

POWER AUSTENITE- A NOVEL σ -PHASE HARDENED HIGH TEMPERATURE ALLOY FOR 700 °C (1292 °F) FIRED BOILERS

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ABSTRACT

The article gives a brief overview of the newly developed austenitic material “Power Austenite”. The microstructure of the Power Austenite is characterized by grain boundary strengthening with boron stabilized $M_{23}(C,B)_6$ and secondary Nb(C,N) in combination with sigma phase and Nb(C,N) as the major grain strengthening precipitates. The material shows a significant creep strength at 700 °C (1292 °F) and 650 °C (1202 °F) as well as fireside corrosion resistance which makes it a possible candidate for 700 °C (1292 °F) power plants.

INTRODUCTION

The principal problem of designing a microstructural stable high temperature material for use in 700 °C (1292 °F) coal fired boilers mainly focuses on finding a synergistic alloying solution which guarantees a significant oxidation and fireside corrosion stability as well as a 10^5 h creep strength of minimum 100 MPa (14,5 ksi). By increasing the chromium content to > 25 wt.% the oxidation and corrosion problem can be reasonably solved. However, the higher chromium contents favours microstructural stability problems after long term service depending on the alloying concept. A strength loss due to the formation of δ -ferrite, z-phase and sigma phase may occur. The formation of these phases is usually connected with weakening of grain boundary adhesion, consumption of a necessary alloying element i.e. Cr and Nb, as well as precipitate coarsening and subsequent embrittlement.

The alloying concept of the Power Austenite is based on Fe-(25-33)Cr-(22-38)Ni with balanced additions of Si, Mo, Nb, B, N and C resulting in a microstructure of sigma-phase, boron stabilized $M_{23}(C,B)_6$ and Nb(C,N) at the service temperatures. Upon heat treatment from solution annealed condition, the material firstly precipitates $M_{23}(C,B)_6$ and Nb(C,N) at the grain boundaries, followed by sigma phase and Nb(C,N) in the interior grain. As the grain boundaries are completely covered with carbides the formation of a δ -ferrite film, which may transfer to σ -phase during long term service, is avoided. Significant coarsening of the sigma phase was not observed after approx. 13.000 h, which may be attributed to a stabilisation of the σ/γ interface by segregated boron. The concept results in an excellent oxidation and hot corrosion resistance as well as significant creep strength evaluated after more than 24.000 h of testing.

DISCUSSION

The aim of the development of Power Austenite was to achieve an excellent Hot Corrosion behavior in the presence of aggressive flue gases as well as in steam, together with a satisfactory creep resistance of 100 MPa (14,5 ksi) at 700 °C (1292 °F). The alloying concept was based on

AC 66 [1], which is known to give a high oxidation and corrosion resistance due to its 27 wt.% of chromium. The major task was, therefore, to increase the creep strength of AC 66.

Sigma phase is known as a detrimental phase in alloys, leading to embrittlement and early fracture. In most reported cases, sigma phase was observed after long exposure times in austenitic alloys, very often at grain boundaries. The phase appears in the Fe-Cr system and is stable up to approx. 800 °C (1472 °F) in the pure binary system. Sigma stabilising elements are besides chromium also Mo and Silicon as well as some nickel.

It is important to note that sigma phase is insoluble for carbon, nitrogen and boron. These elements strongly retard the formation kinetics with respect to carbides and nitrides and it is very difficult to nucleate sigma phase directly within the austenite grain as the lattices are incoherent and the diffusion of carbon and nitrogen in austenite is quite slow [2]. It takes several thousands of hours to nucleate sigma phase in austenite. In most cases, sigma phase forms by precipitation from δ -ferrite islands with a reasonable fast kinetics. This transformation is in particular harmful for the material as δ -ferrite films are usually formed also at grain boundaries. In addition, grain boundary sigma phase is formed much easier also without prior δ -ferrite formation due to the energetic preferable nucleation site. It has been shown in literature that the nucleation of sigma phase within austenite grains enhances the creep strength [3]. The authors have shown that at 700 °C (1292 °F) an increasing volume fraction of sigma phase within the austenite grain enhances the creep strength. With time, however, the formation of grain boundary sigma occurs and the strength strongly decreases.

The aim of the Power Austenite development was to achieve a sigma phase hardened structure by stabilisation of the grain boundaries by precipitation of B-stabilised $M_{23}(C,B)_6$ and secondary Nb(C,N) and grain strengthening by early precipitation of sigma phase and Nb(C,N). The microstructural concept was achieved by the range of chemical composition shown in table 1 [4]. Prior to melting, thermodynamic calculations were performed with ThermoCalc in order to estimate the stabilities of the different phases. The calculation is shown in Figure 1. It shows that after solidification of the austenite, the precipitation starts with Nb(C,N), followed by $M_{23}C_6$ and sigma phase. The stability range of sigma is starting from approx. 580 °C (1076°F) to 1050 °C (1922 °F), with a middle alloy composition shown in table 2.

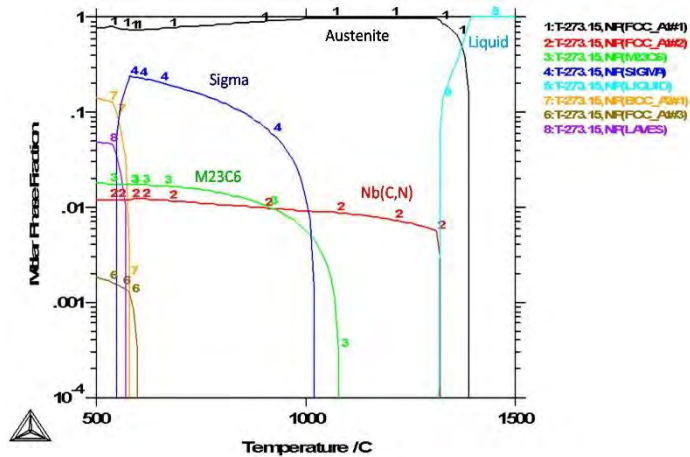


Figure 1: Thermocalc calculation of phases, stable in Power austenite, with composition limits as shown in table 1

Table 1: Composition of Power Austenite(wt.%) –limits of patent application [4].

	C	Si	Cr	Ni	Mo	Nb	N	B
Min	0.02	0.1	25	22	1	0.4	0.01	10 ppm
Max	0.15	2	33	38	6	1.5	0.2	100 ppm

Figure 2 shows the microstructure in an SEM image which was achieved on a heat of Power austenite after annealing at 1150 °C (1922 °F) followed by 700 °C (1292 °F) tempering. Sigma phase, $M_{23}C_6$ and some Nb(C,N) are precipitated in the entire grain. The sigma phase is grown as plates, which appear needle like in the SEM cross sectional view. The crystallographic relationship between austenite and sigma phase has been reported to be (111) γ parallel (001) σ , which can be seen very clearly in figure 3. Adjacent to the plate like σ , also some globular precipitates are formed.

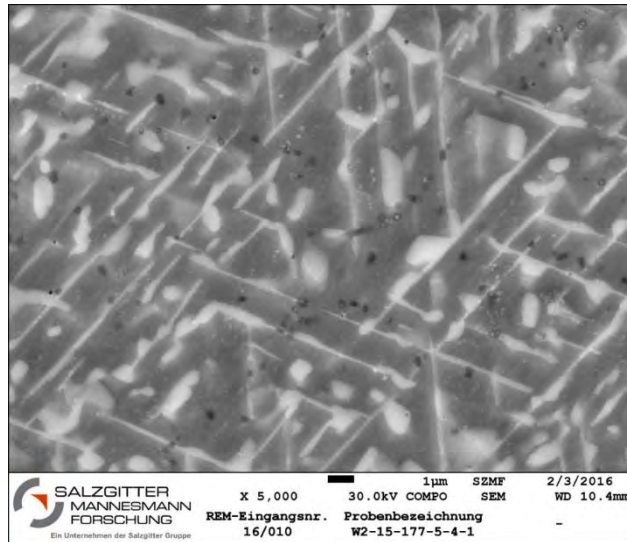


Figure 2: Strengthening concept of Power Austenite – SEM picture showing sigma phase and Nb(C,N) precipitated in the grain as well as $M_{23}C_6$. Note the Widmannstätten type of precipitation orientation

Figure 3 show a creep rupture diagram at 650 °C (1202°F). The broken points at 300 (43,5 ksi) and 265 MPa (38,4 ksi) fit very well to the Sanicro 25 middle values, whereas two other samples at 230 (33,4 ksi) and 195 MPa (28,3 ksi) are still running and approaching the mid values. Figure 4 shows the creep rupture diagram for 700 °C (1292 °F) at stress levels of 180 (26,1 ksi), 145 (21 ksi) and 120 MPa (17,4 ksi) with rupture points in the lower scatter band of Sanicro 25. One sample at 120 MPa (17,4 ksi) is still running. In conclusion, the creep behavior is strongly depending on the stress assisted precipitation of sigma phase in the interior grain.

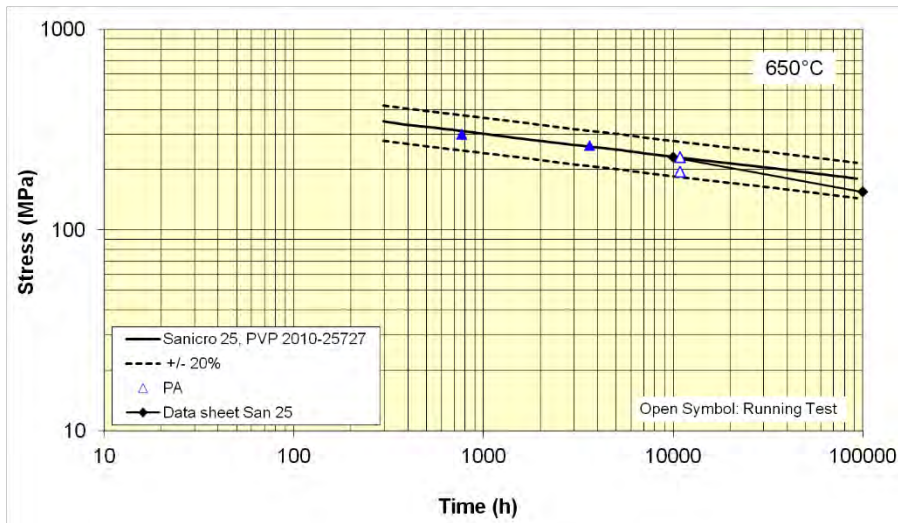


Figure 3: Results of creep tests at 650 °C (1202 °F) with two samples running

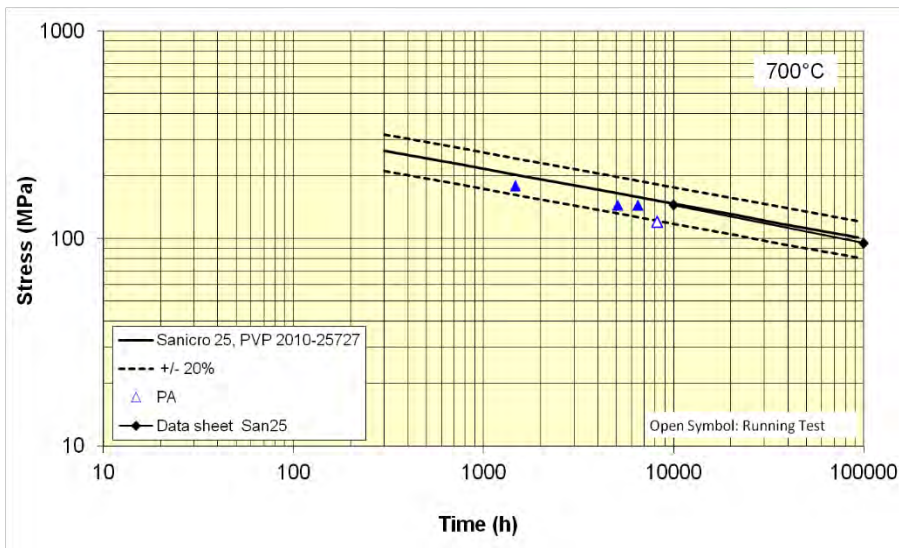


Figure 4: Results of creep tests at 700 °C (1292 °F) with one sample running. Creep values are approaching the Sanicro 25 mid values.

Fireside corrosion issues, especially by sulfur rich deposits have to be considered and are expected to occur much more frequently in the future by increasing temperature. Fireside corrosion processes are complex reaction cycles, consisting of reactions of flue gas components (i.e. SO_2/SO_3 , O_2 , ...) with the material, of reactions of alkali-salts (sulphates, chlorides) within the deposits with the material and reactions of components of the flue gas with components of the deposit. In energy conversion systems, liquid sulfates are usually formed as eutectic mixtures in ashes on superheater tubes. The main constituents of such systems are CaSO_4 , Na_2SO_4 and K_2SO_4 , depending on the chemistry of the coal. Eutectic mixtures usually have lower melting point than the pure substances. This becomes detrimental, if metal components starts to dissolve

in the solid mixture, thereby decreasing the liquidus temperature. This is especially the case if NiSO_4 is formed by reaction of the nickel in the alloy with SO_3 in the combustion gas. The risk of fireside corrosion failures strongly depends on the composition of the fuel i.e. waste, biomass or coal and its conversion to form corrosive species like for example HCl , SO_2 and H_2S , as well as alkali salts (halides and sulfates) within ash deposits.

For the development of a fireside corrosion resistant material the temperature dependence of the corrosion rate is an important issue. The corrosion loss generally shows a so called ‘bell shaped’ behavior i.e. increasing with temperature up to $700\text{ }^\circ\text{C}$ ($1292\text{ }^\circ\text{F}$) and then decreasing again. The highest corrosion loss is generally observed at $700\text{ }^\circ\text{C}$ ($1292\text{ }^\circ\text{F}$) and decreases with the chromium content. Chromia scales formed on the material are generally stable under fireside corrosion conditions, however, they need to be dense and protective. The most important element to achieve a protective chromia scale is chromium, which amount should not be lower than 25 wt.%. The fireside corrosion behaviour of several austenitic steels and nickel alloys beneath sulphate deposits at 650 ° is reported in [5] concluding that a chromium content higher than 25 wt.% is absolutely necessary to reduce fireside corrosion.

The fireside corrosion behavior of the Power austenite was tested in 3000 h tests in simulated coal combustion gas containing N_2 -4% O_2 -15% CO_2 -0.25% SO_2 with deposits of Na_2SO_4 - K_2SO_4 - CaSO_4 at $700\text{ }^\circ\text{C}$ ($1292\text{ }^\circ\text{F}$), conditions which are generally agreed to be proper for lab testing. A typical scale on Power Austenite after the experiment is shown in a metallographic cross section and an SEM micrograph in figure 5. The scale thickness is about $10\text{ }\mu\text{m}$, showing also some internal sulfidation zone underneath. In the SEM micrograph, the microstructure of the scale is shown in more detail. The more dense part close to the metal surface is chromia, giving the necessary stability of the alloy. The upper part of the scale is composed of Fe_2O_3 and some Cr_2O_3 , showing that the chromia scale needs some time to develop during which sulfur ingress is possible into the alloy.

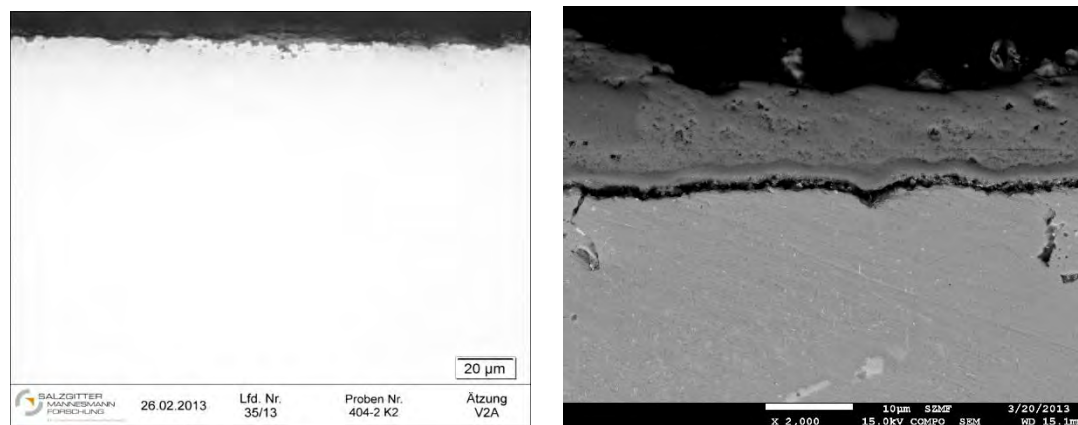


Figure 5: Metallographic cross section after fireside corrosion testing at $700\text{ }^\circ\text{C}$ ($1292\text{ }^\circ\text{F}$) for 3000 h (left: light optical microscopy, right: SEM).

First production trials have show that the material can be produced with a common production route for seamless tubes at Salzgitter Mannesmann Stainless workshops.

CONCLUSIONS

The new austenitic material Power Austenite, a Sigma phase hardened concept, was developed by Salzgitter Mannesmann Stainless Tubes and Salzgitter Mannesmann Forschung GmbH. The microstructure is characterised by grain boundary strengthening with boron stabilized $M_{23}(C,B)_6$ in combination with sigma phase and Nb(C,N) as the major strengthening mechanism. The creep behavior is strongly depending on the stress assisted precipitation of sigma phase in the interior grain. This gives some options to optimize the creep properties by adequate heat treatments after solution annealing. Good creep properties are achieved at 650 (1202 °F) and 700 °C (1292 °F), almost comparable to Sanicro 25. The material shows a significant fireside corrosion resistance which makes it an ideal candidate for 700 °C (1292 °F) power plants.

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