Effect of post-heat treatment on the creep behaviour at 550°C of NiCr+Cr3C2 coating produced by HVOF on the SUS 304 substrate

E Martides1, A Rijaluddin2, D H Prajitno3, E Junianto1, and B Prawara1

1Research Center for Electrical Power and Mechatronics, LIPI
2Metallurgical Engineering, UNJANI
3Science Center and Nuclear Technology Application, BATAN

Email: erie001@lipi.go.id

Abstract. Austenitic Stainless Steel Grade 304 which is used for power plants boiler pipes often occurs creep phenomenon that caused a decrease in performance due to work at elevated temperatures. Surface coating of SUS 304 with Metal Matrix Composites Coating feedstock material 60% NiCr + 40% Cr3C2 is deposited using high-velocity oxygen fuel (HVOF) technique. The post-annealing process at 600°C at an argon atmosphere, holding time for 3 hours, and cooling in the furnace. Creep resistance test was carried out at a temperature of 550°C with a load of 54 kg for 10080 hours on three specimens, i.e. on-spray, as-spray, as-annealed, then followed by microstructure hardness testing and porosity observation. As-annealed specimens were assessed that the lowest creep resistance value, increased hardness in the coating and substrate and decreased the percentage of porosity in the coating.

1. Introduction
Austenitic stainless steel grade 304 is a non-magnetic metal widely used for super-heaters boiler tube in power plants applications, because it has properties that are good formability and weldability without annealing treatment before, and can be used for cryogenic and elevated temperatures applications [1]. SUS 304 has single phase and face-centered cubic (FCC) crystals as the influence of the dominant elements namely Cr and Ni which are intentionally obtained on very large amounts of steel for corrosion resistance and high temperatures stability [2]. However, the presence of high Cr and C elements in SUS 304 is a trigger for sensitization phenomenon by carbides forming, and subsequent stress corrosion cracking in the super-heaters boiler in some power plants [3].

Power plant systems in Indonesia have 4 types based on temperature and pressure operational, i.e subcritical, supercritical, and ultra-supercritical, with operational temperatures between 540°C-760°C and operational operations between 170-350 bars [4]. The application of SUS 304 material at elevated temperatures with a long duration, besides causing sensitization and corrosion phenomena, it also will increase in length depending on the time (creep). Failure on the boiler tube because of localized prolonged heating will occur wall thinning, reducing thickness, fish-mouth opening as visually. As the impact, it will very dangerous for safety and also economic losses because the power plant will be shut down to take corrective action [5].

To avoid sensitization, corrosion and the creep rate of SUS 304, special treatment is needed for SUS 304 materials to be resistant to creep and high-temperature corrosion, so that the material has a longer service life. A fairly effective treatment can be done by adding coatings on the SUS 304 surface with Metal Matrix Composites powder coating using High-Velocity Oxygen Fuel (HVOF) method and continued with post-heat treatment process.
Metal Matrix Composite coating is often used as a protective coating because its properties are suitable for stainless steel part in elevated temperature applications. Metal that used as a matrix usually has high ductility and corrosion resistance, while the reinforcement materials have high hardness and melting point temperature. HVOF sprayed NiCr-Cr3C2 coatings are one of the most popular candidates for protection of material from high-temperature erosion and have been successfully used to protect parts with an erosive and corrosive environment at service temperature up to 800°C. Utilization of carbide, oxide and cermets as a reinforced materials will increase not only hardness value of coating, but also wear and corrosion resistance value which is ideally suited as protective coating in corrosive and erosive environments [6].

Heat treatment after HVOF thermal spray coating process will greatly affects creep properties, because of residual stresses related to the coating process and due to mismatch of thermal expansion and elastic modulus between substrate and coating [7]. Furthermore, the HVOF coating results also will form the porosity, the fraction of melted and partially melted particles which are relatively difficult to avoid, which can degrade the quality of the coating and cause weakening of cohesion bonds on intersplats that are susceptible to corrosion attacks. As a anticipation, post-heat treatment can be carried out to improve microstructure, increase the adhesion of coatings, densification of layers, release residual stress, reduce porosity, increase coating uniformity, reduce oxide in layers, increase carbide precipitates, modify chemical composition.

To sum up, deposition metal matrix composite into 304 stainless steel surface will increase mechanical properties in particular hardness value and creep resistance especially when 304 stainless steel parts are used in aggressive environment. The important thing which determines quality of coatings are coating material selection and coating deposition process.

2. Experimental

Surface preparation of boiler pipes in accordance with SUS 304 specifications as a substrate that is cutting specimens adjusted to the specimen creep resistance test and giving a radius at the sharp end to avoid stress concentration. The blasting process uses 24 mesh of white aluminum oxide powder to clean the surface of the substrate from the impurity and to increase the adhesion of the coating (adhesion).

Ball mill process with 272 rpm rotation speed and sieving process carried out on NiCr powder as a matrix to obtain 45 μm powder sizes. The reinforcing powder of Cr3C2 was added according to the predetermined ratio, NiCr (60%): Cr3C2 (40%), then mixed in a V-type Blending machine for 8 hours with a rotation speed of 64 rpm. Blending powder is heated in furnace at 100°C for 15 hours to remove the moisture content in the powder. Substrate coating using the method of High Velocity Oxy Fuel (HVOF) to deposit each variation of powder by coating gradually with the target bond coat 50-75 μm and top coat 125-150 μm with constant parameters namely; spraying distance of 200 mm, gun angle and substrate of 90°, and pre-heat on the substrate surface at a maximum of 100°C.

In this study, the post heat treatment experiment was carried out in a tube furnace in an argon gas atmosphere with a pressure of 1.25 kgf / cm2 with a rate of 0.6 °C / s at a temperature of 600°C. After reaching the desired temperature, detention was carried out for 3 hours as shown at figure 2.

Creep resistance testing was performed to determine the durability of 3 specimens, i.e non-spray, as-sprayed and as-annealed. The parameters of the creep resistance test on the three specimens were constantly, ie using a static load of 54 kg with a test temperature of 550 °C and long dimension changes was calculated and observed every 15 minutes. Coating characterization was conducted by micro vickers method to determine the hardness distribution in coating with 3 times indentation in the cross-section with 50 gram load. Microstructure of coating and porosity observation are observed in cross section using SEM method, with surface preparation by grinding and polishing uses abrasive paper.
The quality of MMC coating that are already attached on 304 stainless steel surface can be seen from the characterization results using microhardness tester, SEM, and creep resistance machine methods. In this experiment, creep value is the most important mechanical properties of coating that must be observed to prove quality coating, apart from hardness value. The hardness value of MMC coating will increase on average up to 59% of the initial hardness value of stainless steel, if there is no defect or porosity in large quantities [8]. To determine the presence of defects or porosity in the coating can be seen by using optical microscopy which is strongly determined by the parameters that used to deposition coating material into stainless steel surface. Creep value will be related to hardness value, and presence of porosities.

3. Result and Discussion

The results of creep resistance test with a temperature of 550 °C, a load of 54 kg can been seen in strain diagram of the time shown in figure 3 and 4. The minimum value of creep rate (steady state creep) on the specimens from the test creep at a temperature of 550°C and a load of 54 kg is determined by obtaining the slope of the curve (secondary creep). Where at this stage, the creep rate will decrease over time until it reaches an almost stable state, so that the rate of creep undergoes a small change in time.

![Figure 1. Creep resistance test specimens after HVOF process](image1)

![Figure 2. Schematic of post-annealing process after HVOF process](image2)

![Figure 3. Creep resistance specimens (a) initial (b) non-spraying (c) as-spraying (d) as-annealed](image3)
As-annealed specimen has the lowest value of creep resistance which is the lowest elongation and strain, the smallest percent reduction in cross-sectional area and the smallest creep rate value. The creep resistance of the as-annealed specimen is affected by the post-heat treatment which improves the adhesion that can be seen from the visual evidence in figure 3. Post-heat treatment process makes the coating more dense, which increases adhesion automatically due to external energy in the form of heat energy that pushes the atoms to move inward. The crack direction in the necking area occurs following the stress that occurs in the specimen, namely the pulling force.

After creep resistance test, coating on as-sprayed specimen falls out and peels from the substrate that occurs in the necking area. It happens because the specimen is in high pressure and temperature conditions, and finally undergoes coating loss, but in the as-annealed specimen has undergone post-annealing process there is no loss as in the second sample, only in this third sample cracking occurs in the coating.

Figure 4 shows elongation after creep resistance test. Elongation in non-spray specimen is 10.20 mm with strain (ɛ) of 0.10111023. The strain value is obtained from the calculation of the change in length (Δl) divided by the initial length of the specimen which is 100.88 mm. After the stretching test process has been calculated, the reduction in cross-sectional area that occurs in the first sample is obtained by a percentage reduction of 8.05%. While from the calculation of the creep rate obtained the value of the creep rate at steady state creep is 0.0058 mm/hour which means that the non-spray specimens experience a creep of 0.0058 per hour. Using the same calculation, the as-sprayed specimen was 9.86 mm long with a stretch value of 0.098501499 which had an initial length of 100.10 mm. The reduction in cross-sectional area on the second specimen is 4.59%, of course, has a reduction in percent reduction than the first specimen. The creep rate on this as-sprayed specimen is 0.0033 mm/hour. Whereas the as-annealed specimen experienced a 9.51 mm long stretch with a strain (ɛ) 0.0938 which had an initial length of 101.30 mm. Reduction in cross-sectional area in as-annealed specimens has better creep resistance than before, which is 2.44. The creep rate value in the third sample is also lower than the two previous samples with the creep rate of 0.0029 mm/hour.

![Figure 4. Strain vs time diagrams of creep specimens test](image-url)

![Figure 5. Creep rate value of MMC coating on 304 Stainless Steel](image-url)
From Vickers hardness test results, it was found that the increasing of hardness value on the post-annealing results with hardness on the topcoat was 432.97 HVN while the unheated one had a hardness of 396.68 HVN, in bond coat as-spray had a hardness of 306.25 HVN, whereas in bond coat the annealed axles have a hardness of 363.64 HVN. From figure 6, it can be seen the comparison of the hardness between the as-sprayed and the as-annealed specimens. Likewise, the order of hardness from the substrate test point until the topcoat experienced an increase in violence. So, the curve above shows a linear increase in violence. Increasing of hardness value to the coating caused by post-annealing reduces the residual stress in the specimen [9]. This residual stress is in the form of high pressure from the result of spraying powder melt with high speed. Other causes are due to porosity decreasing in the coating will increases violence. The influence of post-heat treatment also affects the formation of fine crystalline as to produce grain uniformity [10].

The study of porosity weight and porosity sizes was characterized using the Image-J program from SEM. The results of this characterization resulted in a porosity decreased at as-annealed specimen. The initial porosity (as-sprayed) is 1.24% with an average porosity size of 12.68 μm, while the porosity of the as-annealed sample is 0.59% with an average porosity size of 6.19 μm. The results of visual observations are also seen from the decrease in porosity in the SEM results which are shown in figures 7 and 8.

![Figure 6. Hardness Vickers value of MMC Coating](image)

**Figure 6.** Hardness Vickers value of MMC Coating

![Figure 7. Porosity measurements using imageJ (a) as-sprayed specimen ; (b) as-annealed specimen](image)

**Figure 7.** Porosity measurements using imageJ (a) as-sprayed specimen ; (b) as-annealed specimen
In the thermal spray coating processes, porosity occurs due to the presence of oxygen gas that trapped in the coating, caused by distance of spraying too far or the presence of contaminants such as oil, grease, air. Besides that, porosity is caused by inadequate pressure on every powder coating to the substrate apart from distance between gun and substrate and powder feed rate, so that the splats shape not uniform and unable to fill the empty space underneath [11]. Basically, the effect of post-annealing on decreasing porosity is due to the presence of heat in the form of energy which pushes the layer more tightly so as to eliminate the porosity in the layer [12,13].

4. Conclusions

Post-heat treatment process has influences to mechanical properties of 304 stainless steel. As-annealed specimen has the smallest creep rate of 0.0029 mm/hour with elongation of 9.51 mm and the highest hardness value of 363.64 HVN (bondcoat), 432.97 HVN (topcoat). Post-heat treatment process has an effect on the decrease in percent of porosity, where the as-spray sample has 1.24% porosity with an average size of porosity of 12.68 µm, while the porosity of the as-annealed sample is 0.59% with an average size of porosity of 6.19 µm. Reduction of cross-sectional area with post-annealing results produces the smallest value of 2.44%.

Acknowledgments

The authors would like to thank to all researcher and technicians at Research Centre for Electrical Power and Mechatronics, All of lectures and students in Metllurgical Engineering, UNJANI, and all of researcher in BATAN. This work is a part of research that have been supporting by LIPI Priority and Advanced Research Projects, sub program development of material, energy and manufacturing engineering

References

[1] Atlas Steel 2013 Stainless Steel Grade Datashee Atlas Steel Technical Department Australia
[2] Aalco 2017 Stainless Steel: Alloys in Stainless Steel Elements Aalco Metals Ltd Cobham-UK
[3] Saad A A, Mahallawi I E I, Abdel-Karim R, Rashad R 2009 Engineering Failure Analysis 16 433-448
[4] Di Gianfrancesco A 2016 Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants Woodhead Publishing Cambridge-UK
[5] Parit A N, Tadamalle A P, Ramaswamy 2014 Thermal stress and Creep Analysis of Failed Tube of Secondary Super Heater (5th International & 26th All India Manufacturing Technology, Design and Research Conference (AIMTDR 2014) December 12th–14th IIT Guwahati, Assam, India)
[6] Bhatia R, Singh H, and Sidhu B S 2012 Asia Journal of Engineering and applied Technology 1(2)
[7] Sudhansu B 2007 *Chapter 6-Oxidation and Corrosion Resistant Coatings* (High Temperature Coatings) 71-154
[8] Tao K, Zhou X, Cui H, and Zhang J 2008 *Material Transactions* 49(9) 2159 - 2162
[9] Hung-Hua, Ting-Yi H, Tzu-Te L, and Ming-Der G *Int. J. Electrochem. Sci.* 13 9399 – 9415
[10] Xiaomei C, Jiangang Q, and Xiaotian H 2017 *Coating* 7(9) 146
[11] Gustavo B S 2015 *Soldagem & Inspeção* 238-252
[12] Jianguo Z and Kang M 2014 *Theoretical & Applied Mechanics Letters* 4 021008
[13] Öz A and Samur R 2013 *Metalurgija* 52 368-370