Effect of Pre Oxidation on Microstructure and Hardness of Low Carbon Steel during Nitrocarburising

Dr. Nirmala L.

Associate Professor, Dept. of Mechanical Engineering, K S Institute of Technology, Babgaluru-560109, India
nirmalal[at]ksit.edu.in

Abstract: ***This paper deals with the effect of pre-oxidation on Nitrocarburizing heat treatment of Low carbon steel (with a carbon range of 0.31wt% to 0.60wt% and a manganese content ranging from (0.60wt% to 1.65wt %). The nitrocarburized steel is used in the applications where corrosion resistance, wear resistance, and lower local stresses properties play a vital role. The purpose of Pre-oxidation in nitrocraburizing process is to develop multi-layer thickness uniformly and to enhance heat treatment (nitriding) kinetics. During Pre-oxidation iron oxide layer forms on the surface, this layer supports the nucleation of an iron nitride layer to develop faster owing to greater nitrogen content in the part of the multifaceted layer adjoining to the surface. The pre-oxidation is performed on the standard specimens by blowing gases such as atmospheric air (O_2), carbondioxide (CO_2), and humidified N_2. The pre-oxidized samples are then preceded to the "Nitrocarburizing" by blowing gases (N_2, NH_3, and LPG) at constant temperature and flow rates with different exposure time in "Fluidized Bed Furnace". From microstructural studies and hardness test results, higher deposition layer thickness and higher hardness is achieved for samples which have undergone peroxidation with humidified nitrogen, due to more amount of nitrogen deposition onto thick oxide layer.***

Keywords: Nitrocarburizing, Nucleation, Pre-oxidation heat treatment kinetics

1. Introduction

With the advance in the industry, the surface heat treatment of steels is an essential technology for enhancing their sturdiness. Over the last few decades, the prominence of surface heat treatment has improved due to easy way of improving chemical and physical properties at lower prices. In meticulously nitriding and carburizing are classic chemical heat treatment methods for surface treatment and have been applied extensively in parts where high wear resistance requires [1]. Nitriding heat treatment of steel is carried out at low temperature range of 550^0c to 590^0c, which is ferrite region. Amount of deformation in nitriding is negligible when compared to carburizing in which high-temperature treatment of 900^0c or more is required. Various nitriding techniques are used such as plasma nitriding, salt bath nitriding, and gas nitriding. Of these methods, gas nitriding is most commonly used. A shallow surface hardened layer in metals 2019, 9, 190 2 of 10 the range of numerous hundred Micrometers can be attained by gas nitriding. The processing time for gas nitriding should be more than 10 hours. Moreover, only high-grade steel is suitable. In addition, the nitride layer must be detached before it is put to use due to its higher brittleness. To overcome this problem in gas nitriding, gas nitrocarburizing heat treatment has been developed.

The nitrocarburizing process comprises the diffusion of nitrogen and carbon onto the surface of the steel instantaneously at the same time. Gas nitrocarburizing is preferred over gas nitriding due to: short heat treatment time of several hours and extensive usage of steel along with low carbon steels[3]. During gas nitrocarburizing in steels two nitride layers are formed, one layer ε phase and second layer γ phase, both the phases' helps to improve wear resistance of the material but deteriorates corrosion resistance.

The concentration of carbon content on the steel surface decides the phase to dominate. In high carbon steels, ε phase is dominant on the surface, whereas in low carbon steels γ phase dominants. To enhance the corrosion resistance, preoxidation of the sample is done before it undergoes nitrocarburizing. This technique involves three steps: pre-oxidation is performed on the standard specimens in two ways by blowing gases such as atmospheric air (O2), carbon dioxide (CO2). The pre-oxidized samples are then preceded to the "gas nitrocarburizing" by blowing gases (N2, NH3, and LPG) at different exposure times with constant temperature in fluidized bed furnace and post oxidation is also performed on the sample surface [4]. Pre-oxidation helps to form an iron oxide layer on the surface of the sample which helps to improve nucleation of iron nitride layer on the sample during gas nitrocarburizing and post oxidation helps to form an iron oxide layer on the sample surface to improve the corrosion resistance of sample by forming an oxide layer on the surface of porous ε phase on the iron nitride layer.

2. Materials and Methods

A commercial steel plate cold of particularly low-carbon steel (SPCC) for cold rolling, manufactured by POSCO, having a thickness of 10 mm, was used as the raw material. Table 1 depicts the composition of the low carbon steel used in this study. A negligible amount of copper and manganese is present as an alloying element in the iron matrix.

Table 1: Chemical composition of low-carbon steel (wt.%)

C	P	S	Mn	Cu	Fe
0.0018	0.093	0.003	0.206	0.051	Bal.

Figure 1 shows a graph of the oxi-nitrocarburizing process. Afore the oxi-nitrocarburizing process, contaminants on the exterior portion of the material were removed by acetone bath in cleaning machine. And then they were oxy nitrocarburized in a gasiform atmosphere by applying different heat treatment cycles.

Oxi nitrocarburizing method was implemented in two stages: Gas nitrocarburizing was performed at 580^0c as the first stage, and oxidation was performed 400^0c a second stage. Gas nitrocarburizing was carried out for two and four hours in ammonia, nitrogen and carbondioxide atmosphere and the purity of the gases was more than 99%. The complete process cycle is shown in table 2.

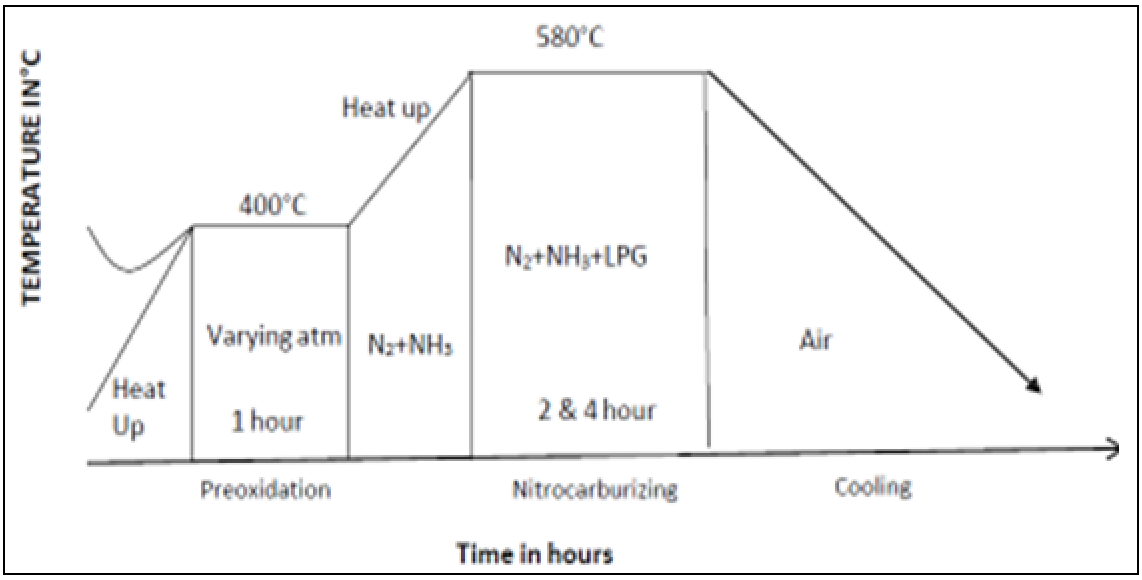

Figure 1: Shows a schematic diagram of the oxi-nitrocarburizing process

Table 2: Process Cycle

Trial No.	Preoxidation temperature& soak time	Preoxidation gas	Nitrocarburising temperature	Nitrocarburising Gas	Soak time
1	-	-	580°C	N2+NH3+carbon donor	2 & 4hrs
2	400°C for1hr	Air	580°C	N2+NH3+carbondonor	2 & 4hrs
3	400°C for1hr	CO2	580°C	N2+NH3+carbondonor	2 & 4hrs
4	400°Cfor1hr	Humidified N2	580°C	N2+NH3+carbondonor	2 & 4hrs

The metallography studies were performed by METJI inverted microscope to examine the microstructure of the hardened layer formed during Oxi-nitrocarburizing. The each sample were carefully cut with an abrasive wheel, the cross sectioned specimen was m olded. The molded specimens w ere initially ground with 120 grade emery paper to eliminate any deep scratches, polishing is done with fine grades of abrasive and finishing is done with alumina and diamond paste on velvet cloth. The samples were etched for 3-10 seconds with Nital (composition is 3% concentrated nitric acid and ethyl or methyl alcohol), then the samples were observed in a metallurgic a microscope with suitable t certification. The resulted microstructures were photographed.

The Nano hardness is investigated using Nano indentation tests to evaluate the effect of Oxi-nitrocarburizing on the surface properties of the selected material. After the specimen is polished with various grades of emery paper, the Nano indentation is carried out using a Vickers hardness tester on the surface hardened layer. The nanohardness was determined by means of an average of five measurements using a minimum load of 10 mN. The loading and unloading duration during the calculation of nanoindentation was 10 s, respectively

3. Experimentation

In-order to characterize the effect of pre-oxidation before nitrocarburising, three selective preoxidizing atmospheres was considered such as air, CO_2, N_2. A process was also carried out without preoxidation to compare the results achieved. The material used for trials is low-carbon steel. The nitrocarburising parameters are kept constant such as temperature and gas concentration. Trials were conducted with two nitrocarburising time cycles and keeping preoxidation time as constant time period followed by normal gas nitrocarburising a s shown in table 2. The samples were processed in FLUIDIZED BED furnace with the amazing flexibility which contributed significantly to the nitrocarburising process and have enabled many variations of the basic process to enhance various properties for diverse applications. The microstructures and hardness were interpreted to understand the behaviour and nucleation of compound layer growth with different pre-oxidation.

4. Results and Discussion

Microstructure analysis shows that, as expected, after nitrocarburizing process the low corbon steel has core microstructure i.e., ferritic and pearlitic. Micrographs of samples undergone nitrocarburizing process consists of compound layers composed of carbonitrides and porous ε phase in the outer part and γ phase adjacent to the layer matrix interface. Below such compounds the diffusion layer is formed, which is hardened due to precipitation of carbonitrides along the grain boundary. Figure2a, b depicts Microstructural images of samples undergone Nitrocarburising process for 2 hr and 4hrs duration of exposure without peroxidation.

The samples which have undergone pre-oxidation before nitrocarburizing process consists of iron oxide layer on the surface, this layer supports the nucleation of iron nitride layer to grow faster during nitrocarburizing process, owing to a higher nitrogen content in the part of compound layer closest to the surface. The compound layer formed is well adherent to the substrate with uniform thickness. Fig 3 and 4 shows microstructural images of material undergone peroxidation with media as atmospheric air, Co_2 and N_2 during nitrocarburizing process.

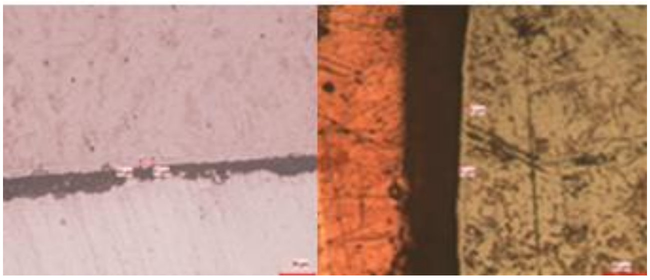

Figure 2: Microstructures of specimens undergone Nitrocarburising without preoxidation a) 2 hr duration of exposure b) 4 hr duration of exposure

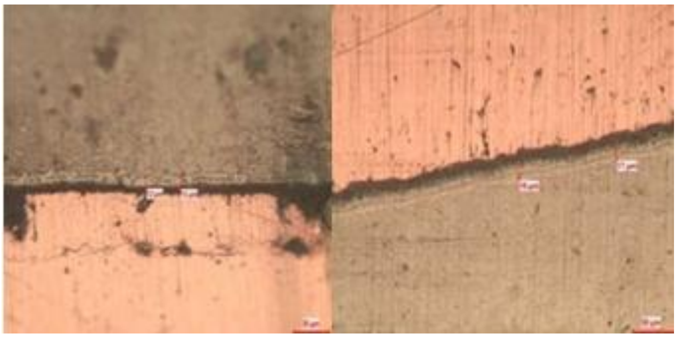

Figure 3: Microstructures of specimens undergone Nitrocarburising with air as preoxidant a) 2 hr duration of exposure b) 4 hr duration of exposure.

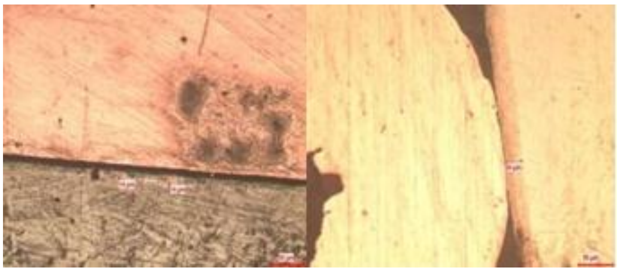

Figure 4: Microstructures of specimens undergone Nitrocarburising with CO_2 as preoxidant a) 2 hr duration of exposure b) 4 hr duration of exposure.

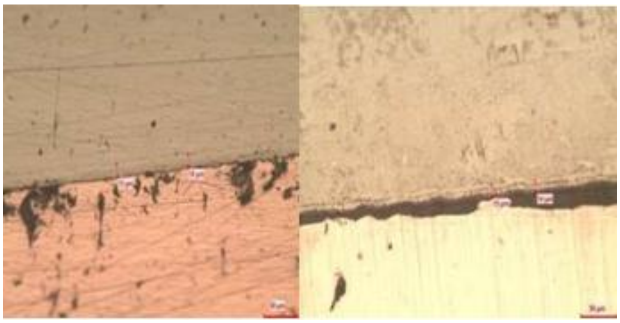

Figure 5: Microstructures of specimens undergone Nitrocarburising with Humidified N_2 as preoxidant a) 2 hr duration of exposure b) 4 hr duration of exposure

Microstructure reveals the samples processed without preoxidant have compound layer with lesser thickness as compared to samples processed with preoxidants. Preoxidation promotes the nucleation of iron nitrides and also reduces the incubation period for the case depth formation. Oxide layer formed on the surface allows the dissolution of carbides and formation of carbonitrides to occur deep in the diffusion layer. Incubation duration is reduced due to peroxidation, this lead to separation of the nitride and carbonitride location and is associated with higher nitrogen content near to the surface zone as compared with the near core zone. Air as preoxidant resulted in thin oxide layer while CO_2 and humidified nitrogen as preoxidant resulted thick oxide layer for the same temperature. Higher hardness and higher deposited layer thickness is achieved for samples which have undergone peroxidation with humidified nitrogen, due to more amount of nitrogen deposition on to thick oxide layer.

Figure 5 depicts microstructure of sample undergone peroxidation with humidified nitrogen, deposited layer thickness is 18μm which is higher than the other two samples which have undergone peroxidation with air and CO_2.

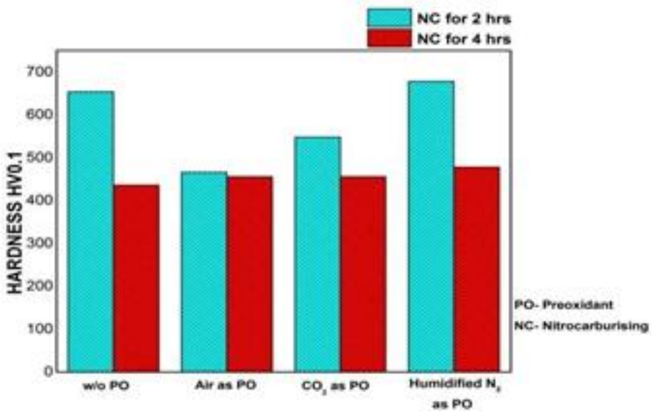

Figure 6: Microhardness profile of low carbon steel specimens treated with the various preoxidants

The fig 6 depicts microhardness profile of specimens treated with the various preoxidants. Microhardness improves when preoxidation is performed on low-corbon steel due to formation of an oxide layer on the surface. The oxide layer formed helps in nucleating of iron nitrides.

Despite preoxidant the specimen's hardness is 650HV and 410HV, respectively, when it undergoes 2hrs and 4hrs of nitrocarburizing. The surface microhardness for the air specimen is 460HV and 440HV, CO_2 specimen is 530HV and 469HVand N2 specimen is 670HV and 470HV respectively, when exposed to nitrocarburisig at 2hrs and 4hrs. Out of all the preoxidants the effect of humidified N_2 showed a substantially effect on microhardness, to a higher value of 670HV when it is exposed to 2 hours of nitrocarburixing, this is because the nitrogen concentration in the ε and γ phase increased as a result of the nucleation effect of preoxidation process and preceded nitrocarburising process. These results suggest that peroxidation is strongly influencing the hardness during nitro carburizing process.

Higher hardness is achieved for the samples undergone nitro carburizing process for 2 hour cycle time, whereas samples processed at 4 hours shows lower hardness due to the formation of porosity in the compound layer. This should be further characterized using XRD analysis.

From the analysis, it is clear that humidified N_2 as pre-oxidant shows better result compared to air and CO_2 as preoxidant

5. Conclusion

The significant finding of this preliminary experiment is Preoxidation helps to enhance formation of uniform compound layer on the treated surface. Samples processed without preoxident have lesser thickness compound layer as compared to samples processed with preoxidants. Higher hardness is achieved in samples nitrocarburised for 2 hour, than the samples processed at 4 hours this should be further characterized using XRD analysis. There is no significant difference in compound layer depth with various preoxidants. Higher hardness and higher deposited layer thickness is achieved for samples which have undergone peroxidation with humidified nitrogen, due to more amount of nitrogen deposition on to thick oxide layer

Generally it is known that air as preoxident result in thin oxide layer while CO2 and humidified Nitrogen as preoxidant results in thick oxide layer for the same temperature and time. The effect of nitrocarburising to the thickness of the peroxidised layer is to be studied during further work

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