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THE EVOLUTION UNDER STRESS OF THE SUPERALLOY/PROTECTIVE COATING INTERFACE

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Abstract

NiCoCrAlYTa coatings are frequently used to protect the components in the hot path of the gas turbines engines. A careful selection of the coating that offers sufficient chemical compatibility with the substrate and a low interdiffusivity is necessary for these high temperature systems. The diffusional phenomena of single-crystals, [001] oriented, of the AM-3 superalloy coated with a Low Pressure Plasma Spray (LPPS) NiCoCrAlYTa coating is described at two fixed times (8 hours and 89 hours) at 1323 K (1050°C) under different types of loading. The experimental conditions comprise oxidation treatments, creep and four point bending stress controlled tests with two different cycles 10-300-10 seconds and 10-10-10 seconds. Using the information obtained from Energy Dispersive microprobe Spectroscopy (EDS) the diffusional phenomena between the coating and the substrate is characterised and correlated with the chemical nature of the substrate and with the different types of loading.

Introduction

The increasing demand for higher fuel efficiency and lower maintenance costs by increasing the components life, have lead the manufacturers of aeronautical engines to develop different materials and their associated coatings for every specific application in the engine. The requirements on every section of the engine are not the same and particular solutions have been given each one of them. In many cases, it is not possible to fit the correct buck mechanical properties and the surface behavior for a given component. It rises them the need for the developing of protective coating. The deposition techniques, the microstructural complexity and the functions of the coatings have evolved allowing to use some component in very demanding and hostile working environments. The initial coating design was a mono-functional, thus the coating was conceived as protection for a particular surface problem. Coating are now facing a new challenge of being designed for coping different simultaneous functions (e.g. protection against high temperature and abradability) The engine hot section components face degradation by erosion and oxidation. These components are normally protected with protective coatings that could be fundamentally of two types: metallic coatings and thermal barrier coatings. The first are used to assure an oxidation protection against the hot gas passing trough the turbine areaand are the focus of interest of this work. This type of coating is applied normally by inert gas plasma spraying also known as Low Pressure Plasma Spraying (LPPS) to achieve coating without oxidation traces and with a elevated degree of compactation. These coatings are 70-100 μm thick and consist basically in alumina formers and stabilisers. The coating design follows the guidelines of keeping the aluminum activity and content as high as possible in the surface-subsurface region so as to form a protective, highly adherable alumina coating

Experimental

Monocrystalline, [001] oriented, samples of the AM-3 superalloy, characterized by a γ ' cube size of 0.7 μm, and with a Low Pressure Plasma Spray (LPPS) NiCoCrAlYTa coating (70-80 μm thick) (measured composition presented in Table 1) were submitted to high temperature tests in order to evaluate the influence of the stress state on the interdiffusion between the coating and the substrate. All the tests were performed at 1323 K (1050°C) and two test times were chosen: 8 and 89 hours. For all the mechanically stressed test conditions the value of the applied stress was fixed at 140 MPa. Three different loading modes were used to stress the samples : four point bending isothermal low cycle fatigue (under stress control using either a 10-300-10 s. cycle, or a 10-10-10 s. cycle) and creep. The diffusion profiles obtained under applied stress were compared to those in the unstressed condition (oxidation tests) as well as to other results under different temperatures and/or stresses for the same times, to establish the contribution of the different parameters (time, temperature , stress, loading mode, stress sign) on the diffusion phenomena. Scanning Electron Microscopy (SEM) as well as Energy Dispersive microprobe Spectroscopy (EDS) were performed at each condition to determine the microstructural evolution and to characterise the interdiffusion phenomena between the substrate and the coating correlating them with the test parameters. The EDS analysis was carried out using a 10 μm x 10 μm scanning area moving it 5 μm at each point of analysis; the resulting 5 μm overlapping of the analysis zones give smoother profiles. K-ratios gain factors were corrected using a reference sample of known composition.

After all thermal treatments (solution treatment + ageing treatments) the microstructure of the coating consisted basically of γ matrix (Ni-rich solid solution) with a dispersion of β phase (NiAl) , along with some Ti an Ta rich precipitates near the coating/substrate interface

Table 1: Measured chemical composition in weight percent of the monocrystalline substrate alloy and the LPPS coating.Ni balance.

	Co	**Cr**	**Al**	**Ta**	**Y**	**W**	**Ti**	**Mo**
AM-3	5.6	8	5.9	3.5		4.9	2	2.2
Coating	23	20	8.5	1	0.4			

Table 2 Standard thermal treatments for the AM-3 superalloy

THERMAL TREATMENT	Temperature (°C)	Time (hours)
SOLUTION (**S1**)	1300	3
AGEING 1 (**A1**)	1050	16
AGEING 2 (**A2**)	850	24

Results and discussion

Some degree of plastic strain was observed for both 89-hour fatigue tests under different conditions. The basic kinematics assumption of the flexure theory asserts that the plane sections through the beam taken normal to the axis remain plane after the beam is subjected to bending. This assumption remains applicable even if the materials behaves inelastically. That means that even with an inelastic material's behaviour and with no further assumptions, the strain in the fibbers of a beam subjected to bending remain being dependent upon their respective distances from the neutral axis. In all the cases no cracks have been detected in the coating

The AM-3 superalloy with a NiCoCrAlYTa coating has noticeable reduction in its creep life. The four-point bending isothermal low cycle fatigue at 1423 K (1150 °C) and 80 MPa was carried out during 89 hours under a 10-300-10 cycle without failure of the coated sample. For the same temperature and stress conditions, the uniaxial creep life of a bare sample (which is longer than for a coated one) is less than 89 hours,. confirming that the high temperature useful life of a component is controlled basically by its creep resistance. However the intensity of the diffusion exchanges is not higher during creep than during other testing modes. Figure 1 shows that for a given temperature, oxidation test samples present a bigger Diffusion Affected Zone

(DAZ) than those submitted to creep. For a given testing mode the key parameter is temperature (see Figure 2).

The mechanical response of the coated samples to the four point bending fatigue tests until 89 hour could be described as follows: during the first 30-40 hours the strain rate remain decreasing until a sudden acceleration and the passage to new stable step .

A very first hypothesis was the transition phase could be the result of the penetration of the four point bending rod inside the coating until reaching the substrate. In order to verify or disqualify this hypothesis, coated samples, in which the coating was mechanically removed from the points of contact, were submitted to the fatigue tests under the same condition with identical results. It seemed evident that a strain mechanisms shift had occurred. More studies are required to clearly understand the precise nature of the strain mechanisms as a function of the formation of dislocation networks and their mobility as a function of the evolution of the gamma /gamma prime misfit stress and the gamma matrix short range chemical order (all this as a function of time).

As a consequence of the relative insignificance of the wave shape for dwell cycles, the frequency and hold time are considered together. The effect of frequency on the strain behavior of the coated superalloy translates into a reduction of 20 percent on the strain rate for the 10-10-10 sec against the 10-300-10 sec. cycle for both the coated and the bare samples. In general this confirms the fact that for many engineering materials, creep is the most important damage mechanism and therefore due attention must be paid to the loading history and the stress state. The curves run parallel and the differences are kept constant during the whole tests times. For a given frequency, the coated samples showed a higher strain rate than the bare samples. As per the frequency effects on the endurance, the results seem to indicate that the factors influencing the creep life or the degree of time-dependant strain (the presence or not of a coating, reducing the frequency for increasing the creep character of the test) are the key factors in determining the creep-fatigue life of the studied four point bending tests. This seems to confirm the fact that the processes of creep and fatigue only co-exist over a narrow range of conditions and any interaction is of minor significance in determining the long term behavior of engineering materials (which are basically determined by the creep factors, without influence of the environment in this case) For every condition, the observed strain rates and strains are lower (for the same period of time) than these observed during creep.

The strain sign inverting tests show that when the sample was rotated for the second half of the test, the strain vs. time curve show signicantelly lower strain rate values. One possible explanation come from the fact that the gamma channels that were normal to the stress axis find themselves parallel to the new stress direction. The gamma channels normal to the stress direction in the tension side in the first half of the tests were those in which the dislocations network were formed (since they were the largest channels and, thus, where the dislocation motion was easier). For the second half of the test, the gamma corridors that were parallel in the tension side of the sample are subjected to the dislocation flow. Since these corridor are narrower , the friction forces on dislocations is higher thus reducing the overall strain of the samples.This observation remains valid whether the samples are coated or not. In the case of the bare samples it could be added that the global strain achieved is lower than for the MCrAlY coated samples.

The driving force for rafting seems to be related with the unequal stress states which develop during stressing-straining in the gamma channels lying parallel or perpendicular to the stress axis [001] as a result of the superposition of the external stress and the coherency stresses. Thus, an external axiale (compressive) stress reduces the compressive strain energy in the vertical gamma channels relative to that in the horizontal gamma channels. The resulting gradient acts as a driving force for diffusional mass transport between the two types of channels. The time dependence of the above mentioned fact leads to an almost not measurable effect of 4 + 4 hours reverse test but for the 44.5 + 44.5 hours tests, it seems clear that the diffusional transport between this type channels is more difficult than at the beginning due to the three dimensional dislocation networks and by the already rafted structures (which means that the chemical potential is such as to refrain the microstructural evolution under changed sign stresses). It has been established that high temperature cyclic damaging can be separated into time-dependent and cycle dependent components. The time-dependent damaging could be either creep or environment controlled. The cycle dependent part is regarded as pure fatigue. As temperature is increased or frequency reduced, time-dependent damaging mechanisms take place.

FIgure 3, shows that even after 89 hours of four point bending fatigue test at high temperature, rafting is not highy in evidence for the neutral and compression fibers of the test samples. This contrast with the rafting behavior of the gamma prime phase under tension condition; after 8 hour, clear rafted plates are observable normal to the stress direction (Figure. 4)

The oxidation concentration profiles for the 89 hours show narrower DAZ than the oxidation concentration profiles for the 8 hours tests. It seems possible to figure out that in the absence of any stress the first atomic movements are driven by the differences in the chemical potential (basically dictated by the concentration differences) between the coating and the substrate ; but for longer times once the coating begins to lose part of its species (those related to formation of the oxide protective coating at the coating's surface and those that have already migrated to the substrate), the tendency may be reverted. If so, the results obtained for the compression side of the fatigue samples (for both the 10-10-10 s. and the 10-300-10 s. cycles) are interesting since for this condition the mechanically driven and the chemically driven diffusion movements are opposed. Since the reduction in the DAZ is not observed for the compression side of the fatigue samples it would indicate that for this condition mechanically driven diffusion prevails preventing (or slowing down) the atomic movements from the substrate to the coating. In order to relatively quantify the influence of each parameter it is necessary to take into account that the chemical potential at a time $t_0 + \Delta t$ is smaller than at t_0 since the differences in composition have been reduced due to the interdiffusion. Practical applications of the previous observation could be interesting, since (if confirmed in real gas turbine working conditions) the blades zones under compression (e.g. leading edges) will have a greater undercoating modified zone and the coating will lose it protective properties faster than in the tensile zones of the blade.

The coating initial γ (Ni rich solid solution) + β (NiAl) microstructure have been transformed into a $\gamma + \gamma'$. system for the regions under stress (whether traction or compression) and to a $\gamma+\beta+\gamma'$ microstructure on the neutral axis of the sample after the fatigue tests. The size of the gamma prime clusters is basically the same for the stressed and unstressed regions. The $\beta \rightarrow \gamma' \rightarrow \gamma$ transformation sequence seems to be confirmed for the NiCoCrAlYTa coating under four-point bending isothermal low cycle fatigue. The size and location of the blocky gamma prime phase remain constant for both tension and compression for a given loading state. For the creep test, only the $\beta \rightarrow \gamma$ transformation is observed. The coating shows a β depleted zone at the outer region of the coating (the beta phase have been dissolved to provide the required aluminum to form the protecting alumina layer)

Bare samples submitted to four point bending fatigue tests develop an oxide layer, 25 μm thick, and the gamma corridors show a significant degree of internal oxidation of the superalloy matrix (Fig. 5).

Figures 6 and 7 show the microstructural development for the stress sign inverssion tests. It seems that after a first half of the test under compression and the second under tension, the microstructure, the gamma prime rafts, are basically oriented as a function of the latest stress sign (tension). However when the sample was first submited to tension and then to compression, no specific γ' orientation (rafting) occures and the structure shows only isotropically coarsen precipitates. The discussion regarding the phase transformation sequences in the coating remaing valid for the stress sign inversion tests (fig. 8).

In the 8 hours tests (4 + 4 hours) the "tension + compression" and the "compression + tension" diffusion profiles are almost identical with the only difference that the Ta enrichment occurs inside the substrate in the case of "tension + compression" and inside the coating for the "compression + tension" samples. the "neutral-neutral" profiles show no significant differences in the equilibrium concentration with respect to the previously described profiles; the Ta distribution is similar to the "compression + tension" samples. The 89 hours tests (44.5 + 44.5 hours) profiles show differences between the "tension + compression" and the "compression + tension" sides of the samples. The "compression + tension" side show smaller equilibrium concentration values in the coating.The "neutral-neutral" sample shows the smallest concentration values even if the DAZ is of the same dimension of the "compression + tension" side. The "tension + compression side show a rather limited DAZ (around 20 μm) with the highest concentration values.

Conclusions

- The interdiffusion phenomena across the substrate/coating interface is not only dependent on the stress state but also upon the nature of zone beneath the coating (e.g. γ ' rafting behavior).
- Two similar rafted gamma prime sub-coating microstructures do not necessary lead to similar interdiffusion phenomena.
- Some microstructural transformation sequences are influenced by the nature of the loading, by the stress state and the frequency of the loading.. In particular the $\beta\rightarrow\gamma'\rightarrow\gamma$ transformation sequence seems to be stress dependent (not observed under oxidation nor under creep test conditions); time dependent, frequency dependent (size of the blocky gamma prime depends on the fatigue test loading frequency) and finally insensitive to stress sign (transformation sequence is followed in all the cases for the stress sign inversion tests)
- The high temperature useful life of a component is controlled basically by its creep resistance.

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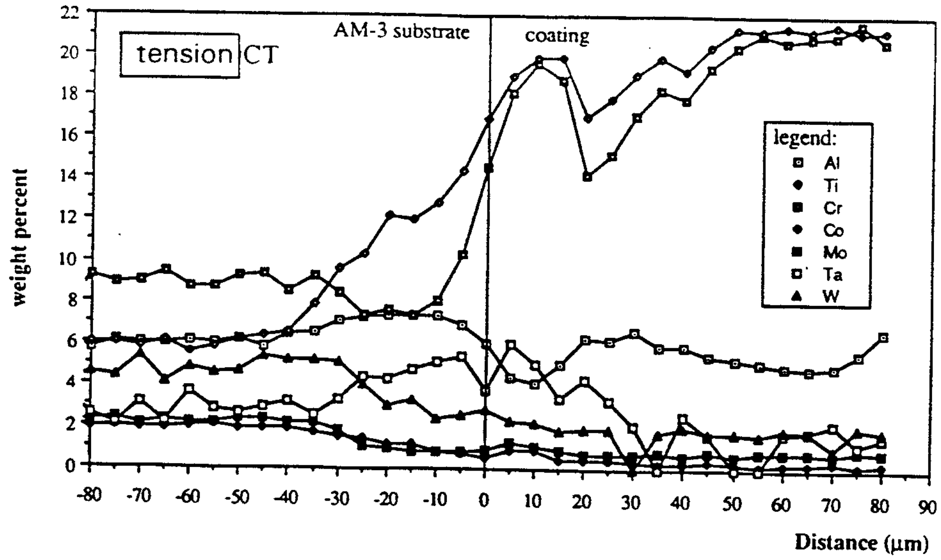

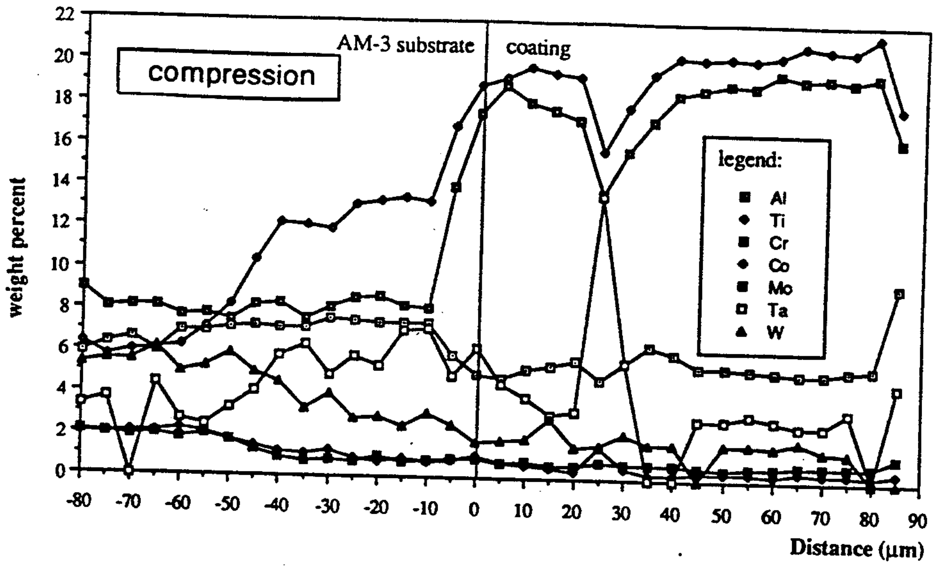

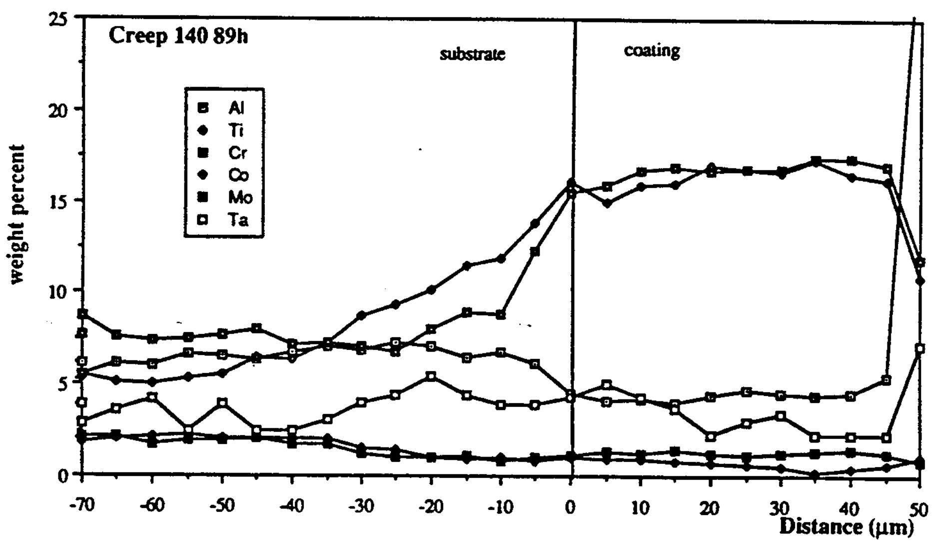

Figure 1 : diffusion profiles for 89 hours at 140 MPa and 1323 K .
four point bending fatigue (a,b) and creep (c)

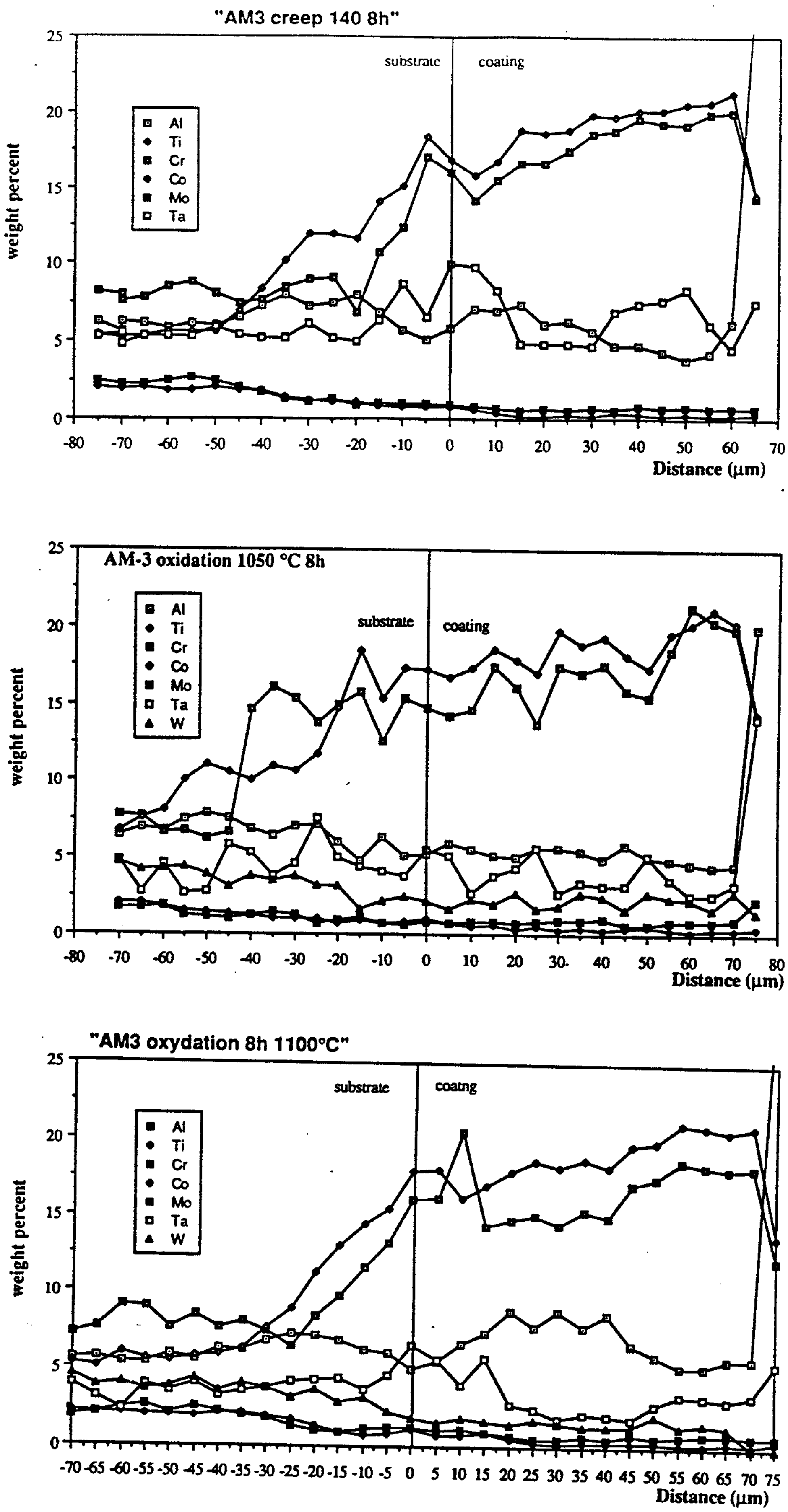

Figure 2 :diffusional profiles for the AM-3 superalloy during 8 hours under different temperature and stress conditions

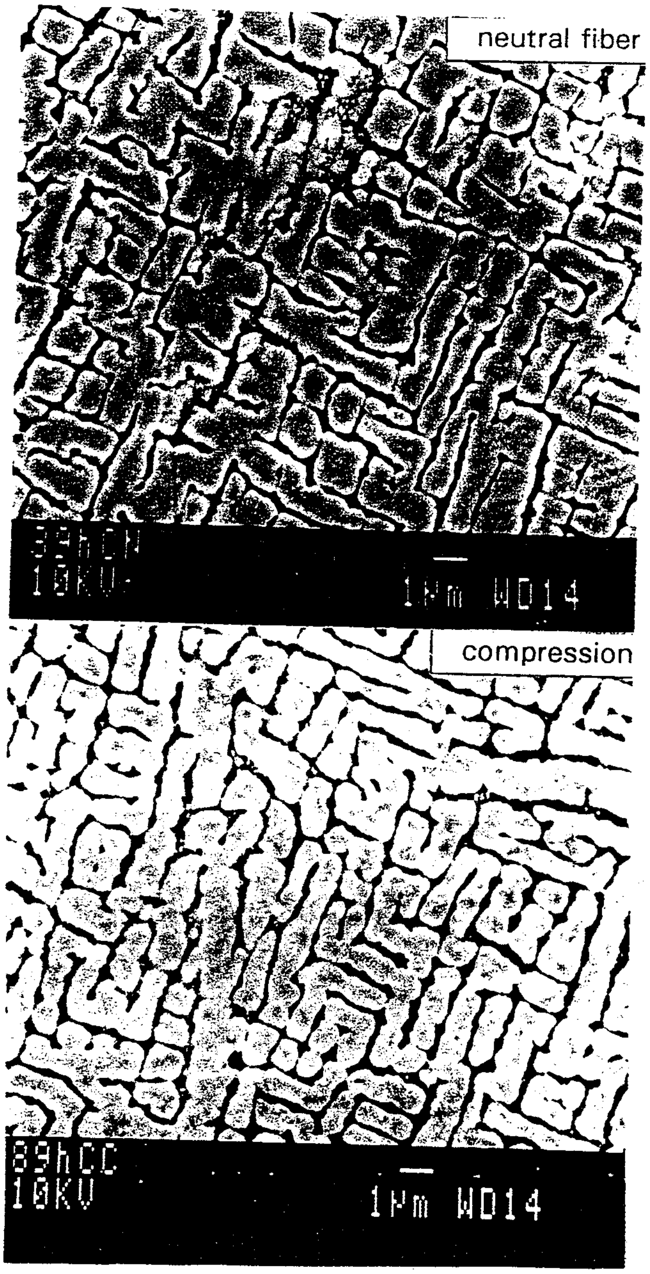

Figure 3: Microstructure after 89 hours of four point bending fatigue test.

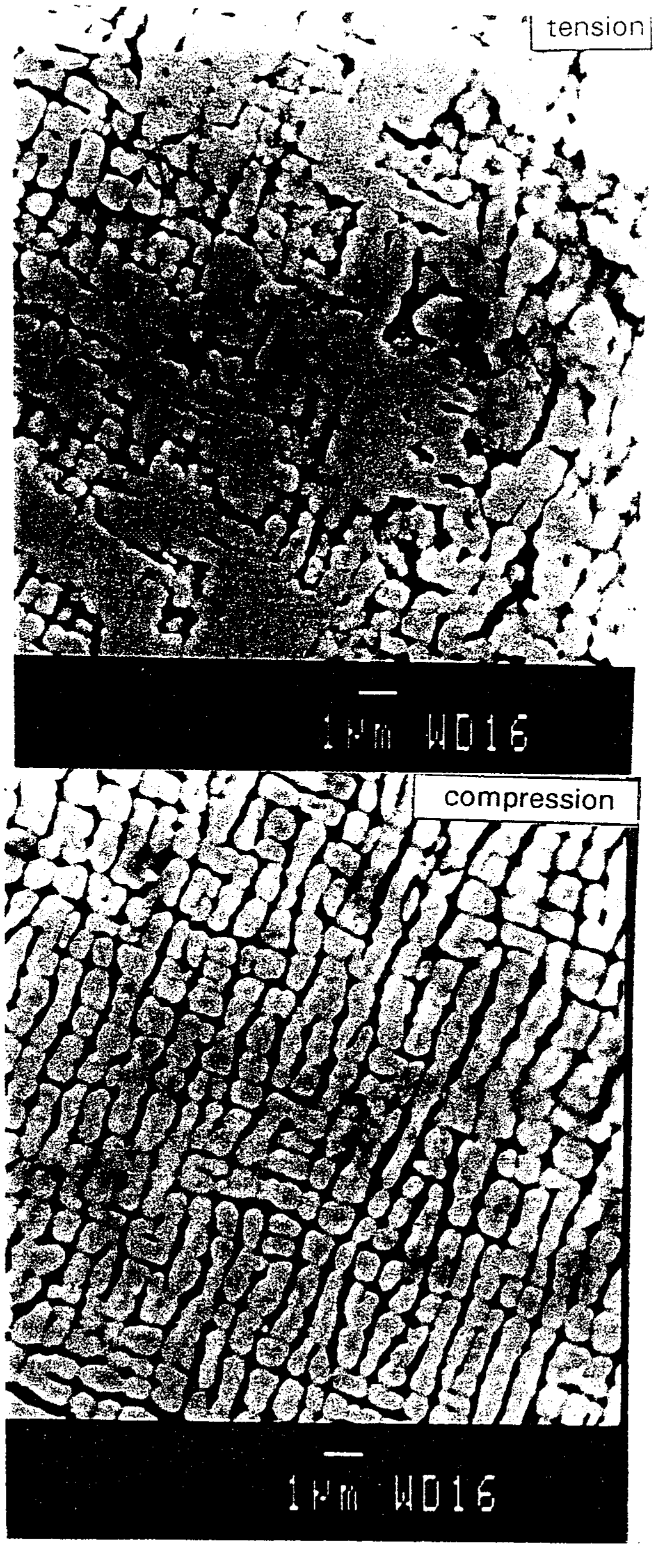

Figure 4: Microstructure after 8 hours of four point bending fatigue test.

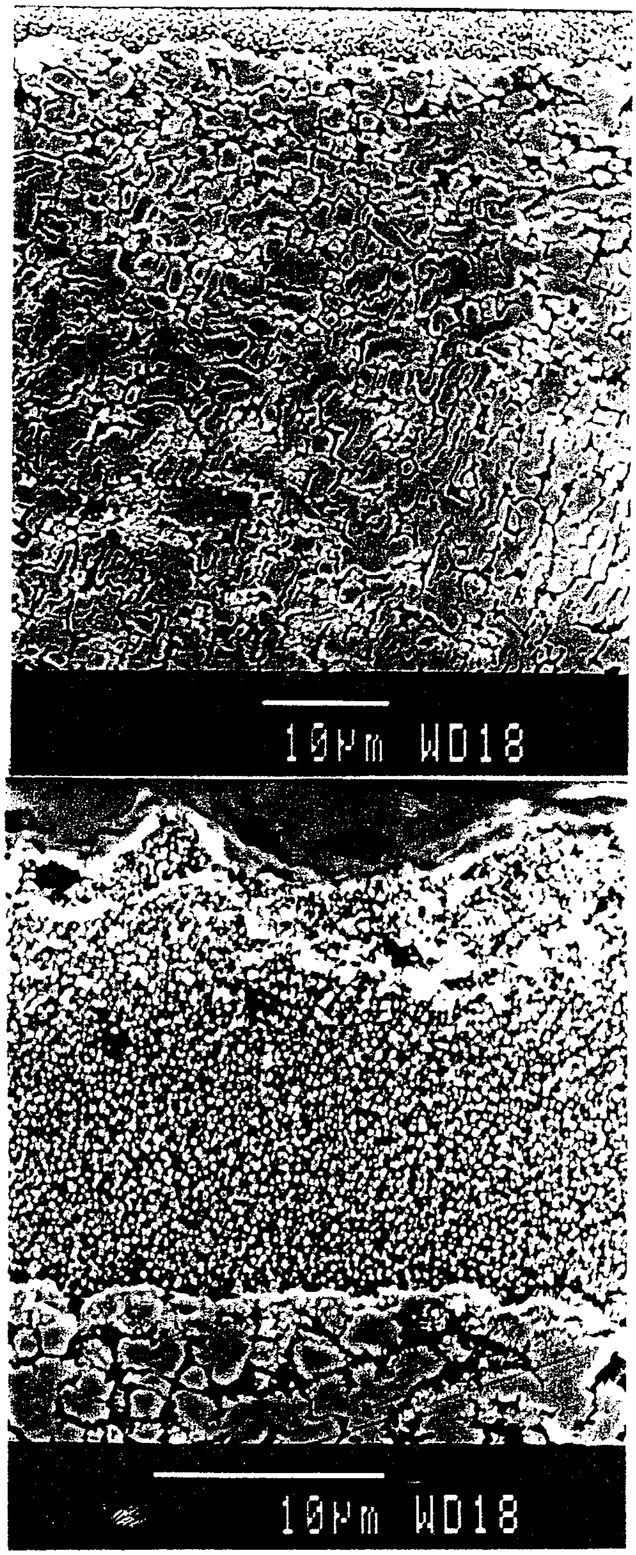

Figure 5: Oxidation phenomena.

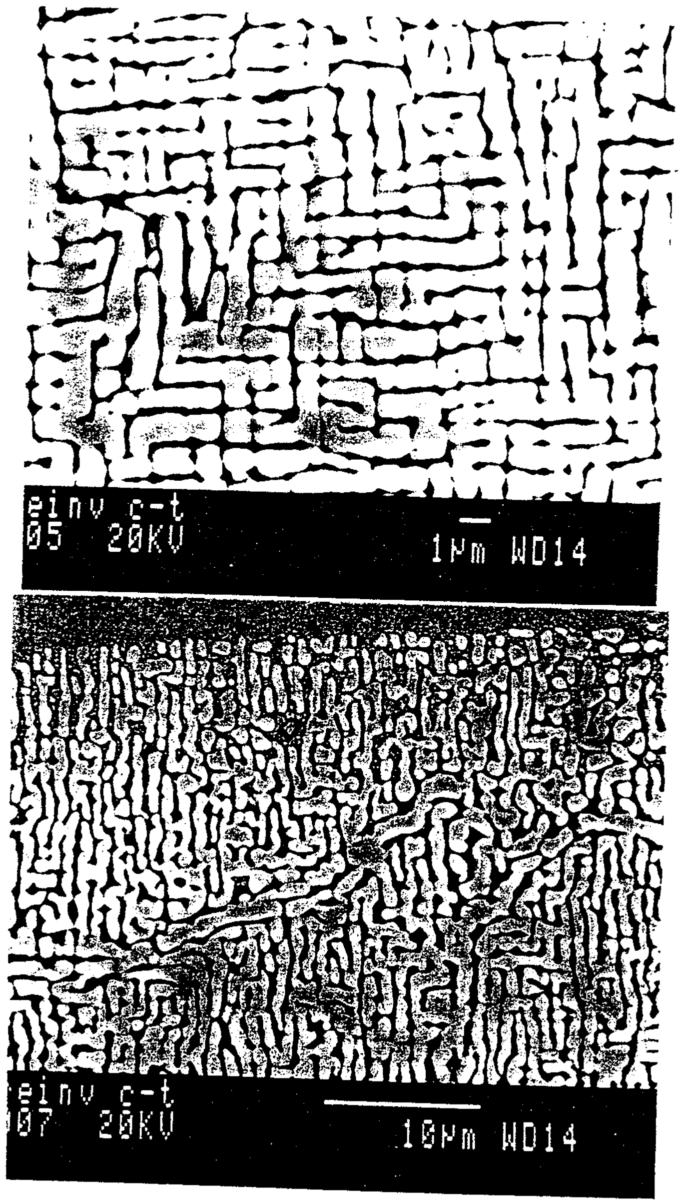

Figure 6: Microstructure after 8 hours reversed of four point bending fatigue test.

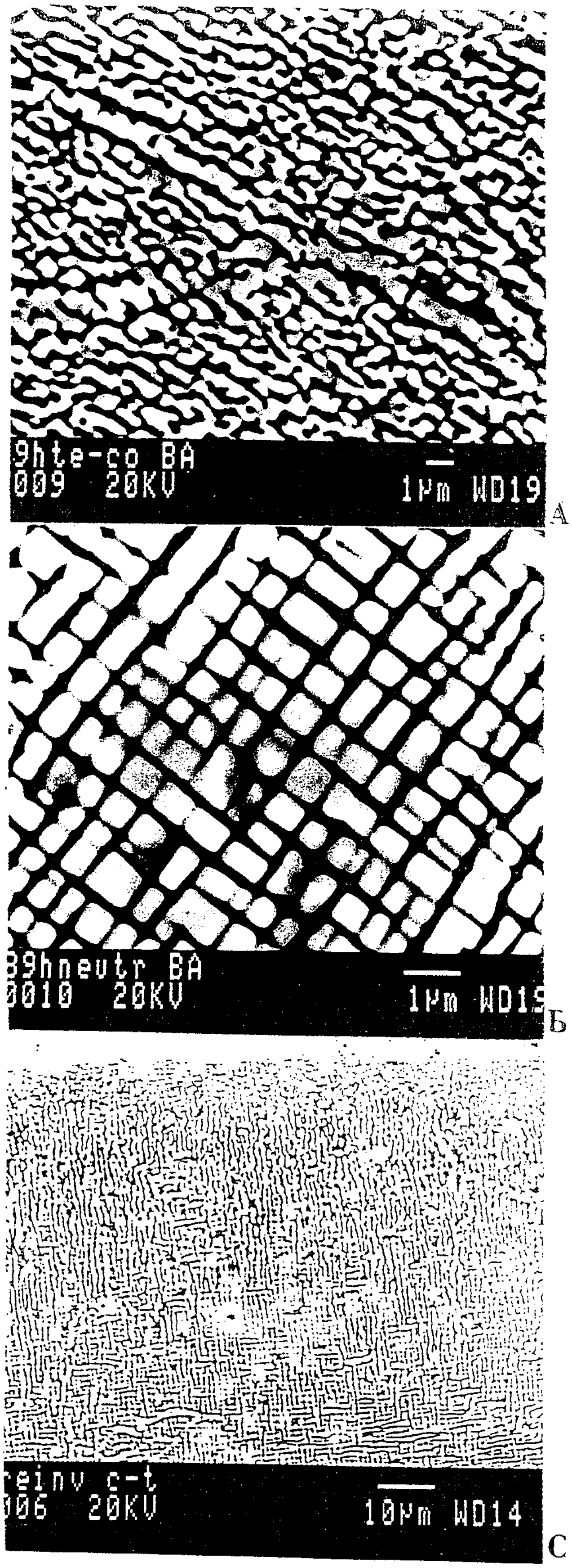

Figure 7: Microstructure after 89 hours of four point bending fatigue test.

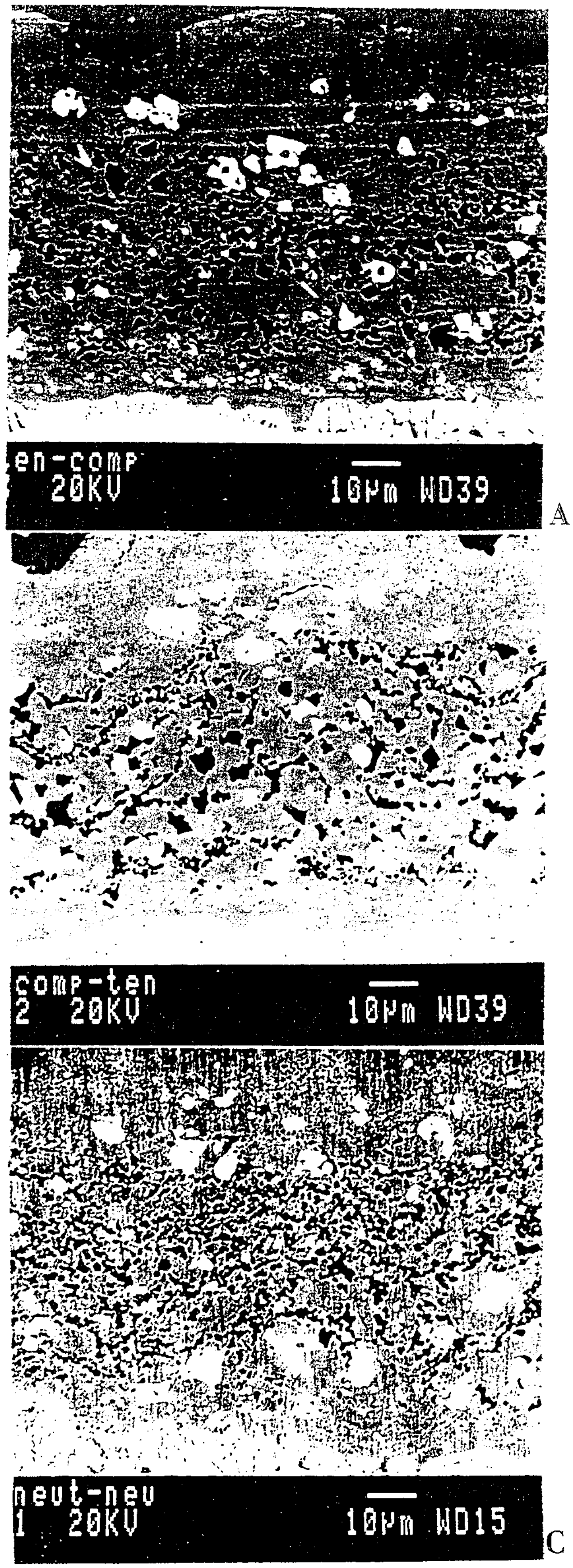

Figure 8: Coating after 89 hours of four point bending fatigue test.