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Cavitation Erosion Characteristics of Nitrocarburized and HPDL-Treated Martensitic Stainless Steels

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This article deals with plasma ion-nitrocarburising and high power diode laser (HPDL) surface treatment of 13Cr4Ni and X10CrNiMoV1222 martensitic stainless steels to enhance their cavitation erosion resistance. These steels are commonly used in hydro turbines and boiler feed pumps. These treated steels have been evaluated for cavitation erosion resistance and it has been observed that the plasma ion-nitrocarburising process has significantly enhanced the cavitation erosion resistance as compared to untreated steel whereas HPDL-treated steels have shown marginal improvement. This is due to formation of high hardness nitrides during nitrocarburising and formation of moderate hardness martensitic phase due to rapid heating and cooling rates involved in HPDL treatment. The cavitation erosion and micro-hardness data of plasma ion-nitrocarburized as well as HPDL-treated steel samples and their comparison with hard deposits such as stellite and HVOF coating form the main part of the article.

Keywords cavitation erosion, diode laser, martensitic stainless steel, plasma ion-nitrocarburising

1. Introduction

It is well known that when the pressure of a fluid drops below its vapor pressure due to an increase in its velocity or otherwise, vapor bubbles tend to form due to the reduced pressure/vacuum thus created. When these bubbles come in contact with regions of high pressure then they collapse, e.g., on the surface of boiler feed pump impeller, runner blade, draft tube, etc. The resulting implosion causes severe erosion of the base material in combination of high pressure wave generated and due to the formation of micro-jets that impinge on the material surface. This phenomenon is called cavitation.

Cavitation erosion is a complex phenomenon that involves the interaction of hydrodynamic, mechanical, metallurgical, and chemical factors. The pressure wave and the cumulative liquid jet generated by the collapsing bubbles interact with adjacent solid surface leading to compressive residual stresses [1]. It is well known that compressive residual stresses cause an increase in micro-hardness [2]. The action of micro-impacts causes an increase in hardness of the surface layer (strain hardening) in all types of tested materials. Strain hardening of metals depends on the ability to form slip planes and on the microscopic effects of plastic deformation. The effects of cavitation lead to the increase in the dislocation density in the steel. Dislocations can move until they meet an obstacle on their way after which dislocation pile up occurs. High amplitude pulses (caused by cavitation phenomenon) put into motion slip systems and also cross slip. The thermal effect that accompanies the bubble implosion can cause the dislocations to climb and also to annihilate. As a result of cavitation, two opposing tendencies occur simultaneously, viz., increase in dislocation density (due to implosion) and annihilation of dislocations (due to thermal effects and micro cracks initiation) [3]. Cavitation phenomena can be reasonably simulated in the laboratory using three methods, viz., cavitating liquid jet (ASTM G-134), ultrasonic vibratory apparatus (ASTM G-32-03), and rotating disc apparatus [4-7]. In the present investigation, the cavitation erosion testing has been carried out using the ultrasonic vibratory apparatus as per ASTM G-32-03.

Several approaches have been attempted to find a solution to the problem of cavitation. Soft polymer coatings, particularly polyurethane, perform well but lack adhesive bond strength with the base material. Stelliting by TIG welding/thermal spraying is another option, but it also has issues regarding design dimensions as well as increased cost. Similarly to overcome this problem, high-quality cermet coatings like WC-Co-Cr by HVOF process were also attempted but achieved an improvement by only a factor of two to three [8]. Also, since there is a thickness limitation in applying these coatings, their protective effect might be lost relatively fast in the case of cavitation [9]. It has also been reported that in the case of martensitic steels, laser surface melting at high laser head movement speeds have resulted in the formation of a large volume fraction of retained austenite [10, 11]. These samples were found to have a better cavitation erosion resistance, a result attributable to the high in situ martensitic transformability of the austenite phase.

Under such circumstances, surface treatment techniques such as plasma ion-nitrocarburising and laser hardening are alternatives which hold potential to overcome the damages occurring due to cavitation erosion. Both these techniques were adopted on 13Cr4Ni and X10CrNiMoV1222 martensitic stainless steel samples and their cavitation erosion resistance was evaluated and it was correlated with their micro-hardness values.

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In addition, for comparison, HVOF coating and stellite cladding were also tested for cavitation erosion resistance and these results are reported in this article.

2. Experimental

2.1 Plasma Nitrocarburising

Plasma ion-nitrocarburising is a process by which the surface hardness of steels can be increased by diffusion of carbon and nitrogen atoms up to a few hundred micron depth (case) under the surface. It is carried out in the ferritic region without any phase transformation. The solubility of carbon and nitrogen in ferrite is small and most of the carbon and nitrogen that enters the steel forms hard nitrides and carbides. In typical gas nitrocarburising, the outer layer formed is called the "white layer" which is hard and brittle. This layer has to be removed by grinding. However, in plasma ion-nitrocarburising this white layer can be avoided by a proper choice of plasma parameters including temperature, and LPG, NH_3 gases flow rates as well as the applied and bias voltage. Plasma ion-nitrocarburising of the steel samples for the reported experimentation was carried out in a furnace is based on cold wall technology and the process was carried out at 550 °C for duration of 8 h at a chamber pressure of 1.8 Torr. Experimental details and parameters are given in Ref [12].

Some of the 13Cr4Ni steel samples were surface textured (shot peened) using fine hard steel shots of size 200 µm at a pressure of 3.5 kg/cm^2 before they were plasma nitrocarburized and studied for their cavitation behavior. It is well known that dislocation densities and grain size are important factors that enhance the nitrogen diffusion process in steels [13-17]. Surface texturing increases the dislocation density and refines grain size of the base material. A surface roughness of Ra 1.159 µm was achieved in textured as compared to 0.509 µm on untextured sample. For the purpose of comparison of cavitation behavior, one of the 13Cr4Ni steel samples was heat-treated at 590 °C for 4 h and tested for cavitation erosion.

2.2 Laser Treatment

HPDL surface treatment was carried out on the steel samples using 4.6 kW Diode Laser System with the laser head mounted on a six plus two axis robot. Optics of "20 mm × 2.8 mm" was used to produce the laser beam controlled in a closed loop by using a two-color pyrometer. Laser treatment was carried out at 1550 °C. The complete system was controlled by the robot controller. The robotic laser treatment details are given in Ref 18. For the purpose of comparison, one 13Cr4Ni steel sample was cladded with stellite 6 powders using laser cladding process in a single pass attaining a thickness of 750 µm after grinding.

2.3 Test Sample Fabrication

Laser hardening and plasma ion-nitrocarburising was carried out on the steel sample blocks having dimensions 100 mm × 50 mm × 20 mm. For the cavitation testing, button samples to the precise dimensions as per the ASTM G-32-03 standard were prepared by wire cutting from these surface-treated blocks. The compositions of the steels are given in Table 1.

2.4 Cavitation Test Set-Up

The various parts of the cavitation test set-up are shown in Fig. 1. It consists of a high frequency-high voltage signal generator which energizes the piezo-electric element in the converter via the transducer RF cable to oscillate at 20 kHz with amplitude of 50 µm. This mechanical vibration is transmitted to the horn made of titanium alloy of matching impedance. The sample to be tested is screwed into the horn tip and securely tightened to ensure that there is no loss of energy transfer from the horn tip to the sample. The sample also oscillates at a frequency of 20 kHz thereby simulating the phenomena of cavitation on its surface.

3. Cavitation Erosion Testing and Characterization

Before the start of the cavitation erosion testing, commercially pure (99.5%) annealed wrought nickel 200 sample was used as the standard reference material for the cavitation test as per ASTM G-32-03. After establishing the accuracy of the

Table 1 The composition of the tested steel samples

Material	C	Cr	Ni	Mo	Si	V	Iron
13Cr4Ni SS	0.05	12.5	3.7	0.5	0.5	…	Balance
X10CrNiMo1222	0.1	12	2.5	1.75	0.25	0.3	Balance

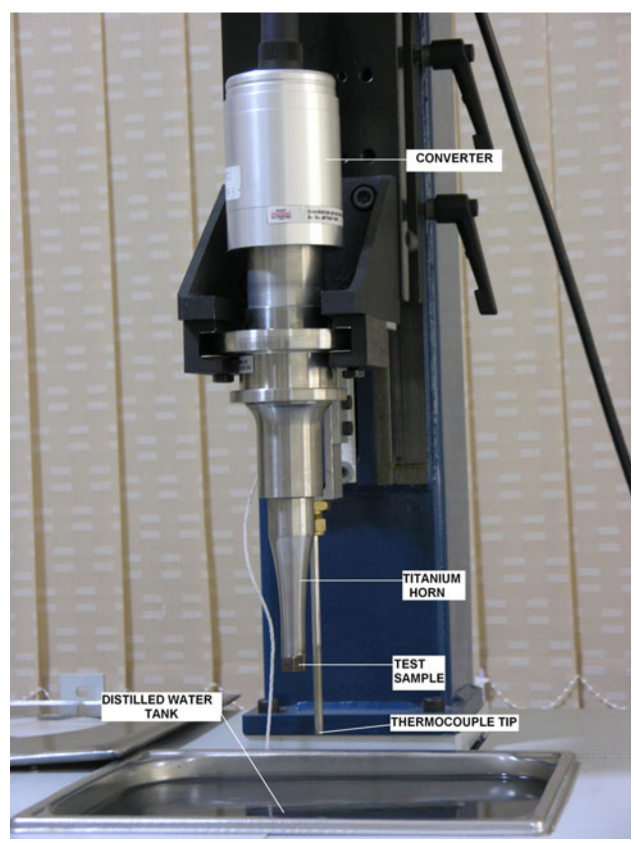

Fig. 1 Ultrasonic cavitation test set-up

cavitation tester with the standard sample, various test samples were then tested for cavitation by weight loss. This method of testing for cavitation is an accelerated test in which data can be obtained within few hours of testing.

The Vickers micro-macro-hardness (Wolpert, USA) tester was used to carry out micro-hardness as well as case depth measurements of the samples. The advantages of the Vickers hardness test are that extremely accurate readings can be taken and just one type of indenter is used for all types of metals and surface treatments.

4. Results and Discussions

4.1 Cavitation Test Results

Various samples tested for cavitation are listed in Table 2.

The results of cavitation for the above-mentioned samples are shown in Fig. 2.

Volume loss data have been calculated from the weight loss: for the 13Cr-4Ni steel sample (ρ = 7.85 g/cc), stellite 6 (ρ = 8.46 g/cc), and HVOF sample (ρ = 12.7 g/cc).

Laser treatment involves very fast heating and cooling of the steel specimens and thus results in an increased volume fraction of martensite in the samples. There is an improvement in cavitation performance of 13Cr4Ni steel (0.05% C) after laser hardening but it is more pronounced in X10CrNiMoV1222 steel (0.1% C). This indicates that the percentage of carbon in the steel plays an important role in improvement of cavitation erosion resistance due to the formation of carbide precipitates in the surface layers after laser treatment. To see the effect of cavitation on the 13-4 (NC) sample on a longer term, it was subjected to cavitation erosion for 30 h (Fig. 3). From the figure it is clear that beyond 15 h, the slope of the curve increases sharply and is closer to the slope of the untreated sample (13-4AS) indicating that the cavitation depth has exceeded the nitrocarburized layer thickness leaving the base material is exposed.

The cavitation erosion is measured by the mean depth of erosion rate (MDER) which gives the relative performance of the samples and is calculated by the following equation

$$\mathrm{MDER}\ (\mu\mathrm{m/h}) = 1000\,\Delta V/(A \times \Delta t)$$

where ΔV is the volume loss in mm^3, Δt is the duration of the test in hour, A is the surface area of the specimen in mm^2.

Table 2 Samples tested for cavitation

Sl. no.	Sample ID	Sample composition and treatment	Comparison after 5.5 h of cavitation testing
1.	13-4 (AS)	13Cr-4Ni as-received steel sample	Untreated
2.	13-4 (HT)	13Cr-4Ni as-received steel heat-treated sample	1.4-fold better than 13-4 (AS)
3.	13-4 (LH)	13Cr-4Ni laser treated at 1550 °C at 2 mm/s	2.9-fold better than 13-4 (AS)
4.	13-4 (SPNC)	13Cr-4Ni shot peened and nitrocarburized steel sample	9 fold better than 13-4 (AS) and 5.8-fold better than HVOF
5.	13-4 (NC)	13Cr-4Ni nitrocarburized steel sample	6-fold than 13-4 (AS)
6.	X10 (AS)	X10CrNiMoV1222 as-received sample	Untreated
7.	X10 (LH)	X10CrNiMoV1222 laser treated at 1550 °C at 2 mm/s	5.6-fold better than X10 (AS)
8.	X10 (NC)	X10CrNiMoV1222 nitrocarburized steel sample	6-fold better than X10 (AS) and 5.5-fold better than HVOF
9.	HVOF	HVOF-coated WC-Co-Cr coating	…
10.	Stellite 6	Stellite 6 laser clad sample	Benchmark for cavitation

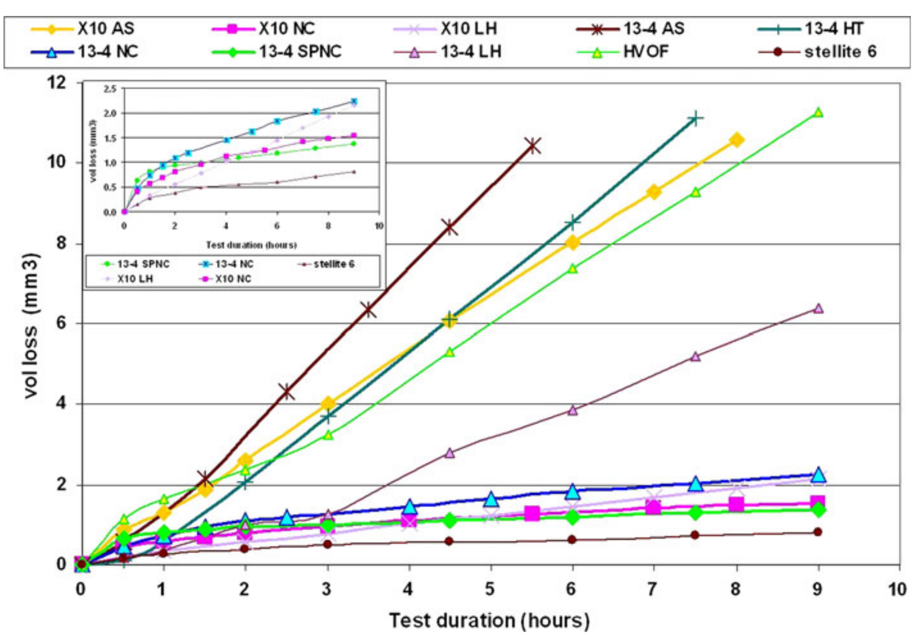

Fig. 2 Volume loss due to cavitation as a function of test duration

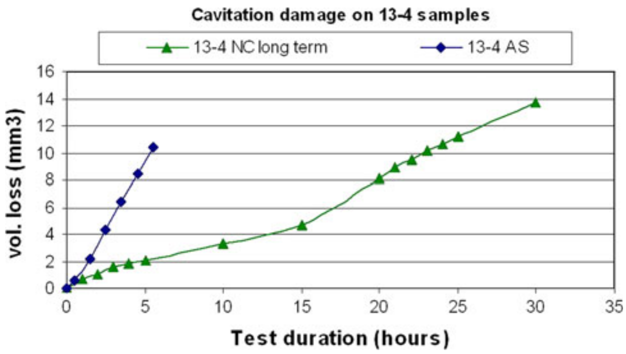

Fig. 3 Volume loss by cavitation erosion after removal of nitrocarburized layer as a function of test duration

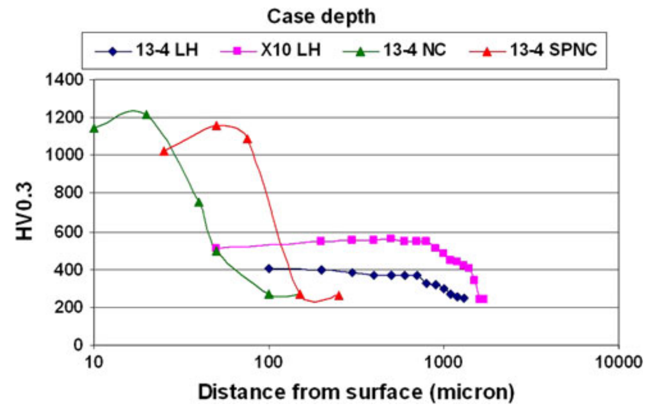

Fig. 4 Vickers hardness as a function of depth below surface

Table 3 Case depth/thickness, micro-hardness, and mean depth of erosion rate of different surface-treated/coated materials

Sl. no.	Description	MDER, μm/h	HV0.3 pre-cavitation	HV0.3 post-cavitation	Case depth/thickness, μm
1.	13-4 AS	12.7	280	285	…
2.	13-4 HT	9.2	260	275	…
3.	13-4 LH	7.4	387	418	700
4.	13-4 NC	1.7	1100	1280	25
5.	13-4 SPNC	1.0	1202	1225	70
6.	X10 AS	8.8	275	300	…
7.	X10 LH	1.6	665	715	1200
8.	X10 NC	1.1	1103	1150	100
9	Laser clad stellite 6	0.6	580	660	750

The mean depth of erosion rate (MDER) is tabulated in Table 3.

4.2 Micro-Hardness and Case Depth

The hardness of various samples pre- and post-cavitation along with the case depths are also given in Table 3. It is seen that in all the surface-treated samples (laser hardened as well as plasma nitrided) that the hardness tends to increase marginally after cavitation. Before start of cavitation, there is a low density of dislocations in the material. Cavitation pulses generate dislocations and set them into motion [3]. Some of the dislocations are blocked by the presence of precipitates, grain boundaries, etc., in the materials. With increased exposure time to cavitation, amount of energy supplied increases and hence dislocation density increases (work hardening) which is responsible for the marginal increase in surface hardness. With dislocation pile up at some discontinuity, the resistance to cavitation is found to increase till a point after which micro-cracks begin to develop and leading to rapid removal of material.

The case depth of hardness for the 13-4LH and X10LH martensitic stainless steel samples as well as the nitrocarburized sample (13-4 NC and 13-4 SPNC) is shown in Fig. 4 (*x*-axis is logarithmic scale). It can be seen from the figure that the depth of hardening is much more for X10 LH sample as compared to 13-4 LH sample. This could be because of higher carbon percentage in X10 as compared to 13-4 steel. The case depth of hardness for the nitrocarburized sample (13-4 NC) shows that there is an increase in hardness from the edge inwards up to a depth of 25 μm after which it starts to fall again. The effect on hardness of the modified nitrocarburized layer is lost after a depth of around 40 μm. This corroborates the cavitation behavior seen in Fig. 3 and implies that hardness plays a vital role in the cavitation performance. The shot peening step prior to nitrocarburising has introduced beneficial residual compressive stresses in the (SPNC) samples that has helped in increasing the depth of hardness unto around 100 μm seen from Fig. 4.

5. Conclusions

The plasma ion-nitrocarburized 13Cr4Ni and X10CrNiMoV1222 steel samples have shown significantly improved cavitation erosion resistance, closest to the benchmark of stellite 6 which is due to the formation of hard nitrides which effectively impede material removal due to cavitation. Laser treatment of the martensitic steels has also improved their cavitation resistance over that of the untreated ones but the improvement is far less than that achieved by nitrocarburising.

Laser treatment of the martensitic steels has also improved their cavitation resistance over that of the untreated ones due to the formation of hard martensitic phase; however, the improvement is marginal in case of 13Cr4Ni steel (0.05% C) whereas it is more pronounced in case of X10CrNiMoV1222 steel (0.1% C). This indicates the important role played by the formation of hard carbides and martensitic phase in the improvement of cavitation erosion resistance. From the long-term cavitation testing of the nitrocarburized 13Cr4Ni samples it is clear that the cavitation depth has exceeded the nitrocarburized layer thickness and the base material is exposed.

WC coated HVOF sample shows improvement in cavitation erosion behavior over the untreated steels (13-4 AS and X10 AS); however, the cavitation erosion resistance is inferior to that of nitrocarburized and stellited samples. HVOF coatings are hard; however, they have a few pores which are the main reason for their inferior performance in cavitation compared to stellite cladded and nitrocarburized steel samples.

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