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Wear Characterization of High Temperature Oxidized Ni Based Superalloys

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Abstract

Objectives: Present manuscript deals with the study of wear performance of nickel superalloys namely Superni-76 and Superni750-X, by means of two bodies dry sliding wear method. **Methods/Statistical Analysis:** The wear performance of the superalloys was noted in as received conditions and after oxidizing the sample at 900°C for 50 hours. Hardened steel balls were used as abrasive body to evaluate the wear volume in each as received and oxidized samples. **Findings:** The wear volume was calculated with respect to time and sliding distance and graphs were plotted for both the superalloys. The weight change and types of oxides formed after oxidation were identified by XRD and EDX/EDS analysis. The wear surface was also characterised by using FE-SEM/EDS analysis to ascertain the mechanism of wear in the samples. From various characterisation results and observations of volume loss, the effect of oxidation was analysed for these superalloys. Oxidation affects the wear behaviour of nickel based superalloys. The wear mechanism changes due to increase in hardness and brittleness after high temperature exposure. **Application/Improvements:** It has been found that the oxidation phenomenon leads to the formation of very fine oxide scale on the superalloys. This oxide layer especially in case of Hastelloy-X (Superni-76) was responsible for the improvement in the wear resistance despite of some initial fast volume loss.

Keywords: Oxidation, Superalloys, Tribology, Wear

1. Introduction

Superalloys are the candidate materials for applications requiring high strength, improved wear resistance, higher fatigue and creep resistance in highly corrosive conditions at elevated temperatures. These materials are particularly important for chemical, automobile, aerospace, chemical/oil sectors to resist the harsh service environment.[1-3] The Ni, Co and Fe based super alloys have been specially developed for application in the hottest parts of the turbines, e.g. combustor in the turbine sections where it experiences highest temperature and pressure. Ni based superalloys are best for these applications due to its increased and constant high temperature strength.[4] It is important to evaluate tribological behaviour of these superalloys as they undergo the wear phenomenon during continuous contact with other surfaces.

The tribological behaviour of CMSX-186 superalloy against hardened steel was studied under dry sliding conditions. The weight loss of the alloy during wear process showed incremental behaviour with respect to applied load at a given sliding speed. Both ductile and brittle fracture mechanism was responsible for the wear loss. The presence of iron (Fe) and carbon(C) due to counter material was confirmed by the XRD results along with In the reported article it was investigated on the dry sliding wear of Ni, Co and Co/Fe based superalloys in their study by using pin on disc method.[5,6] It was summarised that the Ni based superalloys exhibited higher specific wear rate as compared to Co based and Fe based superalloys. Formation of NiO was discovered as the major reason for this behaviour. The comparative wear performance of Hastelloy-C and Refractalloy 26 was carried out by article by using pin-on-disk tests at different temperatures at fixed values of load and speed.[7] They commented about the relationship between microstructure, hardness and wear

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at different temperatures of these super alloys. The heat treated Hastelloy-C possess uniform and fine distribution of precipitates while for Refract alloy 26, these precipitates are not uniform and bigger in size.[7] The wear behaviour of Inconel718 with without surface treatment was studied and the improvement in the wear resistance of Inconel718 was noted after nitriding treatment. It was found that the increased hardness was major factor for reducing friction coefficients after the nitriding processes which ultimately increases the wear resistance of the alloy.[8] Similarly the room temperature tribological behaviour of some of Nimonic and Incoloy were studied and it was noted that the wear resistance in initial stage of above said alloys was associated with their strength. After that the work hardening due to the surface asperities may influence the further wear loss.[9]

The effect of oxides formed during the wear process on the alloys has been reported and explained in different studies.[10,11] It was explained by some proposed models that oxides forms glazed layers between the two contacting surfaces during wear. These glazed layers affect the amount and mechanism of wear. These oxides were found to prevent the contact between the two metal surfaces during rubbing of the surfaces.[10]

Present investigation involves the dry sliding wear study of two Nickel based superalloys namely: Superni-750X and Superni-76. The effect of oxides formation on these materials has been studied after exposure to high temperature environment. This study is particularly important to visualize the amount of wear and effect of oxide scale formation on these superalloys.

2. Experimental

2.1 Sample Preparation

The rolled sheets of Superni-750X and Superni-76 were obtained from MIDHANI, India. The elemental composition of both the alloys is given in Table 1. Samples of 20mm x15mm x3mm dimensions were prepared by precise cutting and grinding process from the corresponding superalloy sheet. It was polished up to 1200 grit and subsequently cloth polishing was done using alumina powder of 1 μm.

2.2 High Temperature Oxidation Studies

As received samples were then cleaned ultrasonically to remove dust and loosely bonded particles. Oxidation was carried out in a laboratory SiC tubular furnace (Digitech, India) at 900°C. The calibration of the furnace was done by using Platinum/Rhodium thermocouple up to an accuracy of ±5°C.

2.3 Wear Studies

The wear test was performed by using hardened steel balls (case hardened En-32 plain carbon steel with hardness of 62-65 HRC) and Multi-Tribo Tester (model TR-25) using Win Ducom-2008 software for data acquisition. Three oxidized and three as received superalloy samples were tested under different load variations of 2 Kg, 4 Kg and 6Kg at a constant speed of 250rpm. Wear rates were calculated by using the Archad equation

$$W=V/(DF)m^3/N.m$$

The volume loss during wear test was calculated by examining the worn tracks which were observed by using the scanning electron microscopy technique. Depth of the track was noted by using surface profilometer (ASTM G99).

2.4 Characterisation Techniques

X-ray diffract meter (Bruker D-8, Cu Kα energy) and with Ni filter (30mA, 40kV) was used to analyze the as received and oxidised superalloy samples. The morphology along with chemical composition of the surfaces was studied under FE-SEM (Carl Zeiss, Germany, ULTRA plus model) with resolution of 0.8nm and magnifications upto 1,00,000X. The EDAX Genesis Software attached to this instrument was used to calculate the concentration of elements at the particular points and in the specific area. The roughness of the worn tracks was estimated by using a roughness profilometer (MITUTOYO, SJ-201) according to JIS-1994 roughness standard.

Table 1. Elemental composition of Superni-76 & Superni-750X as supplied by the manufacturer

Elements	Ni	Cr	Fe	Ti	Al	Mn	Co	Mo	W	Si	C
Superni-750X	Bal	15.28	7.32	2.37	0.59	0.06	0.05	-	-	0.07	0.07
Superni-76	Bal	21.49	19.69	-	-	0.29	1.6	9.05	0.6	0.39	0.86

3. Results

3.1 Microstructure and Hardness of as Received Superalloys

The microstructure of the both superalloys has been shown in Figure 1**.** The microstructure of Superni-750X is showing the presence of two phases (γ and γ') which are coherent with each other with presence of some carbide also. On the other hand the Superni-76 is a solid solution strengthened alloy having uniform γ-phase and the carbides can be seen in larger quantities. The micro hardness of superni-76 and superni-750X was 390Hv and 320Hv respectively.

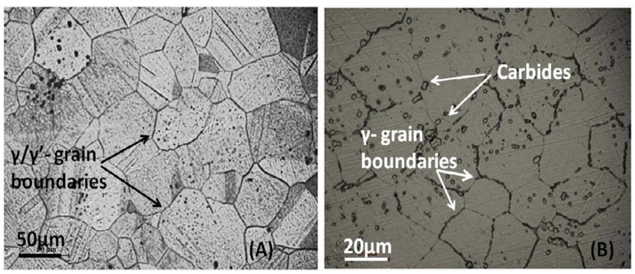

Figure 1. Microstructure of superalloys in as received conditions (a) Superni-750X, (b) Superni-76.

3.2 XRD Analysis

XRD analysis of the as received superalloy and heat treated superalloys has been shown in Figure 2 (a and b). As received superalloy Superni-750X and Superni-76 shows the peaks of theγ/γ' and γ phases respectively. In case of air oxidation of Superni-750X, the major phases present are Cr_2O_3 and TiO_2 only. There was no another oxide observed. The larger intensities of the oxides peaks as compared to intensity of the bare metal peaks give the information that the oxides have been formed in larger quantity. In case of air oxidation of Superni-76, the peaks corresponding to bare alloy are still prominent and other peaks corresponding to the phases: Cr_2O_3, $Ni(Fe,Cr)_2O_4$ and $NiMnO_3$ are observed.

3.3 Morphology and EDS Analysis

The surface morphology of the oxidized Superni-76 and Superni-750X has been shown in Figure 3. In case of Superni-76, one can easily observe the uniform and compact morphology with no signs of spallation in Figure 3(a and b). The composition of the oxidized surfaces has been shown tabulated in Table 2. The main elements detected at the surface were Cr, Ni, Fe and some amount of Mn. However the morphology of the oxidized surface is different in for superalloy750X. The oxides formed are not compact and a unique pattern has been observed Figure 3c. The oxides nodules have been grown on the grain boundaries and these nodules are rich in Ti as shown in Figure 3(d). This pattern indicates that the migration of Titanium is faster along grain boundaries rather than through the grains. Ti and Cr are the major elements which were found in the scale.

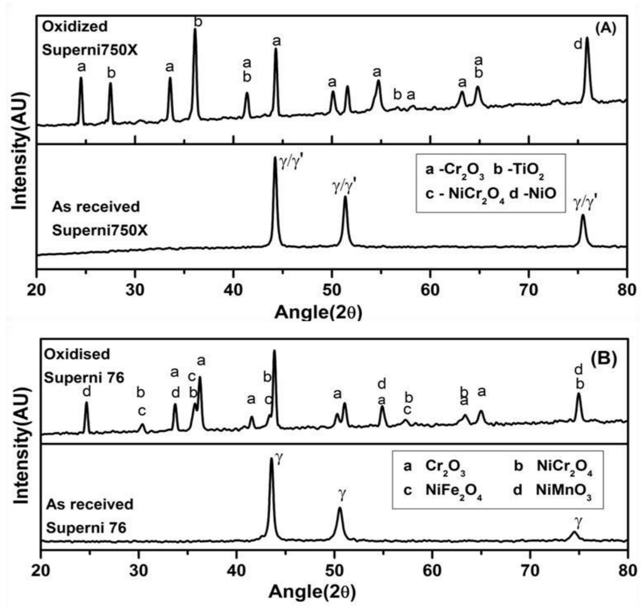

Figure 2. XRD peaks of as received and oxidized (a) Superni-76, (b) Superni-750X.

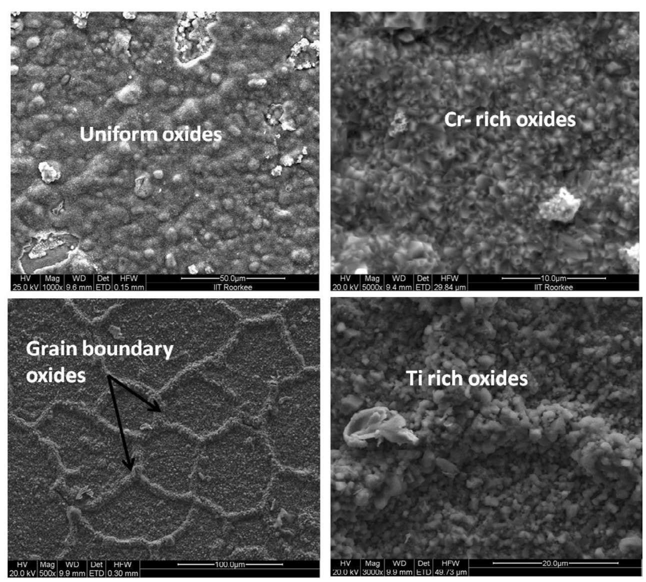

Figure 3. FE-SEM images of oxidised superalloys, (a, b) Superni-76, (c, d) Superni-750X at lower and higher magnification respectively.

Table 2. Composition of the oxidised surfaces (EDX) at same magnification (wt %)

Alloy	Ni	Cr	Fe	Ti	Mn	O
Superni-750X	3	43	3	28	-	21
Superni-76	12	48	7	-	5	22

3.4 Wear Studies

The effect of the sliding distance on the wear rate at loads of 2Kg, 4Kg and 6Kg respectively has been shown for both the alloys in Figure 4 and 5. In case of Superni-76, the as received samples show zig-zag variation of wear volume with sliding speed. However for oxidized samples the specific wear rate increases initially up to 600m sliding distance after which it becomes almost constant. On the other hand in case of Superni-750X the specific wear rate was higher as compared to Superni-76. The oxidized Superni-750X showed increase in wear rate up to 1200m and then it become gradual.

The morphology of the worn alloys has been shown in Figure 6(a-b). In case of Superni-76, the wear grooves can be seen along with some sign of delamination Figure 6(a). On the other hand in case of Superni-750X there was presence of some transferred layers of wear debris Figure 6(b). Similar observations were also noted by Mishra *et. al.* in their study on wear behaviour of Ni based superalloys.[7] The SEM morphology of worn surfaces after high temperature exposure has been shown in Figure 7(a, b). The oxides in case of Superni-750X are showing signs of brittle fracture and production of larger wear debris as compared to Superni-76.

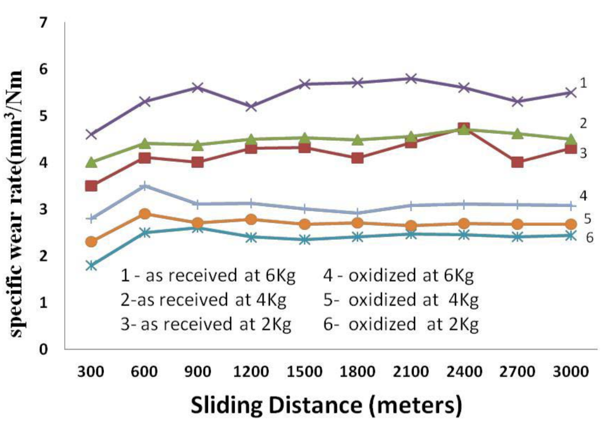

Figure 4. Graph showing dependence of specific wear rate on sliding distance for Superni-76 under as received and oxidized conditions.

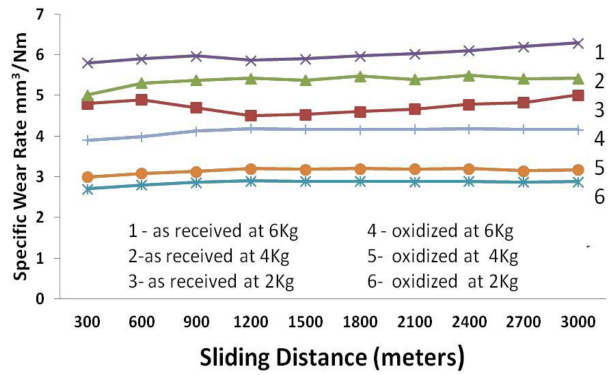

Figure 5. Graph showing dependence of wear rate on sliding distance for Superni-750X under as received and oxidized conditions.

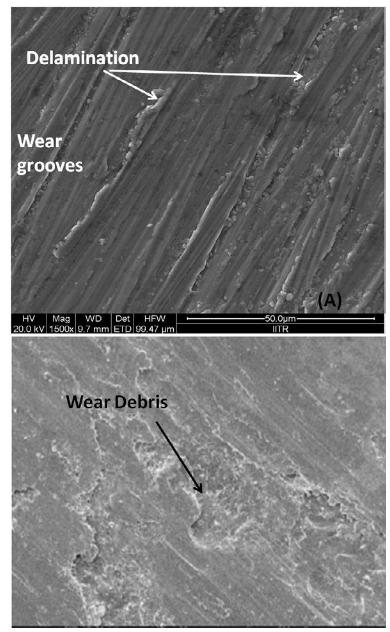

Figure 6. Morphology of worn surfaces of as received (a) Superni-76, (b) Superni-750X.

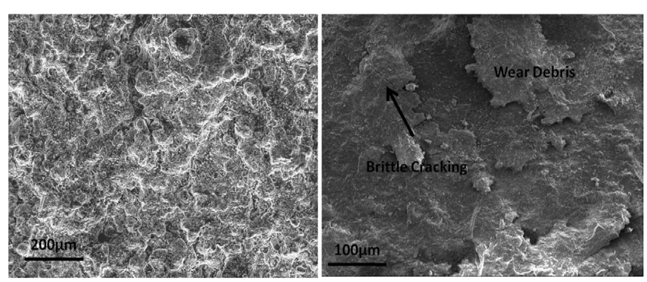

Figure 7. Morphology of worn surfaces after oxidation (a) Superni-76, (b) Superni-750X.

4. Discussions

The hardness of both alloys varies due to difference in microstructure of both the alloys. Superni-76 is solid solution hardening alloy and have presence of strong carbide forming elements. The higher value of hardness in case of Superni-76 may be the consequence of the formation of larger amounts carbide along the grain boundaries as also evident from the microstructure. The oxidation resistance of both the alloys is different due to different composition and morphology of the oxides. The formation of Cr_2O_3 and $NiCr_2O_4$ in case of Superni-76 has been well explained by some previous studies.[12-14] These oxides are highly desirable for high temperature and oxidation/corrosion resistance. Moreover the compact morphology of these oxides has been found to increase the wear resistance as evident from the wear rate curves. In case of heat treated samples, the initial high rate may be attributed to the removal of the outer layer of oxides which is loosely bounded to the substrate. After a certain time the wear rate becomes almost constant which indicate that the oxides are now acting against further wear.

Ti has been found to important in describing the difference in the oxidation behaviour of both the alloys. In case of Superni-750X the effect of Ti is important; it has been observed that formation of TiO_2 exerts a negative effect on the oxidation behaviour of the alloys.[15] Similarly in our study TiO_2 crystals were observed at the surface of the oxidized surface. However in present case the TiO_2 is segregating specially at the grain boundaries. It has been reported by SW Yang that the diffusion of Ti in the Cr_2O_3 is similar to the diffusion of Chromium.[16] Hence Ti is diffusing very fast at the surface through the Cr_2O_3 oxide layer. However the diffusion along grain boundaries is faster than in the bulk. Hence it can be concluded that the Ti is diffusing more along grain boundaries rather than in the bulk. Cr_2O_3 is a protective oxide; however, the amount of Cr in this case is not sufficient to develop a uniform layer on whole surface.

The wear behaviour of Superni-750X after oxidation is also affected by the types of oxides formed. The oxides in case of Superni-750X have shown prominent sign of fracture and spallation after wear test. The wear rate also increases rapidly when compared with that of Superni-76. This difference in wear response of both alloys can be described on the basis of preferential segregation of TiO_2 crystals on the grain boundaries which make the surface more uneven. Moreover it has been also reported that the wear resistance of Cr_2O_3 and Al_2O_3 decreases by addition of TiO_2 in the ceramics.[17]

5. Conclusions

- Superni-76 possesses higher wear resistance than Superni-750X under dry sliding wear despite of fact that both are Ni based superalloys. This difference in the wear behaviour is attributed to the composition and microstructure of the alloy.
- Wear behaviour of the alloys changes after exposure to high temperature oxidation. In both the alloys, the initial wear rate increases after high temperature exposure.
- The wear mechanism changes from plastic deformation/delamination to the brittle fracture of the oxide scale after high temperature.
- The oxides formed in case Superni-76 possess higher wear resistance as compared to the oxides formed in case of Superni-750X.

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