JOURNAL OF MATERIALS SCIENCE 24 (1989) 3699–3706

Mechanical sputtering of structural stainless steels

T. NENADOVIĆ*, N. POPOVIC*, J. FINE†
*Boris Kidrič Institute of Nuclear Sciences, PO Box 522, 11001 Belgrade, Yugoslavia
†National Bureau of Standards, Gaithersburg, Maryland 20899, USA

In this paper the results of an investigation of the beam modification (erosion) of stainless steel are presented. The possible similarity of the martensitic stainless steel degradation for turbine engine blades and austenitic stainless steel used as a wall of the vacuum vessel for fusion reactor application has been pointed out. Changes appearing during the interaction have been investigated on the rotating turbine blade material. Simultaneously morphological changes of the 'target' and the change of shape of bombarding species have been analysed.

1. Introduction

Solid surfaces exposed to ion beams (in fusion devices) or working fluids (in steam turbines) may become modified [1]. Such interactions result in material properties modification due to mainly to thermal, mechanical and chemical phenomena, as well as to erosion and radiation degradation. In all these processes impurities are often generated which can cause further material degradation. At the present time high temperature alloys used in the 'hot sections' can only be selected on the basis of their high resistance to surface degradation since actual methods for material improvement are rare. In the future (due to higher energy, higher densities of working fluids, and longer working cycles) this problem is expected to be more critical. Consequently, materials and coatings with better erosion-resistant properties must be developed [2].

Candidates for wall materials should have low erosion rates during simultaneous interaction with all energetic particles and species (including eroded materials); the material selection and behaviour for non-well defined simultaneous interaction with all energetic particles and species is rather important. Experiments done on well defined target materials together with the use of well defined ion beams should better enhance our understanding of damage mechanisms [3, 4]. In real devices the different mechanisms of surface degradation can play a role and a quantitative statement about the contribution of every mechanism separately is not possible. The contribution of each mechanism is different from the sum of the individual effects [5, 6].

In this paper we will deal with degradation of steel during beam interaction. For such degradation of material properties we used the term mechanical sputtering because it is well known that when solid surfaces are bombarded with energetic particles, their energy is transferred to the surface and target material is removed. Independent of the mechanism, all the sputtering processes depend on the beam characteristics and the bombarded target properties [7]. If the bombarded doses are high enough, the beam modification of surfaces (morphological, compositional etc.) is quite pronounced. Therefore, apart from physical (collisional) sputtering [8] in which atomic collisions are necessary, chemical [9], thermal [10] and laser sputtering [11] have also been investigated. All the above mentioned mechanisms result in material removal, etching, erosion or decomposition. In previous papers, we used for example the term laser sputtering, for laser evaporation and laser damage, while for mechanical sputtering we used the term corrosion–erosion degradation [12].

Materials such as high temperature alloys in hot sections of steam turbines and wall elements in fusion device vacuum vessels are selected on the basis of their high resistance to surface degradation when in contact with the beam (working fluid or, dense plasma). In both cases these materials are stainless steels. The material of turbine-engine blades is martensitic stainless steel; conditioning methods improve the fatigue behaviour of their structure and their resistance to surface degradation (corrosion and erosion) during the working cycle. Contaminants from steam and other working environments (halides, sulphates, oxides, and alkali metals) are deposited on the surface producing material degradation. Walls of vacuum vessels are austenitic stainless steel (protected by an inconel shield); conditioning methods eliminate most impurities (oxides and carbon films). Some contaminants (oil films, sulphur, chlorine, and accidental impurities), however, remain trapped at the surface and in the subsurface zone contributing to erosion of vessel materials, undesirable contamination and cooling of the plasma.

Should the erosion behaviour be simply related to material characteristics then the results of an investigation of mechanical sputtering in the hot section of a steam turbine (blades; boiler tube also) can be of use for the analysis of the degradation of stainless steel in fusion reactor application. Naturally, one should

0022–2461/89 $03.00 + .12

take into account the differences due to the 'beam' and the surface condition characteristics in both cases. In this experiment the investigation of degradation of stainless steel during ion beam interaction has been performed on the material of medium pressure turbine blades.

2. Experimental details

The materials selected for this investigation on surface modification were the rotating (free-standing) blades of a medium pressure 300 MW gas turbine. This study examined:

(1) parts of the unused blade (new blade) 12 row turbine, about 100 mm in length, and

(2) used blade 12 row medium pressure turbine which has been demounted after 52 000 working hours.

Parts of a new blade were exposed to an operating environment similar to that encountered in a working turbine (on the lid of the medium pressure–low pressure cylinder connecting tube). The experiment mechanical sputtering of the target, lasted 8.833 h during which the plant had been running mainly on full load. During the experiment, the turbine had undergone several short break-offs caused by various conditions. The time of delay has not been included in the time of the experiment.

The used blades for laboratory tests were randomly selected by visual examination.

After demounting the blades, we found that:

(i) on previously unused blades, even at small magnification, differences in surface structure could be noticed; surfaces facing the working fluid were suitable for analysis; other surfaces of the blade had been partially corroded due to microgalvanic element formation; all further investigations were performed on the surface facing the working fluid (steam);

(ii) on the used (old) blade further investigation of the whole blade was possible and a comparative analysis with parts of a new blade was feasible.

The investigation of the basis material properties (crystal structure and deposit) were performed using a metallurgical microscope and a SEM. The same methods have been used for the analysis of morphological changes on the surface and erosion. In addition, EPMA and X-ray analysis were used for the determination of chemical composition of the material and of the elemental distribution.

3. Results and discussion

3.1. Material characteristics

The investigation of the target materials included the determination of structural characteristics and chemical composition, the characterization of surface deposits and corrosion–erosion damage. The investigations had been performed on cross-sections and longitudinal sections of turbine blades.

The results of investigating the structural characteristics of blades (longitudinal specimen cut) are shown on micrographs in Figs 1a to c and Figs 2a to c. The material of a new blade is essentially both martensitic crystal structure (Fig. 1) corresponding to wrought heat-resisting steel. Along the edge of the blade (Fig. 1a) and in the middle of it (Fig. 1b) the structure is uniformly distributed. Higher magnification shows the fine substructure of crystals (Fig. 1c). The same investigation of the material of an old blade (Fig. 2) show initial changes on the surface (Fig. 2a) and in some areas of its middle part (Fig. 2b) resulting from working conditions. At higher magnification, fime structure of the material (Fig. 2c) with unaltered austenitic boundaries can be observed.

Quantitative analysis of the chemical composition has been performed by electron microprobe and X-ray analysis. The results of the chemical analysis are shown in Table I.

Attention has been drawn to alloying components, which for the given working conditions improve the corrosion stability (Cr, Ni, Mn and P etc) and mechanical properties (high strength and toughness) of the

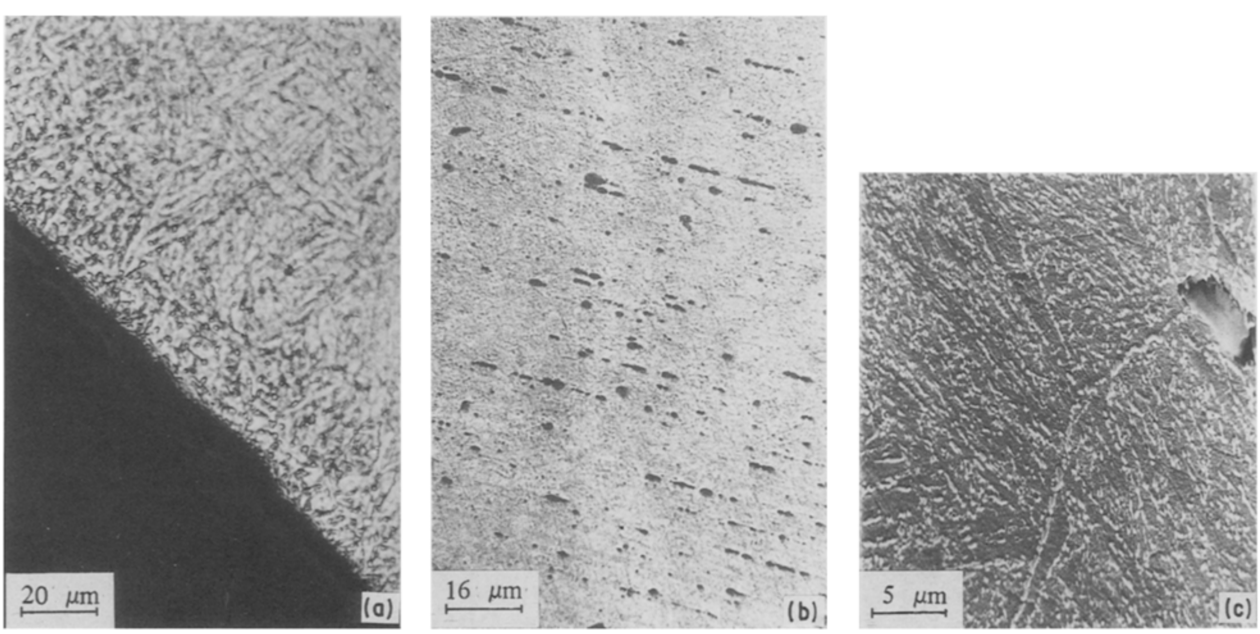

Figure 1 Optical micrographs and scanning electron micrograph showing martensitic crystal structure of a new steam turbine blade at the top (a) and in the middle of it (b) and (c). Elongated sulphide inclusions in longitudinal section are also visible.

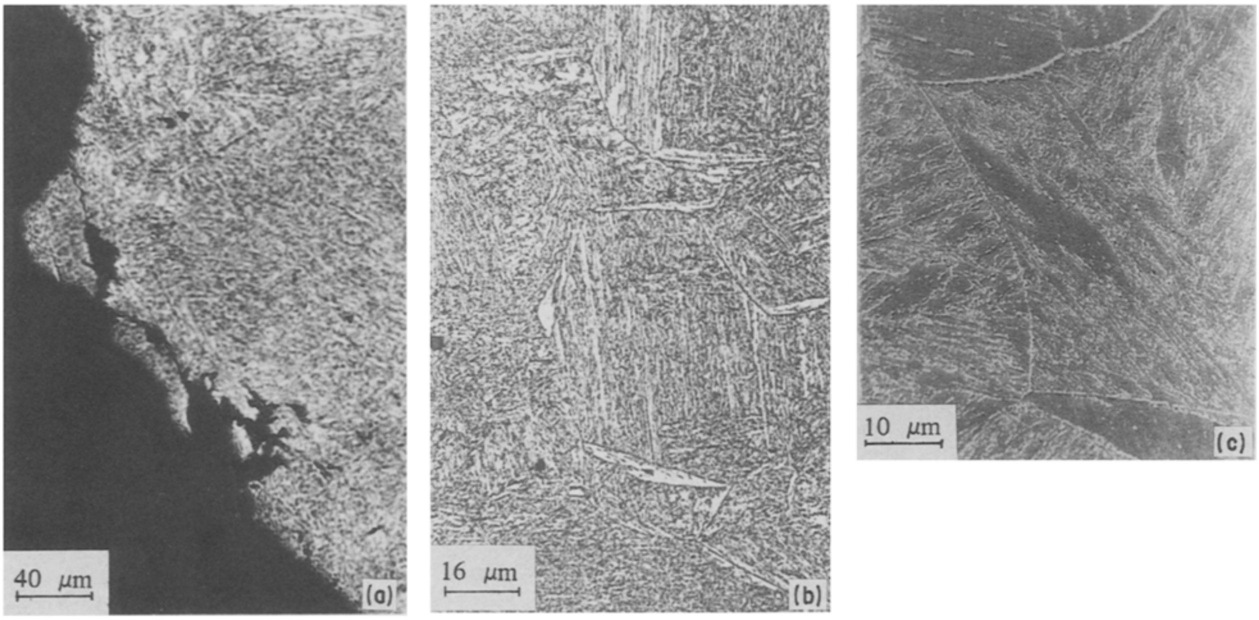

Figure 2 Changes of steam turbine blade (MP) removed from an engine after 52 000 working hours, showing surface degradation (a) and crystal structure (b) and (c) resulting from surface conditions.

material. The results of the investigation show that the material belongs to steel class 400 according to ASTM standards (422 ASTM). This class of steel includes alloys which are hardened by ultrafast cooling, and have exceptional mechanical properties after quenching and tempering. The 12% chromium steel is a widely used steam turbine blade material.

In this way we have investigated the characteristics of the 'target' material (new and old blade). The results obtained represent the zero state on which the mechanical sputtering effects (erosion of material) have been investigated.

3.2. Erosion

Overheated steam when entering the turbine contains dissolved inorganic and suspended organic components which during expansion (steam temperature and pressure are lowered) are deposited out of the vapour steam on the walls (turbine and blades). During operation a wide variety of deposits can form, if the energy of crystal lattice of material is high enough to overcome the erosion effects of overheated steam. The structure and composition of the deposit are subject to change as a function of pressure and as a function of component concentration in the steam, depending on the solubility. After several hours the deposit can be observed as a result of the morphological and other properties changes taking place in the material.

TABLE I Chemical composition of turbine blade material (%)

Element	New	Used	ASTM 422
C	–	–	0.20
Mn	0.48	0.52	0.65
Si	0.26	0.28	0.5
Cr	11.66	11.58	12.0
Ni	0.56	0.56	0.75
Mo	0.86	0.99	1.0
W	0.10	0.08	1.0
V	0.26	0.25	0.3
Fe			
Residual Elements	Nb, Ca S, P	Nb, S, P	

The results of the investigation of deposit properties on new and old steam-turbine rotating blades are shown in Figs 3 and 4. On the new blade Figs 3a to c the localized white and black deposits are structurally and compositionally inhomogeneous. Rounded crystals with spongy structure (Fig. 3a) characterize (or typify) the morphology of the deposit. At higher magnification it is observed that the porousness comes from white needle-shaped crystals, characteristic of the steam-phase deposition (Figs 3b and c). By means of chemical analysis it has been found that the deposit consists of salts (NaCl, Na_2CO_3 and SiO_2) caused by the low quality of steam (improper operating conditions). Other components on the surface of the material are iron oxides (Fe_2O_3 and Fe_3O_4), the major constituent in the black deposits. The distribution of the deposits on the old blade shown in Figs 4a and c is also inhomogeneous. Morphological characteristics of the deposits show spheroidization effects. The concentration of needle-shaped crystals has decreased (Fig. 4a). The distribution of components as well as their thickness is inhomogeneous (Fig. 4b). Qualitative chemical analysis has shown that the basic deposit components are iron, copper and silicon oxides.

The presence of other metallic oxides (Zn, Cr, Mn and Al) is less than 1%; unidentified silicates and SiO_2 are disturbed inhomogeneously in the deposit. It has been found, by means of X-ray analysis, that iron oxides, haematite (α-Fe_2O_3) and magnetite (Fe_3O_4) are uniformly distributed in the deposit. Due to such deposit characteristics and corrosion on some areas of the old blade (piting, transcrystalline and intergranular corrosion) is more pronounced. This effect has not been observed on new blades. As a result of different dilatation on the interface (deposit-base material) and poor adherence, detachment of an oxide coating from the base metal can occur. Thermal stress

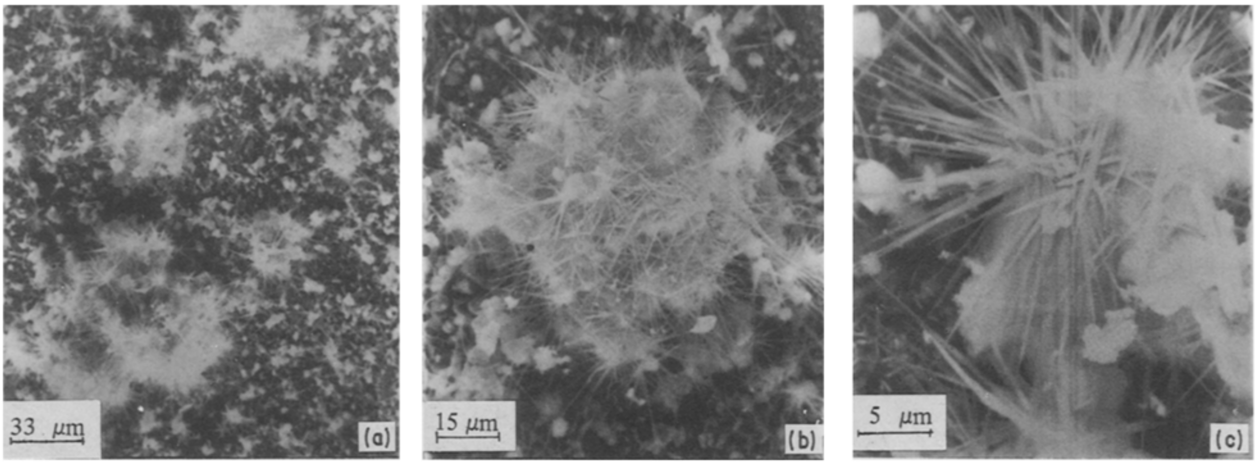

Figure 3 Spongy structure of the deposit on the surface of a new turbine blade (a). White deposit consists of needle-shaped crystals formed as a result of condensation of salts dissolved in steam (b) and (c).

and load are highest during start-up and shut-down of turbine and brittle deposits are spalled mainly in this period. Very hard oxide particles and species are carried forward by the steam which in turn can lead to further material damage is a result of mechanical action.

The results of erosion damage investigations on new blades placed in an MP–LP cylinder connecting tube, until now did not offer sufficient information on erosion changes. The possible cause for this is the 'low dose' e.g. short investigation period (8.833 h). The other possibility, that the eroded particles have been kept at the outlet of the medium pressure turbine engine, is not very probable.

The erosion of old blade has been investigated using rotating blades of a 12 row MP turbine. Three such blades selected after visual inspection, have been used for the investigation. Samples from the top of the rotating blade, from a region about 10 cm down from the top, and from the middle of the foil of turbine blade (concave side) have been used for the investigation. On some blades, erosion was examined on the thermally treated leading edge. It is to be expected that the damage will be most severe at the leading edge where the hydrodynamic intensity is the greatest.

The results of the investigation of erosion on the top of the blade are shown on micrographs in Figs 5a to c. The top of the blade is severely damaged (Fig. 5a). Morphological changes in the damaged zone have shown that the mechanism of erosion is mechanical sputtering. Its direction is from the bottom of the blade to the top (marked by an arrow). Individual collisions with beam particles occurred at glancing angles (high angle is the normal to the surface) and the energy transferred during interaction is dissipated within the surface area. Depth of damage in this zone is small. In zones not directly bordering on the edge of the blade (2 to 5 mm far from the top), two different mechanisms of damage are observed. In the first closer to the top of the blade, craters are formed during the interaction containing irregular oxide species of high hardness. A beam of very fast oxide particles, in this case, strikes the target (rotating blade) at oblique angles (Fig. 5b). The incident angle of beam particles is about 60° and greater. The particle beam path within the working fluid is short and damage due to individual impacts is clearly visible. The last type of damage in this zone (a large width of the erosion spot) occurred during the interaction with spheroidized fast moisture droplets containing oxygen, salts, and oxide particles (Fig. 5c). The initial damage is liquid-impingement erosion. The cavity shape and area depend on the surface conditions and material properties. On the wall of the cavity are trapped oxides and

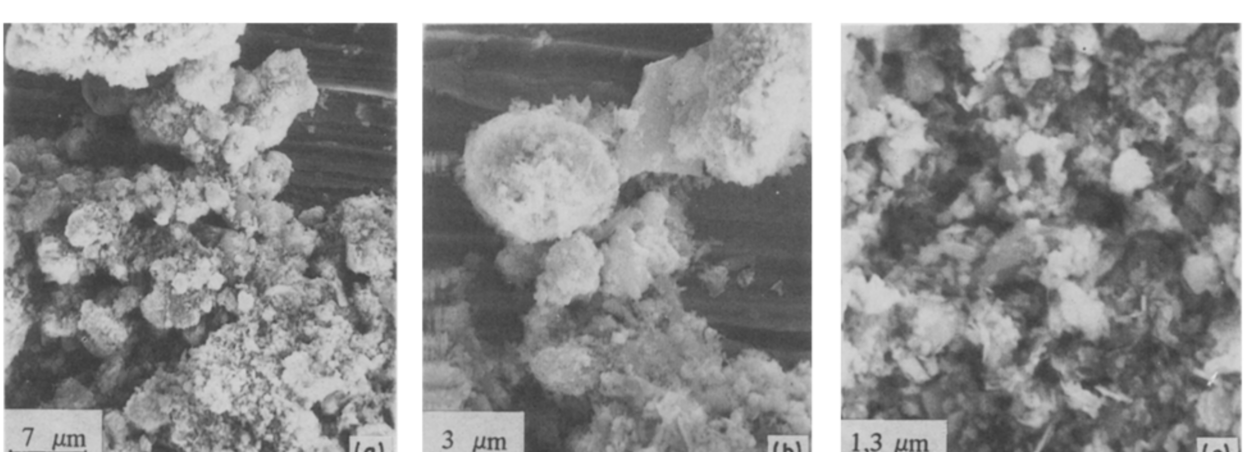

Figure 4 Morphological characteristics of the deposit on the surface of an old rotating blade (12 row). Black deposits area: spheroidization (a) and (b) and non-uniformly distribution of components (b) and (c).

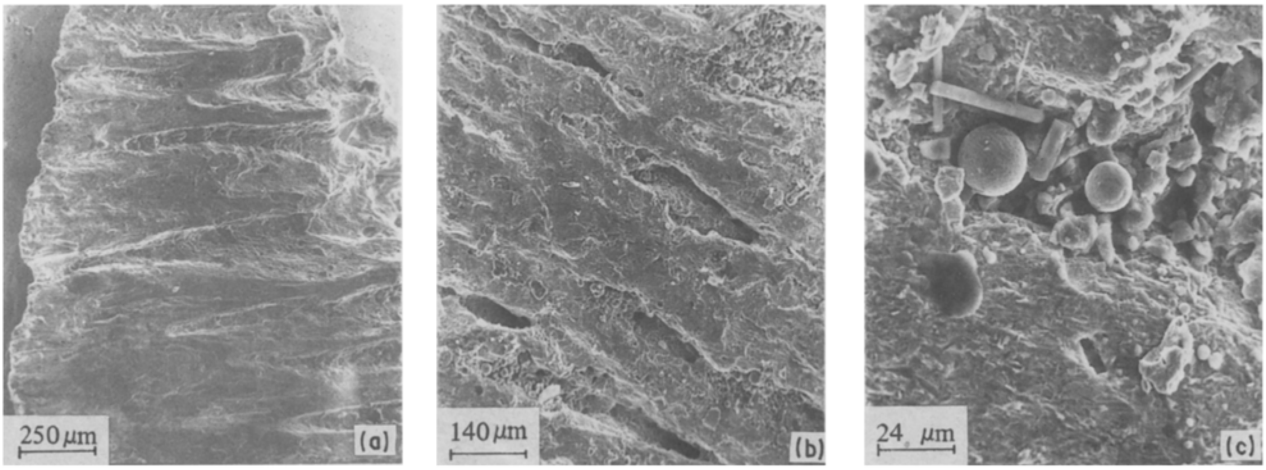

Figure 5 Mechanical sputtering on the top of a steam-turbine rotary blade: mechanical sputtering at glancing angle (a), individual impact damage (b) and fast moisture droplets interaction (c).

inclusion particles which can drastically accelerate corrosion–erosion attack.

The results of investigation in the zone extending 10 cm below the top of the blade are shown on the micrograph in Figs 6a and b. The type of damage appearing in this zone can be classified into two groups. The first group of damage is caused by fast oxide species (particles) together with the working fluid at low angle (normal) striking the target surface (Fig. 6a). The shape of the individual spots corresponds to the shape of individual irregular and polygonal incoming particles. The penetration depth is greater then at the top of the blade. The second group of damage is liquid-impingement erosion caused by liquid droplet collisions and is related to the chemical composition of the steel and its heat treatment (Fig. 6b).

Finally, Figs 7a and b shows damages that took place in the middle of the foil of the blade. The erosion was caused by individual polygonal and spheroidized oxides species going alone with overheated steam; it can be observed that oxide particles are of the same order of magnitude at places of corrosion–erosion damages (Fig. 7b). The beam incident angle is not constant but is more at right angles than at oblique angles. The depth of the damages is variable but the impact velocity of incoming particles is always very high. The second group of damage (large area erosion spot) corresponds as before to droplet collisions and to the electrochemical inhomogeneity of the material.

The erosion of the leading edge of a steam-turbine rotating blade is less pronounced that that of the base material, although the transferred energy in this zone is the highest and the incident angle of the particles is primarily at right angles rather than at oblique angles. The types of damage appearing in this case are shown in Figs 8a and b. A part of the treated surface is covered by oxide species deposited from the working fluid. Polygonal oxide grains which have been implanted into the substrate (Fig. 8a) can be observed at some places. On regions from which the protection has been removed, erosion damage is the same as in the base material (Fig. 8b) and consists of individual impact craters and liquid-impingement erosion damage with the capture of incident beam material. The reduction of the effect of the hydrodynamic intensity in this zone is obtained by local hardening of the leading edge which provides this zone with a highly erosion-resistant surface layer. The microhardness measurements confirm this hypothesis.

3.3. Changes of beam particle shapes

From the analysis of the shape and magnitude of eroded beam particles, it is possible to determine the mean free path and number of collisions. The internal structure of the oxide species of spheriodized particles

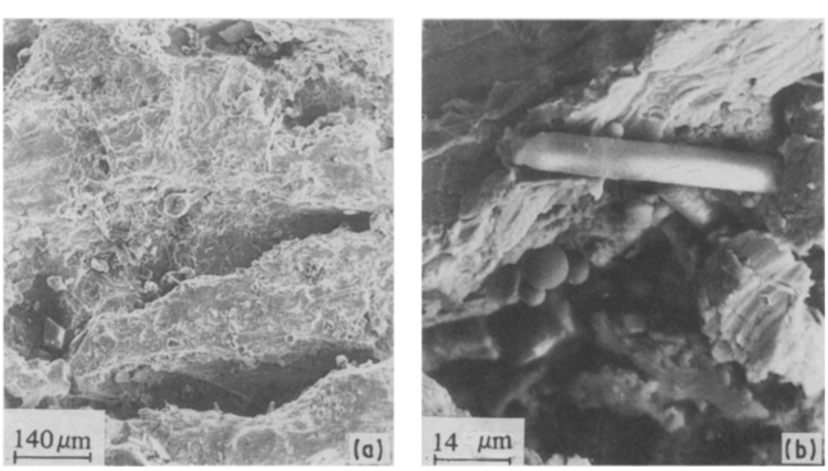

Figure 6 Scanning electron micrographs of the blade surface in the zone extending about 10 cm from the top. Damage is due to fast individual (irregular and polygonal) oxide particles at low incoming angle (a) and to liquid droplets collisions.

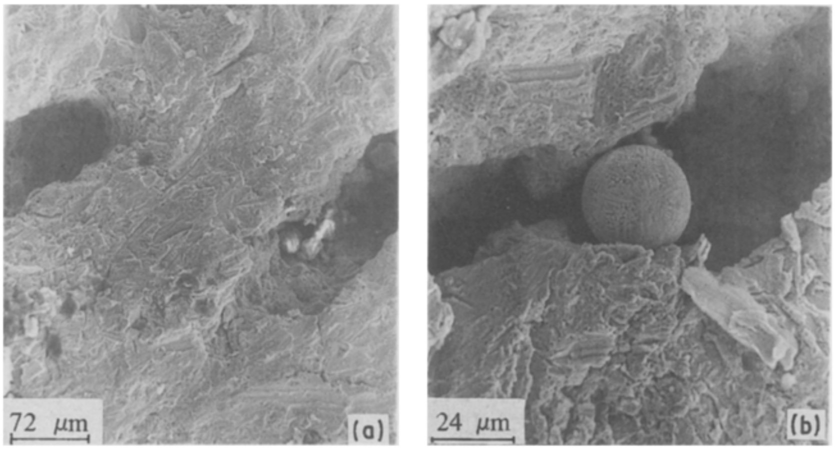

Figure 7 Scanning electron micrographs taken in the middle on the concave side of steam-turbine blade: spots correspond to the shape of individual polygonal and spheroidized fast incoming particles (a) and captured spheroidized beam particle (b).

at certain (determined) conditions can inform us about the state where it appeared, as well as about the conditions on its path. Naturally, better experimental conditions than those provided in the thermo power station are needed. However, on the basis of the statistics, we think that the following analysis can be performed.

Oxide particles and species, separated from the basic material due to the thermo mechanical stress incurred during operation, are carried by overheated steam (working fluid) through the turbine. Their velocity is lower that that of the working fluid. As they interact with the material (target) their interaction energy is changed. The largest part of the interaction energy is transferred during collisions with the rotating blades (3000 r.p.m.). It follows that the shape and magnitude of particle species are considerably changed during this process. Due to this mechanism, some species of determined shapes and sizes appear most often in some turbine zones and blade areas, although not exclusively.

The shape and size changes of 'beam particles' in some rows of medium pressure turbine blades are shown on micrographs in Figs 9a to f. Samples for the investigation have been taken at about 10 cm from the top of the blade. Species removed from the basic material have an irregular shape initially (Fig. 9a). This species is mostly seen in the second row of the medium pressure blades. The total concentration of this species in the row is low. During the interaction with the rotating blades (and other parts) species have been broken due to great brittleness of the material forming smaller polygonal grains; the shape of the polygonal grains in row 4 is shown in (Fig. 9b), polygonal grains may be combined by further collisions; rounded particles are formed mostly in row 6 of the blade (Fig. 9c). Finally, in row 8, a great number of species are spherical in shape (Fig. 9d). This shape is a result of a rather large number of collisions the 'particle' had on its long path. The observations regarding the last rows are also of interest. There a great number of 'particles' (10 at the investigated sample) with a pronounced interval structure have been found. Spherical eroded 'particles' of this type have been found in rows 11 (Fig. 9e) and 12 (Fig. 9f) of the medium pressure turbine blades. Beginnings of perlite structure (Fig. 9e) point to nucleation under conditions of continual cooling; this structure (Fig. 9f) was formed by separating austenite into ferrite and cementite. The question as to whether conditions for this formation were satisfied during the production of blades (probable), during species separation due to thermomechanical stress, or on its way through the turbine (less probable) remain open.

4. Conclusions

Results of the investigation of beam degradation of structural stainless steel used in the 'hot sections' of power plants show the following,

(1) In real devices (steam turbine, fusion devices) different mechanisms of surface degradation play an important role; one of them, mechanical sputtering (removal, etching etc.) takes a great part in erosion damage, particularly of the rotating parts of the plant.

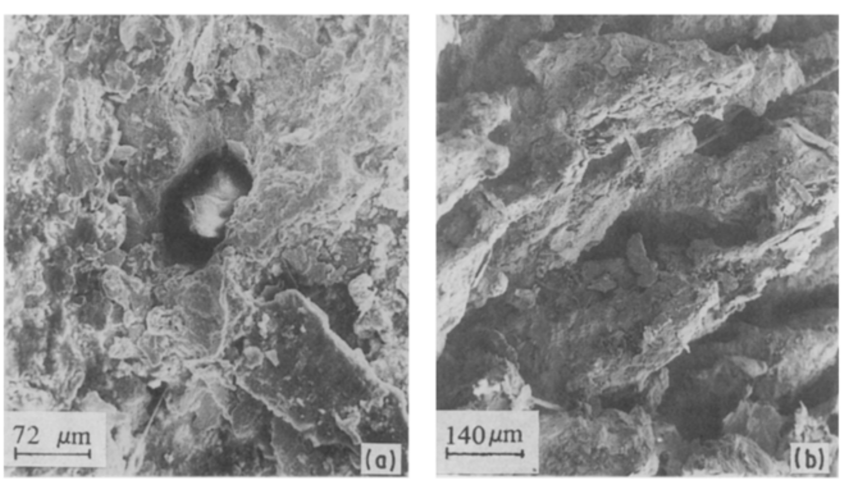

Figure 8 Surface morphology at the leading edge: implanted polygonal oxide particle (a) and a number of individual impact craters in an unprotected region where the hydrodynamic intensity was very light.

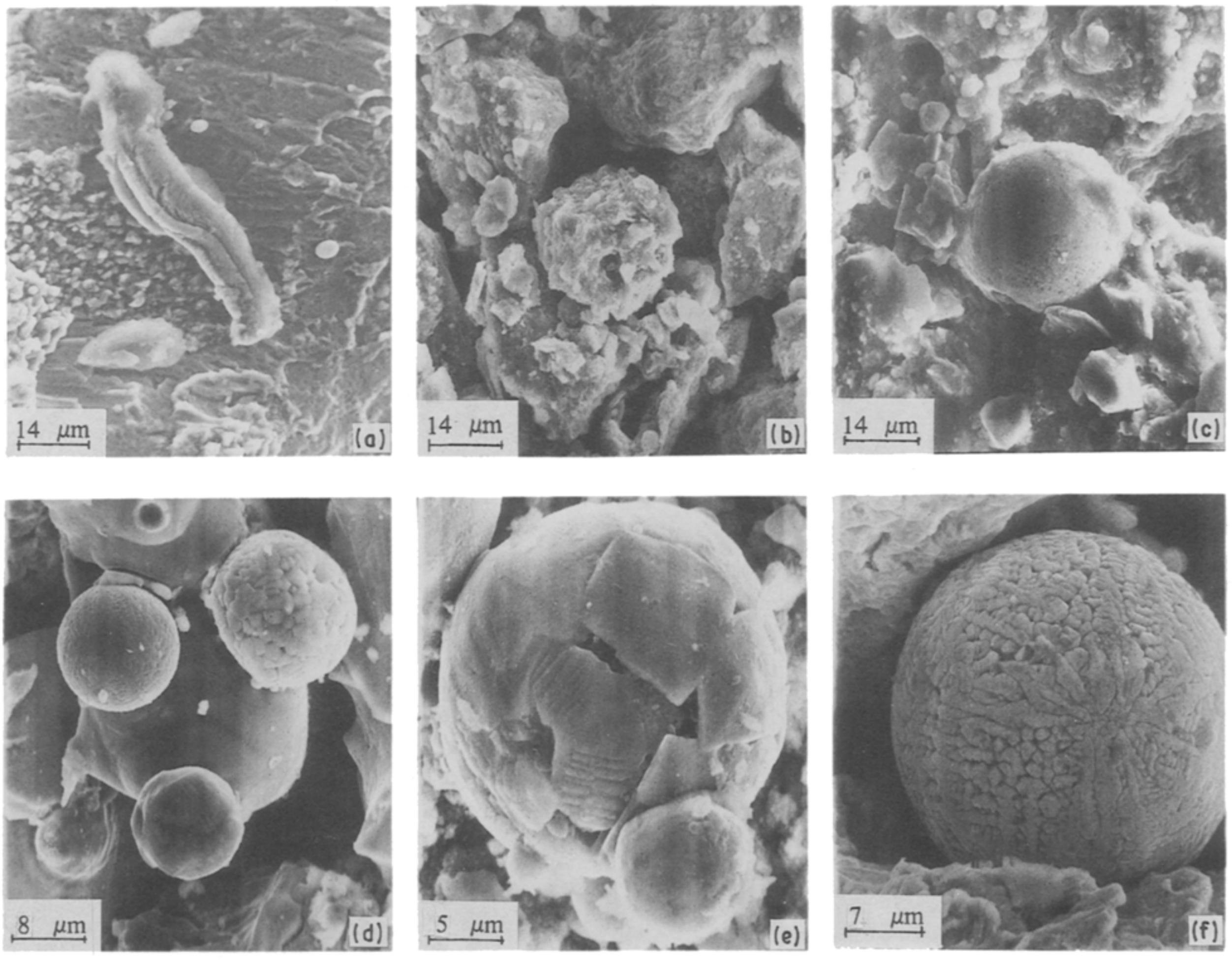

Figure 9 Changes of a beam particle shape: hard irregular oxide species (a), polygonal species-grains (b), rounded polygonal particles (c), spherical particles (d), pronounced internal structure (e) and perlitic structure of particle (f).

(2) Deposits formed on the walls of the plant contain oxides which are very brittle and hard. Due to the great thermomechanical stress, a deposit can be separated from the base material (most probably when the operating conditions change). Separated species move along with working fluid causing further interaction and surface degradation of the structural material.

(3) Morphological changes are most pronounced on rotating components (rotating blades) of the plant. The types of 'target' damage formed during the interaction can be classified in three basic groups: damage caused by individual irregular oxide species, polygonal and spheroidized oxide particle erosion, and liquid-impingement erosion as a result of interactions with spheroidized fast moisture droplets containing oxygen salts and oxide particles.

(4) Shape and magnitude of eroded beam particles change during interaction. In some "target" zones, species of specific shape and size appear more often. For well defined experimental conditions and for well known properties of materials, the change of "beam particle" shape and size can offer important information on the state of the plant and the working conditions in it.

(5) It seems that by analysing the similarities in behaviour of materials in the "hot section" of steam turbines and wall elements in fusion devices (taking care that discrepancies resulting from different beam characterisitcs and surface conditions do not arise) some useful information for the analysis of the mechanism of stainless steel degradation in both cases can be obtained.

Achnowledgements

The authors would like to express their gratitude to the NBS-Yugoslavia Joint Board Project for financial support and useful suggestions; TPS Nikola Tesla, Belgrade for the permission to perform the experiment on their plant; coworkers of the Atomic Physics Laboratory IBK-Vinča, for their help and useful discussions during the analysis of the results.

References

1. O. AUCIELLO and R. KELLY, (Eds) "Ion Bombardment Modification of Surfaces", (Elsevier, Amsterdam 1984).
2. D. M. MATTOX, Proceedings IX International Vacuum Congress, Madrid 1983, *Inv. speaker's volume* (Inst. De Fisica de Materiales, Madrid) p. 309.
3. P. SIGMUND, *J. Mater. Sci* **8** (1973) 1545.
4. B. MECKEL, T. NENADOVIĆ, B. PEROVIĆ and A. VLAHOV, *ibid.* **10** (1975) 1188.
5. T. NENADOVIĆ, N. BIBIĆ, B. MECKEL and M. MILOSAVLIJEVIĆ, *Nucl. Instrum. Meth.* **182/183** (1981) 319.
6. M. KAMINSKY and R. NIELSEN, *Thin Solid Films* **83** (1981) 107.
7. N. BIBIĆ, I. H. WILSON and T. NENADOVIĆ, *J.*

Appl. Phys. **53** (1982) 5250.
8. R. BERISCH, (Ed.) "Sputtering by Particle Bombardment", (Springer, Berlin, 1982).
9. J. A. BORDERS, Sandia Report SAND 82-0601, 1982.
10. J. de JONG, R. L. WANG and F. M. SARIS, *Phys. Lett.* **90A** (1982) 147.
11. J. E. ROTHENBERG and R. KELLY, *Nucl. Instrum. Meth.* **B1** (1984) 291.
12. T. MIHAČ and T. NENADOVIĆ, *Proc. Phys. of Ionized Gases, Šibenik* 1984, (Word Scientific Publishing Co., Singapore) p. 553.

Received 1 August 1988
and accepted 5 January 1989