MODELING OF MARTENSITIC HEAT-RESISTANT STEELS FOR APPLICATION AT 650°C WITH EQUILIBRIUM CALCULATION SUPPORT*

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Abstract

Precipitation of large Z-phase particles, Cr(V, Nb)N, replacing fine MX carbonitrides, Nb(C,N) or V(N,C), has recently been identified as a major cause for premature losses in long-term creep strength in high chromium martensitic steels for power plants applications. For developing a new heat-resistant steel with better creep performance for applications in modern power plants with service temperatures around 650 °C, martensitic steels with 9 wt.%Cr were studied to achieve a chemical composition without the presence of a reversion/formation of detrimental Z-phase from consumption of thermally stable carbonitrides. The alloy composition was design to control deleterious Z-phase precipitation based on extrapolation of conventional vanadium content. The modelling of the alloy content is relied on thermodynamic equilibrium calculations using MatCalc software and Schaeffler modified diagram to achieve a fully martensitic microstructure.

Keywords: Thermodynamical Modelling; Vanadium content; High chromium martensitic steel; heat resistant steel;.

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1 INTRODUCTION

Traditional coal-fired power plants have been emitting high levels of environmentally damaging gases, if compared to other electric power generation options. Adoption of Ultra Super Critical (USC) power plants with increased steam parameters significantly reduces gas emissions, because of its great efficiency. USC power plants require an improvement in creep performance of martensitic steels to allow the use of components operating at 650°C in the next generation of USC power plants. High chromium ferritic-martensitic steels have been studied and tested due to their good thermal properties and low cost, if compared to austenitic steels and Ni-based super alloys [1,2].

The long term creep strength of the 9–12%Cr heat-resistant steels is acquired due to the initial microstructure of the 9–12% Cr steels, composed of tempered martensite without δ-ferrite, formed during the final normalizing and tempering heat treatment. This microstructure is composed of tempered martensitic sub grains, with high dislocations density and distributed $M_{23}C_6$ carbides and MX carbonitrides, which block the movement of sub grain boundaries and dislocations. The creep-resistance relies primarily on precipitation strengthening by MX carbonitrides and secondary effects of other hardening mechanisms, such as solid solution and $M_{23}C_6$ precipitation [3,4].

$M_{23}C_6$ precipitates have a considerable coarsening rate and for this reason they are not able to sustain the creep strength for long periods. On other hand, the carbonitrides MX are small and finely distributed in the microstructure and have a very low coarsening rate at the intended service temperature, providing a good maintenance of creep strength for long periods. However, (V,Nb)N nitrides are not thermodynamically stable and will be replaced with aging by a similar nitride known as the Z-phase, Cr(V,Nb)N, which causes microstructure instabilities. The Z-phase precipitation will not contribute to the strengthening and the consumption of the (V,Nb)N nitrides during their growth, causing a significant breakdown in creep strength [4,5].

To achieve sufficient creep strength, during the entire service life, it is necessary to provide enough solid solution and precipitate strengthening and also reduce the microstructure coarsening. In the last years, emphasis has been put on modelling of microstructure stability mainly with thermodynamic and kinetic models, with the goal to develop predictive tools for life assessment or alloy development. In this context, thermodynamic modelling software, with a validated database of Gibbs free energies, have become a powerful tool which provides useful information for alloy design and development[6,7].

In this research, an alternative alloy composition based on the chemical composition of C12A steel (ASTM A217), is suggested to avoid the detrimental Z-phase precipitation. For that, the vanadium content in this steel alloy was intentionally increased and thermodynamically designed to evaluate phase constituents in equilibrium conditions and an estimative microstructure is predicted using the modified Schaeffer diagram.

2 DEVELOPMENT

2.1 Methodology

Thermodynamic Equilibrium calculations have been carried out with the thermo-kinetic software MatCalc 5.62 including the iron database to investigate effects of the extrapolation of vanadium content on the Z-phase dissolution temperature and phase stability of deleterious phase.

Complex multi-component systems were specified to simulate the new alloy composition (Table 1) based on the chemical composition of C12A cast steel. The vanadium content rage is delimited between 0.2 – 0.8 wt. %.

Table 1. Composition of multi-component system using in MatCalc and FactSage simulations

Steel	C	Mn	Si	Cr	Mo	W	V	Nb	N	Al
C12A	0.08 0.12	0.3 0.6	0.2 0.5	8.0 9.5	0.85 1.05	-	0.18 0.25	0.06 0.10	0.03 0.07	- 0.02
Simulated	0.1	0.5	0.3	9.0	-	2.0	0.2 0.8	-	0.04	0.02

To obtain a complete austenitic microstructure during heat-treatment process and the final martensitic microstructure after tempering, it is necessary to balance the content of austenite and ferrite forming elements. In order to produce a martensitic matrix, the new alloy composition was recalculated to be in accordance with the empirical relation of $Cr_{eq(A)}<6.5$ [4], avoiding δ-ferrite and regarding the martensitic field in the modified Schaeffler Diagram [7] as presented is figure 1.

$$Cr_{eq(A)}=Cr+6Si+4Mo+1.5W+11V+5Nb+12Al-40C-2Mn-4Ni-2Co-30N-Cu \qquad (1)$$

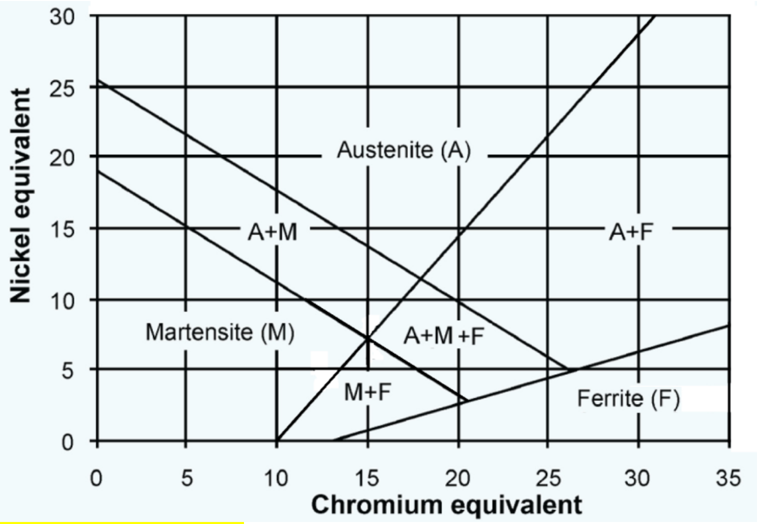

Figure 1. Modified Schaeffler Diagram. $Cr_{eq(B)}$= Cr+2Si+1.5Mo+5V+5.5Al+1.75Nb+1.5Ti+0.75W and $Ni_{eq(B)}$=Ni+Co+0.5Mn+30C+0.3Cu+25N.

2.2 Results and Discussions

The simulated data suggests the new composition of the steel with an extrapolation of the usual vanadium content is more thermodynamically favorable in comparison with C12A steel, since it maintains the nitrides stable. Also, the Z-phase content is inferior in the high vanadium steel in comparison with C12A. Above 660°C, alloys with vanadium content superior to 0.5 wt. % are not expect to show the detrimental Z phase thermodynamically, as showed at Figure 2, and for this reason does not reduce the long-term creep-resistance. However, the vanadium is a powerful δ-ferrite former, then it is necessary to adequate the chemical composition with austenite stabilizers, in order to obtain a fully martensitic structure, after the heat treatment process [8].

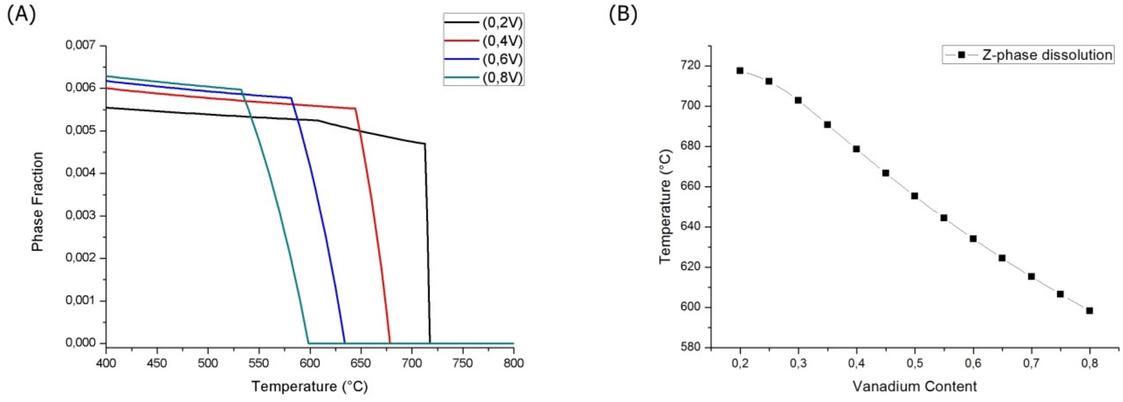

Figure 2. (A) Phase fraction of detrimental Z-phase for different contents of vanadium. (B) Temperature dissolution of Z-phase for different contents of vanadium

Composition with vanadium superior to 0.6 wt. %, in theory, do not present Z-phase at temperatures above 650ºC, and for this content of vanadium the $Cr_{eq(A)}$ = 14.75, which is approximately 2.3 times bigger than the limit value. Combination of reduction of the ferrite stabilizers elements, such as Si and W, and additions of austenite stabilizers, such as C, Mn, Ni, Co and Cu, are an alternative way to adequate the $Cr_{eq(A)}$ value.

The new alloy, with composition showed in Table 2, based on simulated steel with 0.65 wt. % vanadium content, presented $Cr_{eq(A)}$ = 6.5, for modified Schaeffler diagram $Cr_{eq(B)}$=14 and $Ni_{eq(B)}$=7.4. This composition respects the empirical relation to avoid δ-ferrite and is delimitated in a martensitic region in modified Schaeffler diagram (Figure 3).

Table 2. Final composition of new alloy in accordance with the contour conditions.

Steel	C	Mn	Si	Cr	Co	W	V	Ni	N	Cu
LFN	0.12	0.8	0.2	9.0	2.0	1.8	0.65	0.5	0.04	0.35

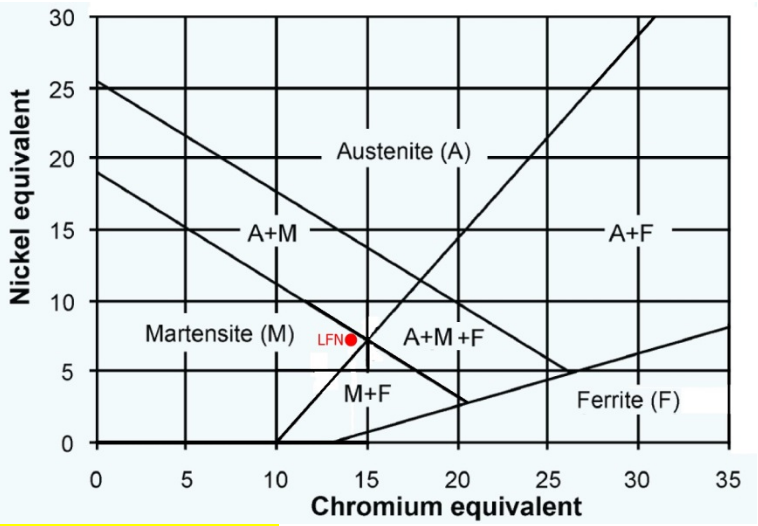

Figure 3. Modified Schaeffler Diagram for new composition alloy ($Cr_{eq(B)}$ = 14 and $Ni_{eq(B)}$ = 7.4).

3 CONCLUSION

The approach for controlling the deleterious Z-phase precipitation with extrapolation of vanadium content was thermodynamically plausible based on results of equilibrium calculation in MatCalc software.
Based on these results it is possible to avoid the reversion of stable carbonitrides at high temperatures and to increase the temperature operation, consequently improving the power plants efficiency and avoiding a significant drop in creep strength.

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