.072	0.20	0.52	57	300	41	<20	50	290
1954	0.121	8.45	1.43	0.077	0.19	0.50	54	300	69	<20	50	290
1954bis	0.077	7.68	1.38	0.065	0.20	0.50	54	280	26	18	60	210
1955	0.125	8.67	1.43	0.066	0.20	0.52	64	250	57	18	60	210
1956	0.14	8.59	1.42	0.12	0.20	1.48	<4	300	57	12	60	210

For all Steels Mo < 160 ppm, Nb < 25 ppm, Al < 85 ppm, Cu < 60 ppm, Sn < 25 ppm.

products. Metallographic examinations of samples drawn from the central zone of plates showed their fully martensitic nature.

Normalization treatments were performed on samples cut from casts 1951, 1954 and 1955 in order to study their effects on grain size. After a proper selection, critical temperatures A_{C1} and A_{C3} were measured using an Adamel D124 dilatometer while M_S and M_F were obtained from continuous cooling tests performed with Dilatronic III dilatometer.

Samples coming from casts 1953–1955, were thermally treated to study the effect of austenitisation temperatures and cooling rates on impact properties. Impact tests have been carried out on micro-Charpy KLST-type samples, using a fully instrumented Wolpert PW5 pendulum (50 J max capacity).

Optical and scanning electron microscopy were used to characterise morphologies and inclusions as well as primary precipitation.

Semi-automatic image analysis for quantitative metallography, performed for grain size distributions determination, was done by means of the public domain Software NIH-Image [11], running under a Macintosh® platform.

3. Physical metallurgy

3.1. Normalization treatments and grain size

In order to maximise fracture toughness, several normalization treatments in the temperature range 970–1040°C were performed on the three casts already mentioned for studying grain refining heat treatments. Results are plotted in Fig. 1. These results indicate that a second normalization before tempering is very effective as refining treatment, at least for the temperature range here investigated. The second normalization treatment not only reduces drastically the mean grain diameter but also sharpens the grain size distribution (Fig. 2). This behaviour is enhanced by the increase in titanium content. Moreover, the grain refinement and the sharpening of distribution function increase as normalization temperatures decrease. Within the experimental error, the second heat treatment seems to dominate these effects. Some reference microstructures are shown in Fig. 3.

3.2. Phase transformation and tempering behaviour

Determination of A_{C1} and A_{C3} was performed using a heating rate of 2°C/min, while M_S and M_F were measured from dilatometric curves obtained under a constant cooling rate. About eight samples for each cast (two samples for A_{C1} and A_{C3} determinations) were tested to evaluate critical cooling rates that induce formation of perlite. Optical metallography and hardness measurements were performed to verify and quantify dilatometric results.

Principle results can be summarised as follows:

- 1% manganese addition (comparison between Casts 51 and 52) decreases A_{C1} of about 50°C and, with a lesser extent, A_{C3}, whereas M_S and M_F increase. The main effect is the shifting of the perlitic nose toward lower cooling rates.
- Carbon addition (Comparison between cast 54b and 53) decreases A_{C3} ($\approx$34°C) and A_{C1} ($\approx$10°C), M_S and M_F, and shifts the onset of the perlitic nose towards the right-hand side of the CCT diagram.
- Titanium addition (Comparison between casts 55 and 52) increases A_{C3} and, in a lesser extent, A_{C1} decreasing in the same time M_F ($\approx$20°C) and speeds up the onset of the perlitic nose, as expected from an α-forming element.
- Chromium (comparison between cast 53 and 55) addition does not induce significant changes on A_{C1} and A_{C3} while M_S and M_F slightly decrease.
- Boron addition (comparison between casts 56 and 51) increase A_{C3} ($\approx$15°C), M_S ($\approx$20°C) and M_F ($\approx$10°C); it shifts the onset of the perlitic nose toward lower cooling rates.

Tempering behaviour of these steels (Casts 1955 and 1953) is summarised as follows: recovery behaviour starts at about 550° (soaking time 1 h), reaching a minimum hardness value of 200 kg/mm^2 at 800°C. Transformation temperatures and estimated critical

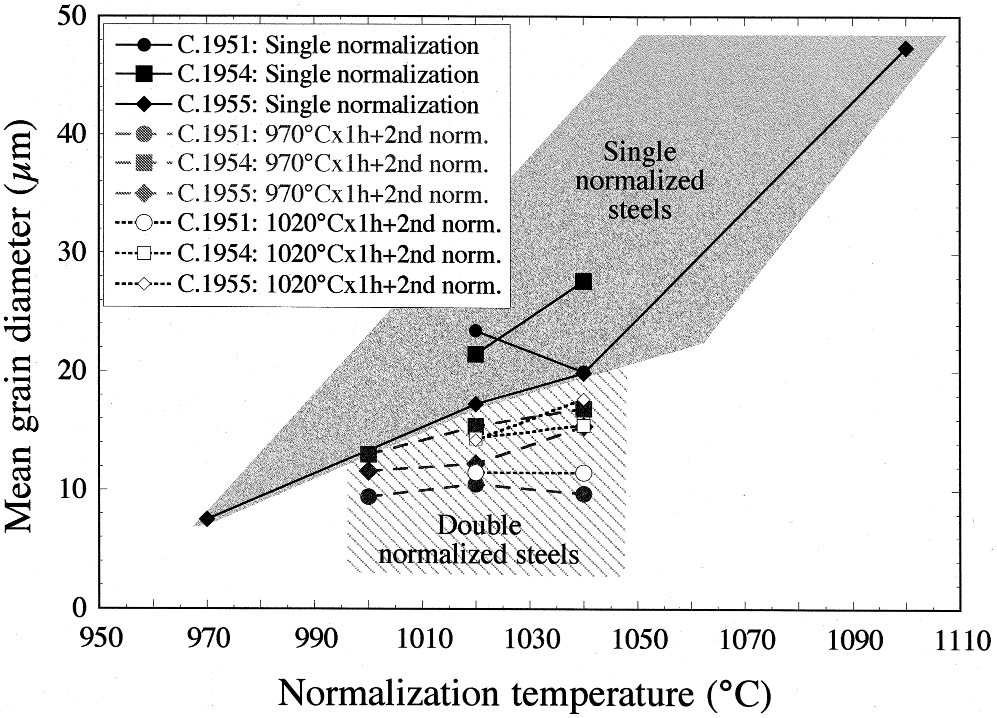

Fig. 1. Grain size as a function of normalization temperatures (Casts 1951, 1954 and 1955). Here, the mean grain diameter is plotted versus the temperature of the ultimate normalization treatment for double normalized steels as well as for the single normalized ones. Grey and white markers represent double normalized steels previously normalized respectively at 970°C and 1020°C.

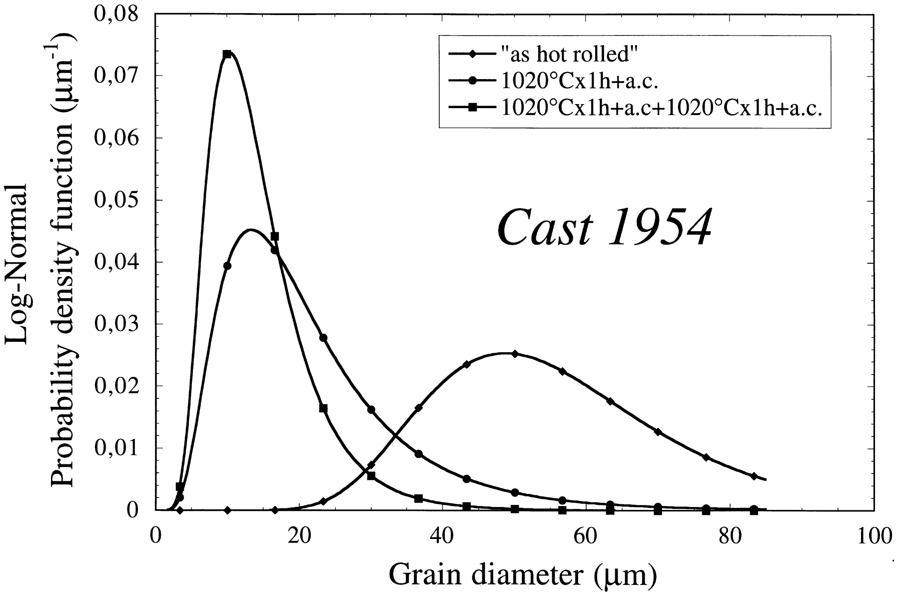

Fig. 2. Fitted Grain diameter distribution function of Cast 1954 for different normalization conditions.

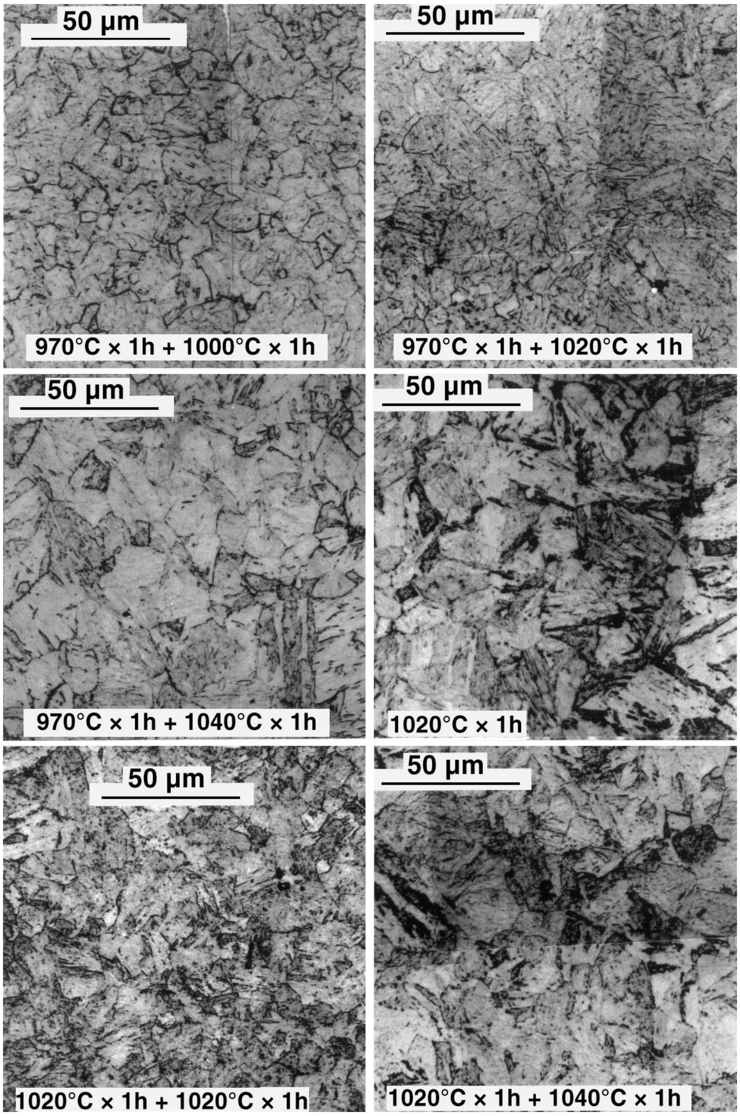

Fig. 3. Microstructures of Cast 1955 obtained by different normalisation treatments.

cooling rates are reported in Table 2, while CCT diagrams are shown in Fig. 4.

3.3. Impact behaviour

Mechanical properties of these steels in "standard state" are reported in a companion paper [12]. The "standard state" is defined as follows:

- 1st normalization: 1020°C × 1 h followed by air cooling;
- 2nd normalization: 1020°C × 1 h followed by air cooling;
- Tempering: 730°C × 1 h followed by air cooling.

A common tempering treatment was chosen for comparison purposes and to have a sufficient mechanical strength (i.e. ≈0.3 times the hardness).

Other heat treatments were performed on casts 1955 and 1953 in order to study their effects on fracture toughness, namely:

state bi (bii): Normalization at 1100°C × 1 h + a.c.(w.q.) + 730°C × 1 h + a.c. (w.q)
state ci (cii): Normalization at 970°C × 1 h + a.c.(w.q.) + 730°C × 1 h + a.c.(w.q.)
(a.c. = air cooling; w.q. = water quenching)

The impact test results obtained from micro-Charpy specimens are reported in Figs. 5 and 6. They show that normalization treatments influence greatly impact

Table 2
Critical temperatures of BATMAN II steels

Cast No	A_{C1}(°C)	A_{C3}(°C)	M_S(°C)	M_F(°C)	V_C(°C/min)
1951	794	921	450	220	$V_C < 0.7$
1952	847	929	430	210	$3 < V_C < 0.7$
1956	796	906	430	210	$V_C \approx 0.7$
1953	837	911	440	230	$V_C \approx 0.7$
1955	843	913	430	215	$V_C \approx 0.7$
1954b	846	945	450	250	$V_C \approx 6$

resistance while cooling rate seems to have only a minor effect (more accentuated in cast 1953). This behaviour is related to the grain size.

Fast cooling processes (e.g. water quenching) generate non-equilibrium segregation phenomena [13] which likely increase toughness. In our case, they seem to have

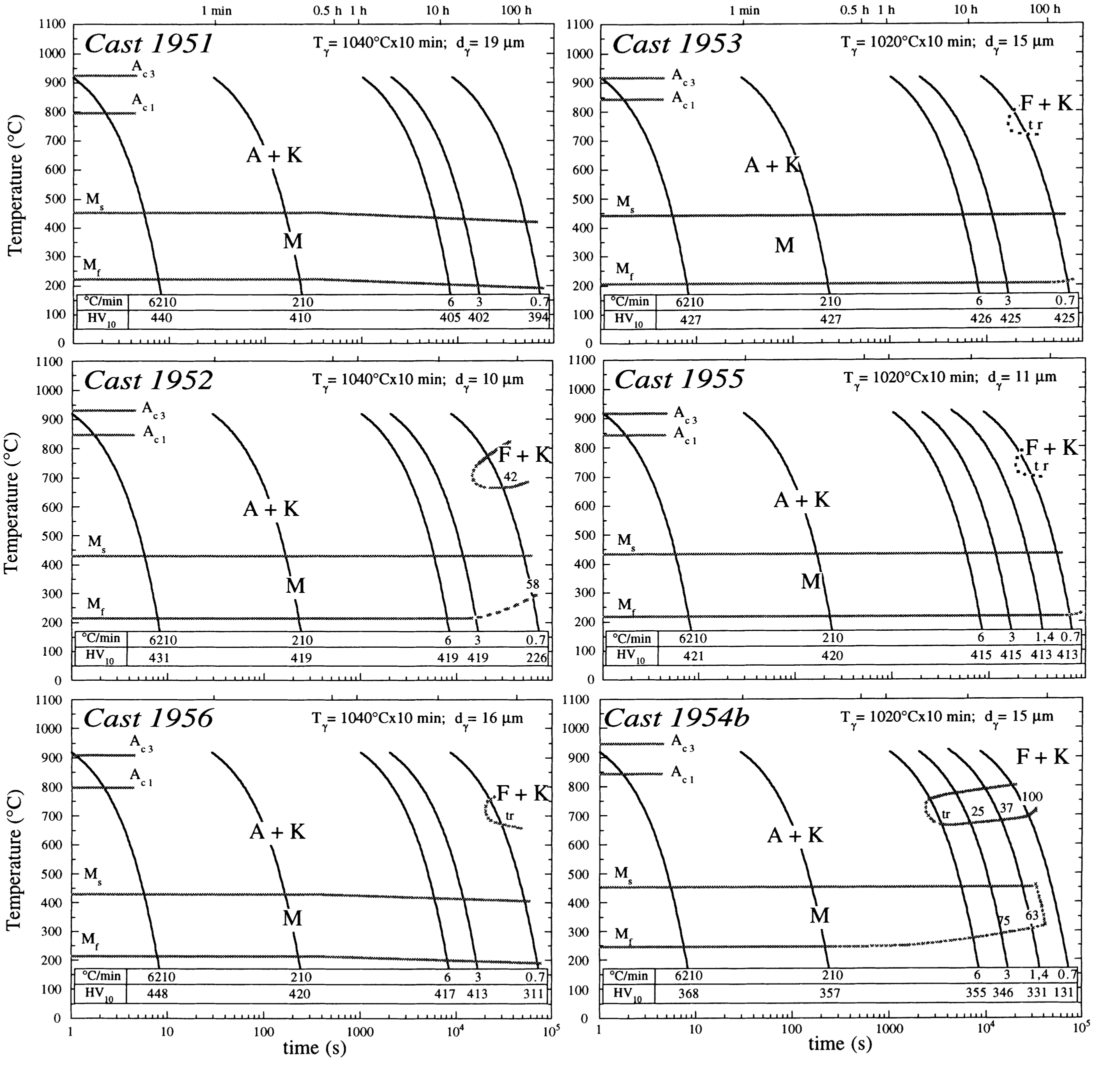

Fig. 4. Continuous Cooling Transformation diagrams of BATMAN II steels.

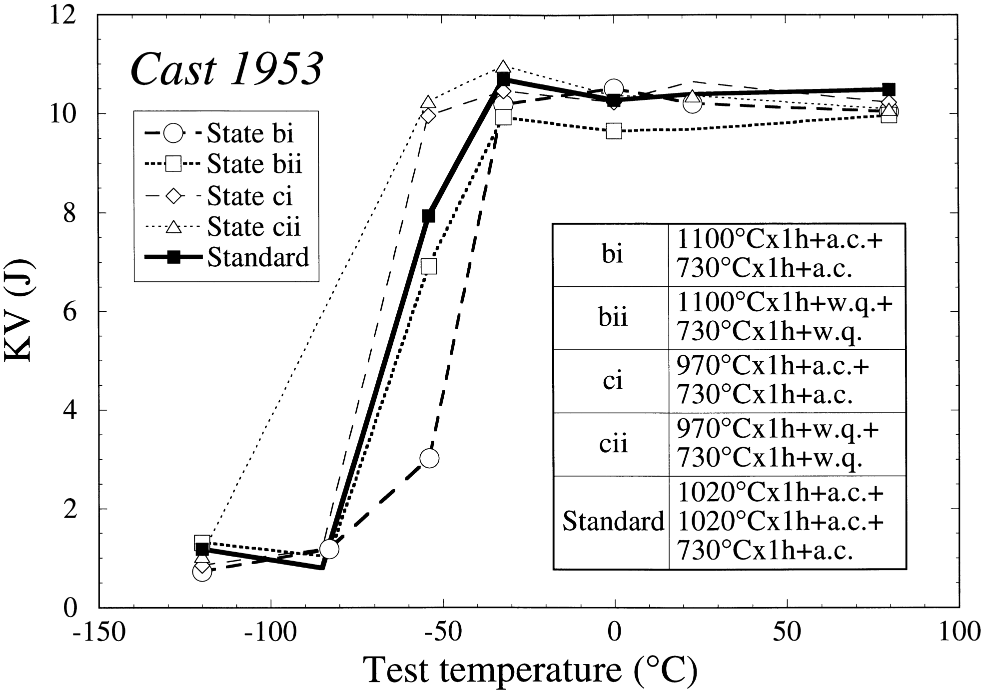

Fig. 5. Impact properties of Cast 1953 for different heat treatments.

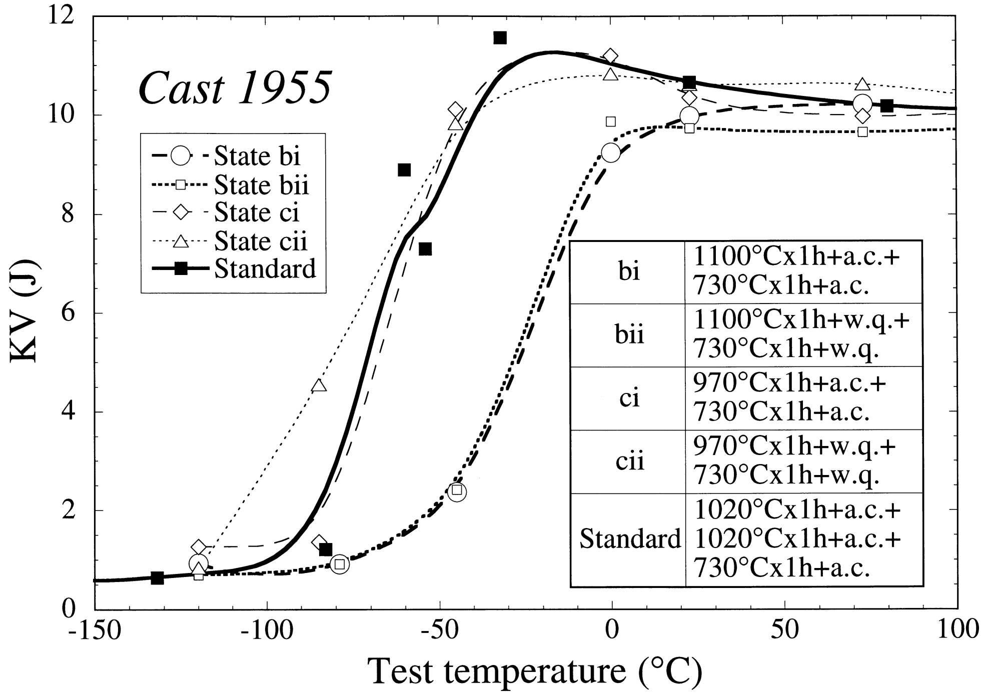

Fig. 6. Impact properties of Cast 1955 for different heat treatments.

a minor influence, at least for the compositions here investigated.

4. Discussion

Prior austenite grain size is one of the microstructural features controlling fracture toughness in a fully martensitic alloy and refining agents, as titanium or tantalum carbonitrides, must be used to reduce grain size in such an amount and to such a level so as to increase their fracture resistance. From this point of view, low normalization temperature (≈50°C greater than A_{C1}) are preferred [8].

Regarding titanium-doping, its use is limited by nitrogen levels so as to avoid large nitride precipitation. Compared to the compositions we studied, taking into account the mechanical results elsewhere reported [12], titanium content should be in the order of 0.02–0.03% (equivalent to a tantalum content of ≈0.12%) linked to a nitrogen level lower than 30 ppm.

Solution temperatures of titanium carbides and nitrides in austenite can be estimated from solubility laws [14]:

$$\log_{10}[\mathrm{wt\%Ti}]\,[\mathrm{wt\%C}] = 4.03 - \frac{8720}{T(\mathrm{K})}$$

$$\log_{10}[\mathrm{wt\%Ti}]\,[\mathrm{wt\%N}] = 3.82 - \frac{15020}{T(\mathrm{K})}$$

For a titanium level of $\mathrm{Ti} = 0.03\%$ and a nitrogen amount of $\mathrm{N} = 20$ ppm, the calculated solution temperature of TiN is about 1594°C. This implies that titanium nitride precipitation starts in the liquid phase, well above the solution temperature of TiC. The titanium content available for "low temperature" TiC precipitation would be about $\mathrm{Ti} \approx 0.023\%$.

The estimated solution temperature of these carbides, for a carbon content of $\mathrm{C} = 0.1\%$, is about 1035°C. So, these levels could be sufficient to guarantee a fine recrystallisation at single or double normalization temperature in the order of 950–970°C.

The consequent reduction of primary Ti (C,N) precipitation, and the drastic boron reduction [12], should bring a better impact behaviour in the transition region.

5. Conclusions

- Thermodynamic properties of Ti-bearing martensitic steels are similar to those of other reduced activation ferrous alloys. They exhibit high values of A_{C1} and their critical cooling rates enable air cooling of very thick products too.
- Prior austenite grain size control is one of the way to increase fracture toughness and to have a low ductile brittle transition temperature. Single or double normalization treatment slightly higher than A_{C3} greatly improves the impact resistance. Reduced titanium and nitrogen levels that we studied would be sufficient to obtain at the same time a very fine structure and further decreased DBTT.

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