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Material advancement used for 700°C A-USC-PP in China

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ABSTRACT

This paper briefly introduces the state-of-the-art of the research and development of candidate heat resistant materials used for the manufacturing of 700°C advanced ultra-super-critical (A-USC) fossil fuel power plants (PP) in china, especially, focus on the impressive progress in the past three years. The detailed advancements (technical exploration and industrial investigation) of candidate materials spectra for the boiler system of A-USC PP will be presented in the current paper, including novel ferritic heat resistant steels, advanced austenitic heat resistant steels, Fe-Ni-based alloys and Ni-based alloys, which serve and cover the steam temperature scope from 600°C to 720°C. Some newly available data associated with above materials will be released.

INTRODUCTION

In recent years, the construction of advanced ultra-supercritical (A-USC) fossil-fired power generation plant with higher efficiency has been accelerated by the demand of reducing CO2 emission for the protection of global environment. The story is especially true in China in the past years. Since the first 600°C USC power plant was successfully launched in the November of 2006, more than 80GW electric capacity of 600°C USC units has been commercially installed in china mainland by the end of 2011 and more 600°C USC units will be constructed in the near future. The steam parameter evolution of Chinese USC power plants was schematically plotted in Figure 1.

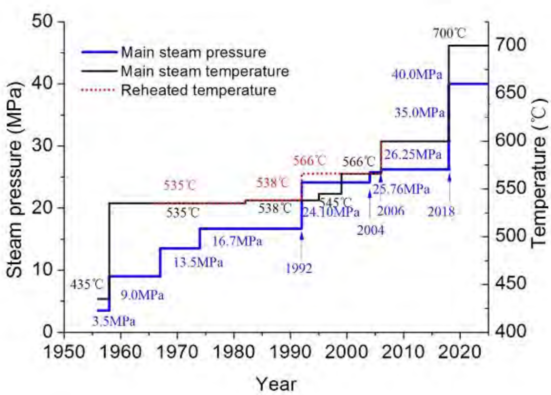

Figure 1 Steam parameter evolution of Chinese USC power plants

On July 23, 2010, Chinese government officially announced a national program to build a demo 700°C A-USC power plant in the near future, probably starting from the year of 2018, depending the availability and maturity of heat resistant steels and alloys. To fulfill such a goal, a national consortium has been directly organized by the National Energy Administration (NEA) of China, including seventeen research facilities, manufacturers and power plant operators, which all are the leading player in their own sectors. Well known, the critical challenge of 700°C A-USC technology lies in the R&D of high-temperature materials, not only for boiler system but also for turbine system. Due to the space limitation, the current paper will mainly address on the recent boiler materials advancement in china, which may be hopefully used for Chinese 700°C A-USC demo plant.

BOILER MATERIALS SPECTRA FOR 700℃ A-USC PP

Basically, those mature materials successfully used in 600°C USC power plant will still be applied in 700°C A-USC power plant, in where the working temperature is below 600°C. When the steam temperature increases from 600°C to 700°C, different novel materials are necessarily required for various temperature scopes. According to published literature and our knowledge, the materials R&D sub-committee of Chinese consortium for 700°C A-USC power plant has discussed, evaluated and summarized the candidate materials spectra used for 700°C boiler of A-USC power plant in China, as schematically shown in Figure 2.

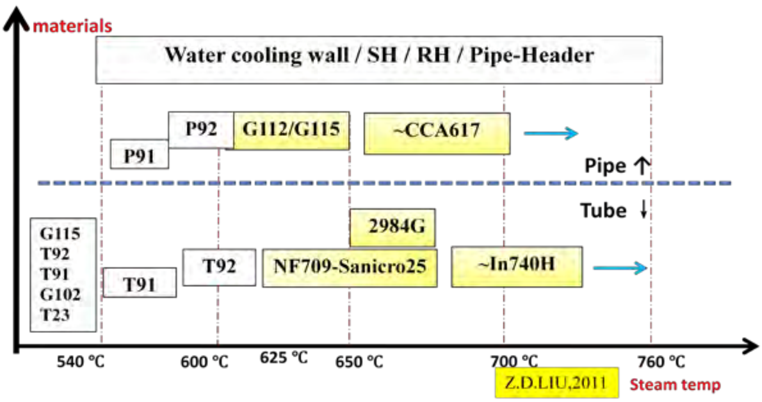

Figure 2 Candidate materials spectra used for 700°C boiler of A-USC PP in china

For water cooling wall tubing, T23 and T91 are considered to be base-steel, on which some modification for the improvement of on-site welding performance during plant manufacturing and following maintain has to be carried out. G102 may be the alternative choice for the replacement of T23 and T91, upon certain modification and improvement which are under investigation at CISRI and BaoSteel. Most recently, T92 and G115 were selected as one of candidate materials by Chinese boiler designers to make tube at superior temperature scope of the water cooling wall tubing system, due to its outstanding creep strength, which make it possible that all tubes from lower temperature to higher temperature of the system are of similar outside diameter and wall thickness. Alloy 617 is not necessary to be a candidate material for the water cooling wall system, unless the hidden weakness of T92 and G115 for such an application occurs during manufacturing and in service in the future. Welding is a key concern for the making of water cooling wall tubing.

For the tube-making of super-heat (SH) and reheat (RH), the candidate materials spectra are T91, T92, NF709R, Sanicro25 (GH2984G), and Inconel740H equivalent (or an Inconel740HM alloy), with the increase of steam temperature from 580°C to 700°C. GH2984 was developed by Institute for Metals Research of Chinese Academy of Sciences some years ago, and 2984G will be an upgraded iron-nickel based super-alloy on the basis of GH2984, which is supposed to be used to make tube or pipe up to 680-700°C. Thus, GH2984G and Sanicro25 are competitive materials.

For the pipe/header-making, the candidate materials spectra are P91, P92, G115/G112, (GH2984G), and CCA617 equivalent alloy, with the increase of steam temperature from 580°C to 700°C. G115 was originally developed and patented by the Central Iron and Steel Research Institute (CISRI) of China in the past years, which is proposed to be used to make pipe or header up to 650°C, although it was selected to be a candidate for water cooling wall tube.

Table 1 The time-table of R&D of materials used for 700℃ A-USC PP in china

Phase	Task	2010	11	12	13	14	15	16	17	18	19
1A	Candidate material selection	→	→								
1B	Materials laboratory investigation	→	→	→	→						
2A	Materials pilot plant trial		→	→	→						
2B	Product industrial trial					→					
2C	Materials/product application study					→	→	→			
2D	Evaluation of product						→	→	→		
3	Product supply to the market								→	→	→

The milestone and time-table of research and development of candidate materials used for 700°C A-USC power plant in china were included in Table 2. Hopefully, the final products of aforementioned candidate materials will be commercially available within five more years from now on, subject to the determination and certainty of designing requirements. The typical chemistry of candidate materials used for 700°C A-USC power plant was listed in Table 2 and the typical mechanical property of candidate materials used for 700°C A-USC power plant was listed in Table 3. The desirable creep rupture strength of candidate materials is around 100MPa under its service temperature for 100,000 hours.

Table 2 Typical chemistry of candidate materials used for 700℃ A-USC PP

Alloy	C	Cr	Mo	W	Co	Nb	V	Al	Ti	B	Cu	Ni	Others
G102	0.12	2	0.6	0.4			0.35		0.13	0.005			Fe
G115	0.08	9		3.0	3.0	0.05	0.20			0.015	1.0		Others
NF709R	0.08	21	1.5			0.25						25	Others
Sanicro25	0.08	22.5		3.6	1.5	0.50					3.0	25	Others
GH2984	0.06	19	2.0			1.00		0.4	1.0			43	33Fe
CCA617	0.06	22	9.0		12			1.0	0.4	0.003		55	Others
In740H	0.03	25	0.5		20	1.50		1.35	1.35			48	Others

Table 3 Typical mechanical property of candidate materials used for 700℃ A-USC PP

Alloy	Room temperature				Elevated temperature				
	$Rp_{0.2}$	R_m	A	Z	$Rp_{0.2}$	R_m	A	Z	T, ℃
G102	345	630	>18	>40					
G115	623	763	23	72	325	375	30	83	650
NF709R	330	700	44.5	74.5	171	454	40	65	700
Sanicro25	366	760	48	68	209	513	44	57	700
GH2984*	686	1107	26.6	46.6	539	745	34.4	52.3	700
CCA617	330	750	66	70	188	555	80	56	700
In740H	705	1110	36	42	630	850	23	28	750

* Data based on published literature

G115 FERRITIC HEAT RESISTANT STEEL

In recent years, the Central Iron and Steel Research Institute (CISRI) of China successfully developed G115™ and G112™ ferritic heat resistant steels, which have been industrially made and qualified, showing the imposing potential to manufacture pipe and steam container in the temperature scope from 620 to 650ºC.[1] Among them, G115 is of higher creep rupture strength at 650ºC and G112 is of better steam oxide resistance at 620-650ºC.

G115 tube and pipes have been industrially made at BaoSteel of China since 2008 by various processing routines. The specimens investigated in the current paper were from hot-extruded G115 pipe, with the dimension of $\Phi 254 \times 25 \times 3500$ mm.

Table 4 Mechanical properties of G115 steel pipe

Temp	Rm, MPa	Rp0.2, MPa	A,%	Z,%	Akv2,J		HB
R.T.	763	623	23	72.3	115	112	210
650℃	380	338	26.5	85			

The mechanical properties at room temperature and 650℃ of the G115 pipe were listed in Table 4. Obviously, the steel is of reasonable impact energy, implying that the steel is of potential to make heavy thickness pipes. The impact energy is higher than 112J at room temperature. The photo-graphics of G115 pipe after aging at 650℃ up to 8000 hours were shown in Figure 3, in which, it is clearly that the martensitic lath width keeps stable, thinner than 425nm. However, when the aging temperature is 700℃, the martensitic lath width grows much faster, as indicated in Figure 4. The 650℃ should be the upper limitation of the steel.

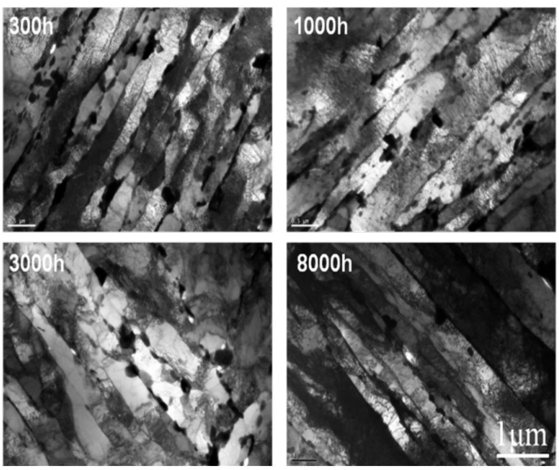

Figure 3 TEM photos of G115 steel after aging at 650℃

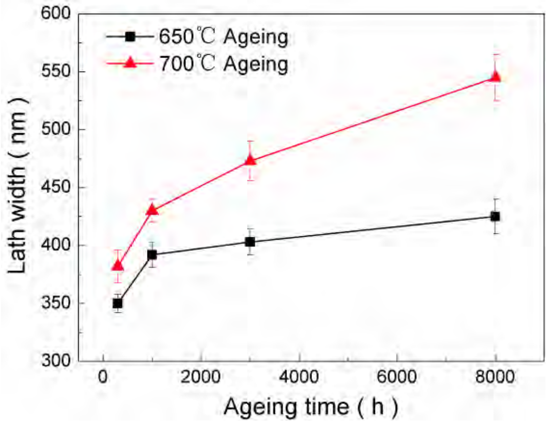

Figure 4 Evolution of G115 martensitic lath width during aging

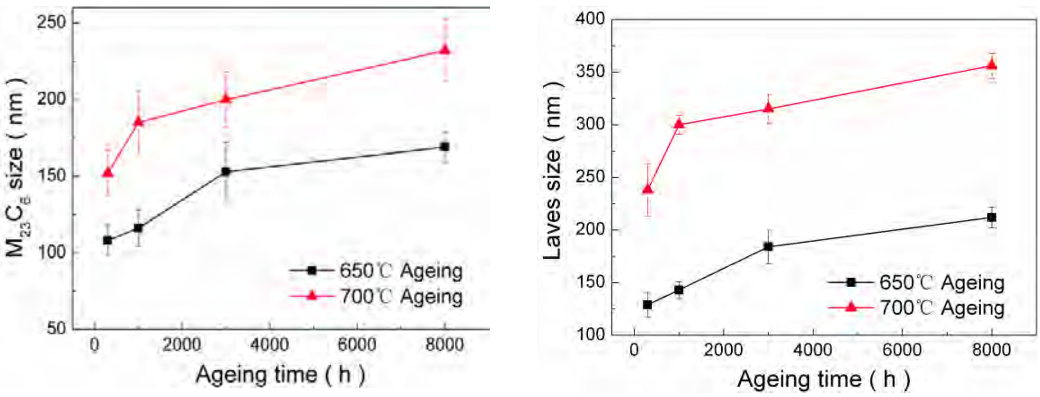

Figure 5 Evolution of $M_{23}C_6$ and Laves phases of G115 steel during aging

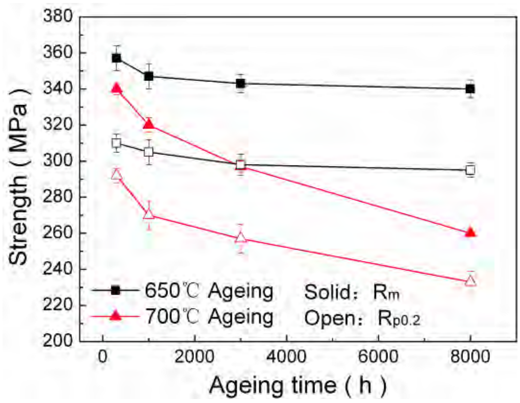

Figure 6 High temperature strength of G115 steel during aging

The major precipitation of G115 steel during 650-700℃ aging includes MX, Cu-rich precipitate, $M_{23}C_6$ and Laves phase. Among them, MX and Cu-rich particles are very fine, basically in nanometer-scale, and very stable during aging. From the viewpoint of precipitation hardening, the deterioration of creep strength of the steel results from the coarsening and aggregation of $M_{23}C_6$ and Laves phase particles. The evolution of $M_{23}C_6$ and Laves phase during aging was shown in Figure 5. The velocity of coarsening of $M_{23}C_6$ and Laves phase under 650℃

aging are much lower than that of 700℃ aging The size of $M_{23}C_6$ is less than 170 nm and Laves phase is about 200 nm under 650℃ aging up to 8000 hours. Correspondingly, the yield strength and tensile strength of G115 at 650℃ and 700℃ after 650℃ aging were drawn in Figure 6. The mechanical properties of G115 under 650℃ aging are very stable.

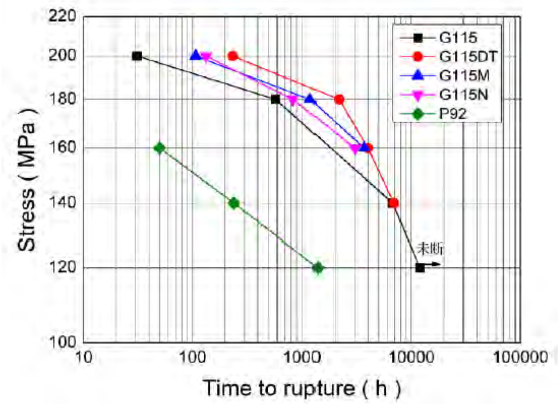

Figure 7 Creep rupture strength of G115 steel pipe

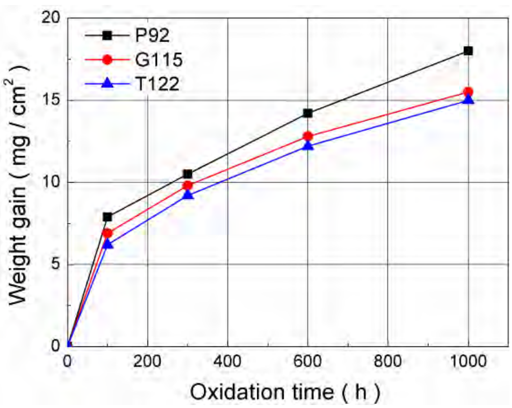

Figure 8 Oxide resistance of G115 steel pipe

The curves of current available creep test results of the G115 steel pipe and other G115 trial samples under 650℃ were plotted in Figure 7. Longer time creep tests of G115 are undergoing at CISRI. In fact, the G115 is of excellent creep strength among all commercially available ferritic heat resistant steels worldwide so far, much higher than that of P92 steel. Meanwhile, G115 has a reasonable oxidation resistance as shown in Figure 8, comparing to P92 and T122 steels. Various welding trial and verification of G115 steel are also under the way at CISRI and Chinese boiler makers.

CN617 NICKEL-BASED ALLOY

Although alloy 617 was developed as early as in 1960s, it was frequently addressed being a candidate material for 700℃ A-USC power plant in Europe since 1990s. Alloy 617 was not suitable to make superheat and reheat tubes due to the poor ash-corrosion resistance resulting from the addition of about 9% molybdenum, however, the alloy was considered to be an important candidate for the manufacturing of pipe and header. Being a solid solution hardening dominated alloy, alloy 617 is more difficult to be hot-deformed, comparing to alloy 740. The operational temperature window is very narrow and the flow stress is higher during pipe-making. Further, relatively lower creep strength is another weakness of alloy 617. Modified 617 (or so-called 617B) alloy has been developed at ThyssenKrupp VDM, mainly by the boron addition of 10-50ppm, through which the creep strength is evidently increased. Big 617B alloy pipes were successfully made and had been qualified in various European test loops. Cracks in the base metal of an injection cooler, made of 617B alloy, in Scholven power plant were found and the cracks was analyzed to be stress relaxation cracks. Proposed solution to eliminate the cracks is to apply stress-relief annealing at 980℃for 3 hours.[2] In spite of aforementioned problem, alloy 617B is still one of most possible candidate materials for the pipe and header making of 700℃ A-USC power plant, because of its accumulated creep data and rich engineering experiences. Alloy 263 and 740H are of higher creep strength, but both alloys are in the early stage in the course of feasibility verification used to make pipes and headers of 700℃ A-USC power plant.

Figure 9 CN617 alloy ingot after VIM+VAR
(Courtesy of CISRI and Fushun Special Steel, 2013)

In recent years, CISRI systematically and experimentally investigated the optimization of chemistry, hot-deformation and heat treatment of 617B alloy. Optimized chemical composition and processing parameters were proposed against the available results, which led to an industrial trial of the novel alloy, tentatively termed as CN617, at the FuShun Special Steel Company in China. A 6-ton CN617 alloy ingot was made by VIM and VAR melting routines with the dimension of 660 mm (outside diameter) and 1940 mm in length, as shown in Figure 9. The ingot had been transferred to Inner Mongolia Heavy Industries Company of China, in where the ingot will be hot-extruded into a big pipe with the dimension of Φ460×80×4000 mm in the coming July 2013, with the help of 360MN press.

INCONEL740HM ALLOY

It was well known that the brittle eta (η, Ni3Ti-type) phase precipitates along the grain boundaries of Inconel740 during 750℃aging. After aging at 750℃ for 1000 hours, small amount of eta phase was observed near the grain boundaries. After 5000 hours, not only eta phase initiates at grain boundaries but also a significant amount of eta phase forms inside the grains as Widmanstatten pattern structure.

The eta phase is rich Ti-containing, which partly attributes to the degradation of creep strength. To improve the microstructure of Inconel740, the researchers from University of Sciences and Technology Beijing (USTB) and Special Metals Corporation (SMC) modified the content of critical elements (i.e. Nb, Al, Ti, Si, etc) and named the modified alloy as

Inconel740H. After the modification, it was reported that there is no acicular eta phase in the microstructure of Inconel740H after 700-750℃ aging.

With the light of the modification of USTB and SMC, CISRI melted some heats of Inconel740H in Laboratory for verification. Among them, one heat of Inconel740H contained 1.98%Nb, 1.08%Al, 1.64%Ti and 0.050%Si. As seen in Figure 10, acicular eta phase clearly exists along the grain boundaries of the specimens after 5000-8000 hours under both 750℃ and 800℃, which implies that the microstructure of Inconel740H should be further modified and improved.[3]

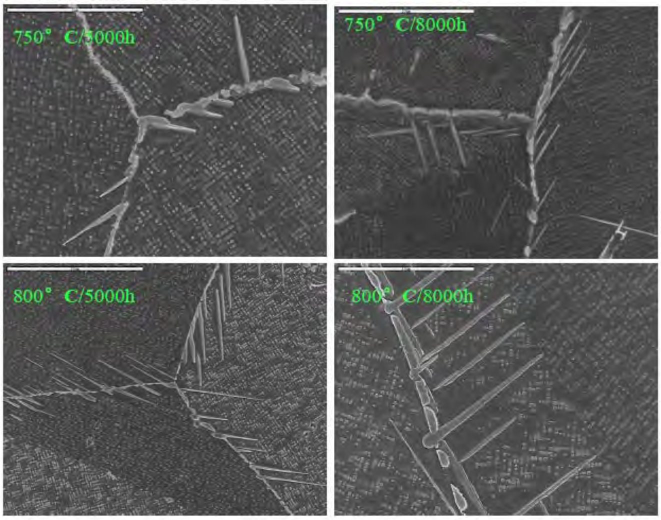

Figure 10 TEM photograph of Inconel740H during aging up to 8000hours

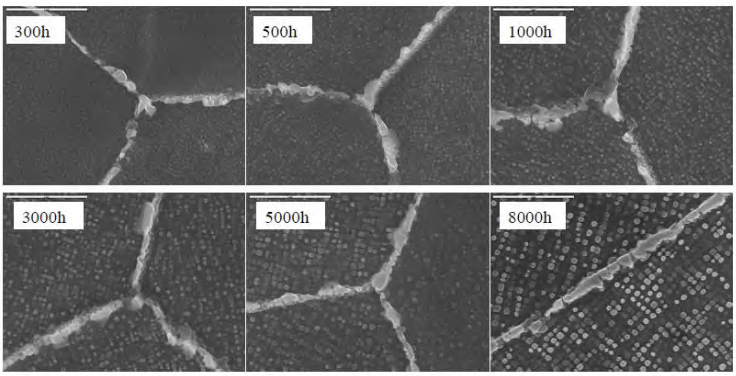

Figure 11 TEM photograph of Inconel740HM during 750℃ aging up to 8000hours

When further decreasing the content of Titanium to 1.38%, meanwhile with 1.48% Niobium and 1.47% Aluminum, together with some other modification, the microstructure of the alloy after aging at 750℃ up to 8000 hours was shown in Figure 11. Clearly, no eta phase precipitates, the carbides along the grain boundaries of the specimens keep in very stable, the size of gamma prime increases. This indicates a much better microstructure (Figure 11) comparing to that in Figure 10. The improved alloy was marked as Inconel740HM. More experimental findings on this interested and important alloy will be published soon.

CONCLUSIONS

(1) Candidate materials spectra used for 700℃ boiler of A-USC demo Power Plant in china was carefully discussed and summarized. The research and development in laboratory and industrial trials of all tubes and/or pipes associated with the selected materials spectra are under their way now.

(2) G115 has been successfully developed at CISRI and BaoSteel and it is an imposing material for the making of boiler pipes at the temperature scope from 620℃ to 650℃ and the water wall tubing of 700℃ A-USC power plants, due to its excellent creep rupture strength and reasonable oxide resistance as well as its economic competitiveness.

(3) Although Inconel740H has been recognized as an excellent candidate alloy for 700℃ boiler, the further optimization of chemistry and processing techniques is still necessary and possible, based on existed and characterized weakness of the imposing alloy.

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