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Influence of thin coatings deposited by a dynamic ion mixing technique on the fatigue life of TITANIUM ALLOYS

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The technique of dynamic ion mixing involving a physical vapour deposition method and a simultaneous ion implantation has been used in order to improve the fatigue resistance of two titanium alloys. This process allows the deposition of adherent NiTi and SiC amorphous coatings of the order of 1 μm thick. Both treated substrates have been tested at room temperature in the low cycle fatigue range, revealing significant fatigue life improvement. NiTi and SiC films modify the surface deformation mechanisms of fatigued materials and largely suppress or delay crack initiation. These effects depend, however, on the nature of the film, the microstructure of the substrate and the stress amplitude applied during the fatigue tests. To explain the fatigue results, the mechanical properties of these thin films have been characterized by different techniques: scratch-tests, micro-Vickers indentations, Young's modulus measurements by a resonant frequency method and "fracture stress" determination by *in situ* tensile tests. The results have shown that their mechanical properties are very different to those of the corresponding classically deposited solid materials and are influenced by the film thickness. The results are discussed according to the mechanical properties of the coatings and the substrate deformation and damage modes associated with their microstructure.

1. Introduction

In titanium alloys, as in most homogeneous metallic materials when cyclically deformed, microcrack nucleation takes place from the surface and cracks grow progressively into the bulk. Indeed, the free surface modifies the strain and stress state of the first atomic layers and allows the emergence of slip bands within the surface grains [1, 2] or the development of microsteps at grain boundaries or others interfaces [3, 4]. It is well known that such processes constitute preferential sites for fatigue crack nucleation [5–8]. Consequently, the application of surface treatments is a potential way of limiting or suppressing fatigue crack nucleation sites by modifying the mechanical, physical and chemical properties of surface layers.

Over the past few years, we have studied the influence of thin films fabricated by the dynamic ion mixing (DIM) technique on the fatigue resistance of metallic materials. This technique, which has been described previously [9], has been developed in the "Laboratoire de Métallurgie Physique" of the University of Poitiers. It involves a coating deposition method (physical vapor deposition) combined with a simultaneous high energy ion implantation. Such a method permits the fabrication of amorphous or nanocrystalline films with thicknesses of the order of a micrometer [10–12]. These thin coatings exhibit a gradual and mixed interface with the substrate, resulting from a spatial redistribution of atoms over relatively long distance which favors their adhesion [13, 14].

It has been shown previously that DIM coatings, specially NiTi films, have considerable beneficial effects on the fatigue resistance of ductile substrates such as stainless steel [15, 16]. For the stainless steel studied, the coatings had to accommodate longitudinal deformation due to the cyclic loading conditions. They had also to accommodate shearing deformation due to the localization of the plastic deformation in the substrate. Indeed, the persistent slip bands in the bulk which tend to emerge at the surface induce stresses at the interface coating/substrate and in the coating. The best results have been obtained when a good compromise was reached between the mechanical properties of the films (low Young's modulus, ductile or brittle character) and the deformation conditions imposed upon the coating by the substrate during fatigue tests [17].

The aim of this paper was to investigate the effects of DIM NiTi and SiC coatings on the fatigue properties of two different ($\alpha + \beta$) titanium alloys. On such substrates, which have strong elastic properties, the coatings have to accommodate higher cyclic total deformation than on steel substrates. On the other hand, the deformation of the coatings in the shearing mode is much smaller.

The first part of the paper presents the fatigue results for coated materials and also the mechanical properties of the DIM films. The following discussion will take into account these specific properties and the different deformation and damage modes of the titanium substrate, which differ according to its microstructure.

2. Experimental procedure

2.1. Fatigue tests

Smooth cylindrical specimens with a diameter of 6 mm were used; they were mechanically polished with a 0.25 μm diamond paste. Fatigue tests were carried out at 0.25 Hz, in air, at room temperature, in a symmetrical uniaxial push-pull mode ($R = -1$), under stress control. Tests were performed at an amplitude of $\Delta\sigma/2 = \pm 750$ MPa for Ti–6A1–4V alloy or at ± 750 MPa and ± 850 MPa for the lamellar Ti 6246 alloy. These stress amplitudes were lower than the yield stress for each alloy (Table I).

2.2. Materials

The Ti 6A1 4V type titanium alloy (80% of primary α) presents a heterogeneously globulized structure consisting of important colonies of aligned coarse α platelets surrounded by small equiaxial grains [18]. The second titanium alloy is Ti–6A1–2Sn–4Zr–6Mo β forged (Ti 6246) with a lamellar structure, the primary α platelets having lengths between 3 and 50 μm. Some mechanical properties of both alloys are indicated in Table I.

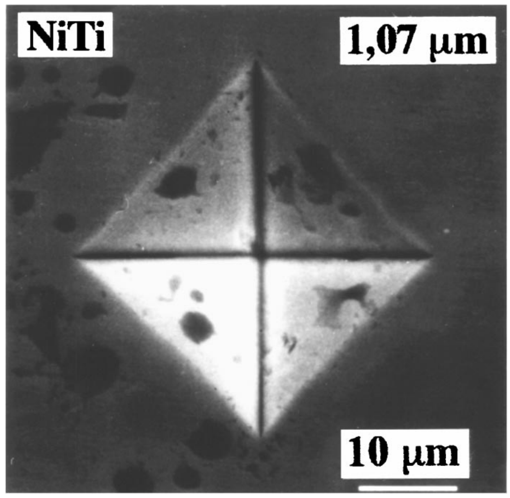
2.3. DIM coating technique

DIM NiTi ($Ni_{55}Ti_{45}$) and SiC ($Si_{58}C_{42}$) coatings, 0.2 to 1.35 μm in thickness, were deposited at room temperature by a sputtering method using a broad beam Ar^{+} ion source of the Kaufman type. During the deposition process, the film was simultaneously bombarded with high energy Ar^{++} ions (320 keV), which were selected and accelerated in an implanter of type "Medium Current Implanter". To ensure good homogeneity of the coating, the cylindrical fatigue specimens were rotated about their axis during the treatment.

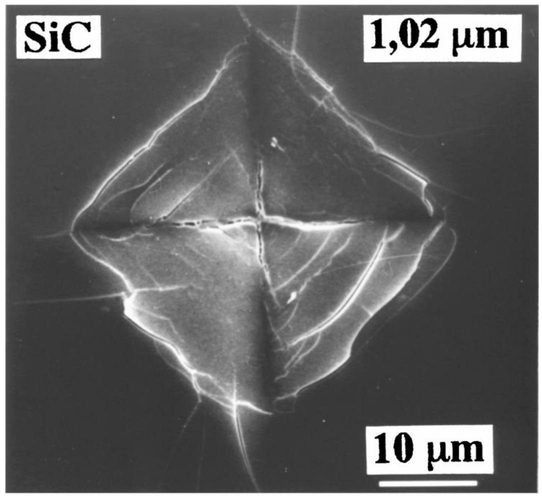
Some characteristics and properties of these thin coatings have been determined previously.

TABLE I Mechanical properties of the two titanium alloys

	TA6V	Ti6246
E (GPa)	123	125.4
E (%)	16	10.1
σ_{YS} (MPa)	975	993
σ_{UTS} (MPa)	1035	1061



(a)



(b)

Figure 1 SEM micrographs of deformation of DIM NiTi and SiC coatings for equivalent indentation conditions. (a) NiTi film 1.07 μm thick; (b) SiC film 1.02 thick.

Transmission electron microscopy (SEM) and secondary ion mass spectrometry investigations have shown that DIM NiTi and SiC films are dense and homogeneous. Both coatings have an amorphous structure [19] with, for SiC coatings [20], some areas exhibiting the first stage of β-SiC nanocrystallization.

Scratch-tests have been applied to characterize the adhesion of NiTi and SiC films. Both coatings remained perfectly adherent to the titanium substrates.

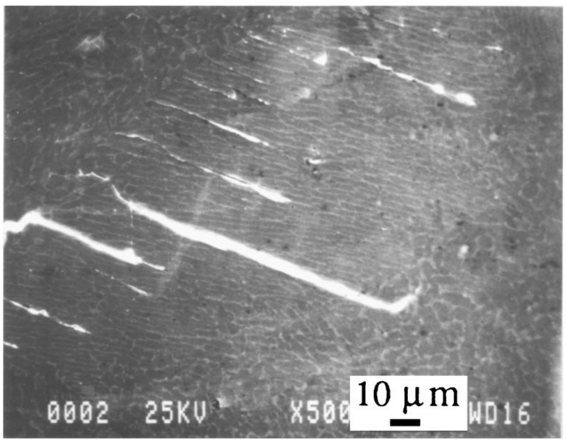
Micro-Vickers indentations have been performed on each coating. The deformation appearance of the indentations and also of the scratch-tracks revealed the good properties of NiTi coatings (ductile and/or superelastic), which were able to accommodate very high plastic deformations of the substrate (Fig. 1a). In contrast, the brittle nature of SiC coatings was revealed (Fig. 1b).

3. Results

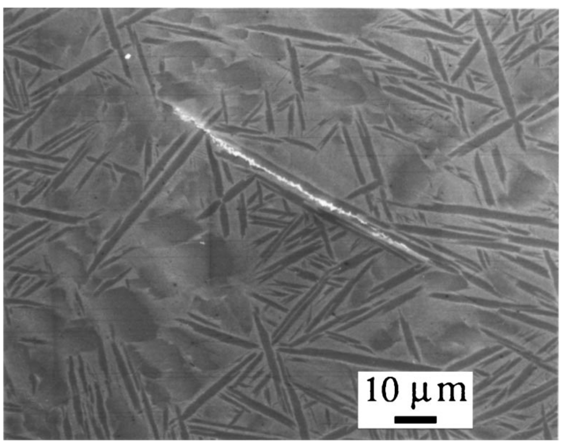
3.1. Cyclic deformation and damage of untreated materials

Ti–6A1–4V titanium alloy was tested under a cyclic stress amplitude of $\Delta\sigma/2 = \pm 750$ MPa ($\simeq 0.75\,\sigma_y$) in air, at room temperature. Under this amplitude, the material was cyclically deformed in the elastic field and the number of cycles at failure was about 5000 cycles. Moreover, regularly interrupted tests and SEM observations of the specimen surface have shown that crack initiation occurs at a number of cycles lower than 10 per cent of the total number of cycles to failure [18]. Consequently, for the testing conditions investigated here, the fatigue lifetime was mainly determined by the duration of the crack propagation stage. The fatigue damage of this alloy was also characterized at failure by a high number of surface-initiated cracks, about 10 cracks per mm^2 for the studied cyclic stress amplitude. Crack initiation sites were localized within the α platelet colonies, either perpendicularly to the α grains or following the α/β interfaces. Rapid subsequent crack propagation occurs within the colonies (Fig. 2a).

For Ti 6246, two cyclic stress amplitudes have been used: $\Delta\sigma/2 = \pm 750$ MPa and ± 850 MPa; the corresponding fatigue life was 12 000 cycles and 4000 cycles, respectively. A regularly interrupted test, at 750 MPa, has shown that cracks appear at half-fatigue life, later than for Ti–6A1–4V, and the total surface crack density at failure was lower (0.8 cracks per mm^2) [21]. For the two investigated stress amplitudes, crack initiation occurs mainly at the α platelets-matrix interface (1–50 μm) accompanied by some extrusion



(a)



(b)

Figure 2 Fatigue crack initiation sites in untreated titanium alloys for $\Delta\sigma/2 = 750$ MPa. (a) within elongated α platelets colonies on Ti6Al4V; (b) at the α platelets-β matrix interface on Ti6246.

emergence (Fig. 2b). The fatigue damage was distributed in accordance with the ex-β grain texture. The same crack initiation sites have been observed for a cyclic stress amplitude of 850 MPa; however, the number of extrusions and microcracks was higher. Therefore, for the same cyclic stress level, the greater resistance of the Ti 6246 alloy compared to the Ti–6A1–4V alloy is due to a higher resistance to crack initiation.

3.2. Characteristics of fatigued NiTi and SiC coated materials

The results for the fatigue lifetime of both treated titanium alloys are given in Tables II and III. These results show that an important improvement of the fatigue resistance can be obtained with thin DIM coatings, especially for the treated Ti 6246. Both NiTi and SiC coated Ti 6246 samples tested under $\Delta\sigma/2 = \pm 750$ MPa have been cycled up to 18 times the reference fatigue life without developing any damage. After obtaining to this beneficial effect on the fatigue life at 750 MPa, subsequent fatigue tests have been carried out under a higher cyclic stress amplitude of 850 MPa. For this amplitude, rupture of the specimen occurred. For the Ti–6A1–4V alloy, the influence of the treatment at $\pm$750 MPa was weaker, since no effect or only small effects on the fatigue life were observed.

In all cases, except for the thickest SiC film, most of the microcrack sites were suppressed. The number of cracks which formed was frequently reduced to only one crack, sometimes accompanied by a few secondary cracks.

For the thin NiTi coatings (0.2 μm), SEM permits us to observe the substrate microstructure through the coating and consequently to detect the first stages of fatigue damage. Fig. 3 shows the nature of the crack initiation sites for the thin NiTi-coated Ti 6246 sample.

TABLE II Number of cycles at failure for the treated Ti–6A1–4V titanium alloy

Coating	Coating thickness (μm)	N_f (cycles)
SiC	0.25	10 800
SiC	1.00	5545
NiTi	0.35	5140
NiTi	1.50	14 400

N_f reference = 5000 cycles ($\pm$750 MPa).

TABLE III Number of cycles at failure for the treated Ti 6246 titanium alloy

Coating	Coating thickness (μm)	$\Delta\sigma/2$ (MPa)	N_f (cycles)
NiTi	0.2	750	160 865[a]
SiC	0.2	750	216 000[a]
NiTi	1.0	850	12 600
NiTi	0.2	850	5600
SiC	0.2	850	9012

[a]Stopped before failure, no surface damage.
N_f reference: (750 MPa) = 12 000 cycles − (850 MPa) = 3900 cycles.

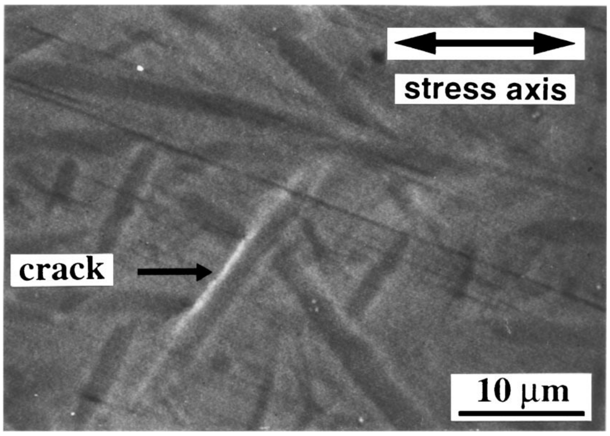


Figure 3 Fatigue crack initiation site at the α platelets-β matrix interface for a Ti6246 sample coated with a thin (0.2 μm) NiTi film after failure at $\Delta\sigma/2 = 850$ MPa.

As in the reference material (Fig. 1b), cracks initiate at the α platelets-matrix interface. The energy of the electrons used in SEM is not sufficient to allow the observation of the substrate deformation state through thick NiTi films after cycling. But no deformation has been revealed on the external surfaces of these films.

For the SiC coatings, fatigue tests results show that thin coatings lead to a great improvement of the fatigue life, even greater than that obtained for thin NiTi coatings. However, the beneficial effect depends on the film thickness. Indeed, the fact that the thickest SiC films are not effective is due to the brittle behavior of this ceramic film, which leads to multicracking at the beginning of the fatigue test. Fig. 4 shows a large number of brittle cracks perpendicular to the stress axis which have revealed after cycling the treated specimen.

In contrast to the fatigue results obtained with the SiC coatings, the fatigue tests carried out on NiTi-treated titanium alloys have shown the thicker the coating, the greater is the improvement of the fatigue life. A similar result had previously been obtained on a 316 L austenitic stainless steel, for which the greatest effect of a NiTi coating on the fatigue life had been observed for the lowest strain amplitude and for the thickest deposit [15].

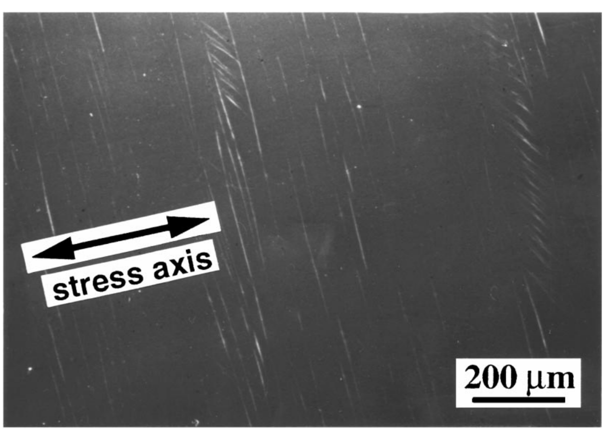


Figure 4 Brittle cracks perpendicular to the stress axis on a thick (1 μm) SiC-coated Ti6Al4V sample observed at failure for $\Delta\sigma/2 = 750$ MPa.

3.3. Mechanical properties of DIM NiTi and SiC coatings

Initial studies have shown that DIM coatings have good adherence to the substrate, which is an essential property for the film to be useful. Knowledge of the mechanical properties of the coating is essential for evaluating the stress and the strain imposed on the coating during the fatigue tests and to explain the fatigue results. Among these properties, the determination of the Young's modulus is of prime importance. For this, we have performed experiments by a resonant frequency technique which has been described elsewhere [22]. This work has shown that the Young's modulus values of NiTi and SiC coatings, at room temperature, are respectively 105 GPa and 235 GPa ($\pm$10%), i.e. twice as low as the corresponding solid materials [23].

The fatigue results have shown that to obtain beneficial effects on fatigue life with this surface treatment, the coating must be able to accomodate the total longitudinal deformation imposed by the cycling without reaching its "breaking point" (appearance of the first microcracks). So, one important mechanical property to be determined is the "fracture stress" of the films. For the brittle SiC coatings in particular, this property must be determined for different thicknesses in order to explain the influence of the thickness on the fatigue results. With this aim in view, tensile tests were carried out using an *in situ* tensile test apparatus in the "Physique des Surfaces" Department of the ETCA. These experiments, performed in an SEM and/or under an optical microscope, permitted a direct study of the deformation mode of NiTi and SiC films. In particular, the load corresponding to the brittle fracture of SiC films was recorded for each thickness. The results showed that the "fracture stress" of the thin coatings was much greater than that of the thick coatings: 1720 MPa instead of 800 MPa [24]. For NiTi films, whatever their thickness, the "fracture stress" was much greater than 830 MPa.

4. Discussion

We have shown that the DIM technique enables us to engineer thin amorphous NiTi and SiC coatings which remain adherent to both titanium alloys during cycling with significant improvement of their fatigue resistance. This fatigue life improvement, which corresponds to an improvement of the crack initiation resistance, depends on different parameters such as the nature and the thickness of the film, the stress amplitude applied during the fatigue test and the substrate deformation characteristics.

The fatigue tests on thick DIM SiC-coated specimens have shown that the "fracture stress" of such films is reached at the start of the tests (first quarter of cycle) leading to a multicracking process. These cracks, which in the first stages occurred only in the SiC coating without penetrating into the substrate, did however destroy the expected beneficial effect of the treatment. Consequently, no improvement of the fatigue life was obtained under these conditions. It must be noted that the Young's modulus of the SiC coating (235 GPa), which was lower than that of the corresponding SiC solid material (440 GPa), remained twice as high as than of the DIM NiTi films. As a consequence, if we consider that the substrate and the coating are cycled in their elastic domain, the stress induced in the SiC film during equivalent fatigue conditions are twice as high as that of the NiTi. The high Young's modulus associated with the brittle character of the SiC coatings is for fatigue applications. However, the fatigue results have shown that the resistance of SiC films depends on their thickness. Indeed, no crack was for the thinnest SiC coating, and in this case a fatigue life improvement was obtained contrary to the case of the thick coatings, which presented a multicracking for the same fatigue conditions.

The Young's modulus and the "fracture stress" values of the SiC coatings, which accordance to their thickness, explain these fatigue results. During the fatigue tests carried out at $\Delta\sigma/2 = \pm 750$ MPa on the SiC coated titanium alloys, the total strain amplitude was of the order of 6×10^{-3} and induced a stress in the film on the order of 1460 MPa. Thus it is clear that the thick SiC films, which have a "fracture stress" of 800 MPa, will fracture in the first quarter of cycle. On the other hand, a thin SiC film tested under the same conditions, which has a "fracture stress" of 1720 MPa, will be cycled in its elastic domain. Consequently, such a thin film may be efficient at prolonging the fatigue life of the titanium alloys.

In contrast, SEM observations of DIM NiTi-coated fatigued specimens led us to conclude that the NiTi films were cycled in their elastic domain. Indeed, generally, no trace of plastic deformation was observed on the coated samples for which the total strain amplitude reached respectively 6×10^{-3} and 6.8×10^{-3} for both stress amplitudes investigated. If we consider that the film is elastically deformed, the value of the longitudinal stresses applied to the coating are lower than those applied to the substrate, because of the lower value of the NiTi Young's modulus (105 GPa instead of 120 GPa for Ti alloys). The low Young's modulus of DIM NiTi films and the "high elastic" and/or ductile properties revealed by Micro-Vickers indentation and scratch-tests are the main reason why these coatings have a high propensity to be deformed under the fatigue conditions investigated here. Thus, it is clear that to obtain maximum reduction of fatigue damage, the film should be able to accommodate the longitudinal deformation induced by the cyclic tension-compression which is imposed on the specimen without reaching its "fracture stress".

Another result was the greater improvement induced by the thin SiC films compared to the effect of the NiTi films, even though both coatings had been cycled in their elastic domain. Such a difference may be attributed to the low chemical reactivity of SiC with regard to environmental effects. Indeed, it has been shown [25] that NiTi films are influenced by the atmospheric environment, since thin NiTi coatings (0.2 μm) lead to a considerable fatigue life improvement in vacuum, but to a negligible effect in air. It seems, with regard to this property, that DIM SiC coatings are more suitable for limiting environmental effects. Therefore, to obtain beneficial effects with such a surface treatment, both the film mechanical properties and its chemical nature must be taken into account. However, to explain the differences in the improvement of the fatigue life which have been obtained for both substrates treated and tested in the same conditions, it is also essential to consider the deformation and the damage modes, which differ from one titanium alloy to the other due to microstructural differences.

The microstructure of the Ti–6A1–4V titanium alloy studied in this work is favorable to a rapid microcrack initiation stage which appears at a number of cycles lower than 10% of the fatigue life. Indeed, trans-or intergranular α/α cracks can initiate easily in the large colonies (300 μm) of aligned α grains in the reference material. This phenomenon is associated with large slip lengths, which facilitate the shearing of the coatings. In contrast, the fine and homogeneously distributed structure of the Ti 6246 alloy is more resistant to crack initiation. The low deformation which appears at α/β interfaces does not lead to the high surface steps which improves the resistance of the coating to shearing. Moreover, the first small cracks which appear at the surface do not initiate before the fatigue half lifetime. The Ti 6246 structure exhibits, therefore, a better intrinsic resistance to crack nucleation, which makes the beneficial effect of the coatings even greater than that obtained on the Ti–6A1–4V alloy. In all the cases, the fine Ti 6246 microstructure leads to a great improvement of the fatigue life, in contrast to the heterogeneously globulized structure of Ti–6A1–4V alloy.

5. Conclusions

Thin amorphous NiTi and SiC films generated via a Dynamic Ion Mixing technique have been used with success to improve the fatigue resistance of Ti–6A1–4V and Ti 6246 titanium alloys in the Low Cycle Fatigue range.

The mechanical properties of the DIM coatings have been characterized and determined by different techniques adapted for the thin film thicknesses (<1 μm). The results of this parallel study allow us to explain some fatigue results and to estimate the applying field of the mixed coatings in terms of fatigue conditions.

It has been shown that significant beneficial effects (fatigue life improved by a factor of 20) can be obtained when a good compromise is reached between the specific mechanical and chemical properties of these DIM films and the deformation conditions imposed on the coating by the cycling and the deformation mode of the bulk material.

For the experimental conditions presented here, improvement of the fatigue life of the titanium alloys has been analysed in terms of decrease of the surface damage and delay in the microcrack nucleation process.

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References

1. J. M. FINNEY and C. LAIRD, *Mater. Sci. Eng*. **54** (1982) 137.
2. U. ESSMANN, U. GOSELE and H. MUGHRABI, *Philos. Mag. A* **44** (1981) 405.
3. W. H. KIM and C. LAIRD, *Acta Metall*. **26** (1978) 789.
4. Y. MAHAJAN and H. MARGOLIN, *Metall. Trans. A* **9** (1978) 427.
5. A. S CHENG and C. LAIRD, *Fatigue. Eng. Mater. Struct*. **4** (1981) 331.
6. J. POLAK, K. OBRTLIK and P. LISKUTIN, in "Basic Mechanisms in Fatigue of Metals," Materials Science Monograph **46**, edited by P. Lukas and J. Polak (Elsevier, Amsterdam 1988) pp. 101–109.
7. H. MUGHARABI, R. WANG, K. DIFFERT and U. ESSMANN, in "Fatigue Mechanisms: Advances in Quantitative Measurement of Physical Damage," ASTM STP 811, edited by J. Lankford, D. L. Davidson, W. L. Morris and R. P. Wei (American Society of Testing and Materials, 1983) pp. 5–45.
8. Y. MAHAJAN and H. MARGOLIN, *Metall. Trans. A* **13** (1982) 257.
9. M. JAULIN, G. LAPLANCHE, J. DELAFOND and S. PIMBERT, *Surf. Coat. Technol*. **37** (1984) 225.
10. J. P. RIVIERE and J. DELAFOND, *Mater. Sci. Forum* **102** (1992) 485.
11. *Idem., Surf. Eng*. **9** (1993) 59.
12. J. P. RIVIERE, *Mater. Sci. Forum* **163** (1994) 431.
13. J. VON STEBUT, J. P. RIVIERE, J. DELAFOND, C. SARRAZIN and S. MICHAUX, *Mater. Sci. Eng. A* **115** (1989) 267.
14. S. PIMBERT-MICHAUX, C. CHABROL, M. F. DENANOT and J. DELAFOND, *ibid*. **115** (1989) 209.
15. P. VILLECHAISE, J. MENDEZ, P. VIOLAN and J. P. RIVIERE, *Nucl. Instrum. Methods* **B59/60** (1991) 837.
16. P. VILLECHAISE, J. MENDEZ and J. DELAFOND, in "Surface Modification Technologies IV," edited by T. S. Sudarshan, D. G. Bath, and M. Jeandin (The Minerals, Metals and Materials Society, 1991) pp. 335–347.
17. S. PERAUD, P. VILLECHAISE and J. MENDEZ, *Mater. Sci. Eng. A* **225** (1997) 162.
18. X. DEMULSANT, L. LEGENDRE and J. MENDEZ, in "Fatigue'93," edited by J. P. Bailon and J. I. Dickson (Engineering Materials Advisory Services Ltd, 1993) pp. 171–176.
19. M. THEOBALT, L. BOURDEAU, T. MAGNIN, J. MENDEZ, P. VILLECHAISE and J. DELAFOND, Rapport de contrat, convention MRT n° 89.P.0477 (1992).
20. J. P. RIVIERE, M. ZAYTOUNI, A. NAUDON, M. F. DENANOT and A. LeROY, *Mater. Lett.* **16** (1993) 79.
21. X. DEMULSANT, PhD thesis, Poitiers, France (1994).
22. P. MAZOT, J. DEFOUQUET, J. WOIRGARD ET J. P. PAUTROT, *J. Phys. III* **2** (1992) 751.
23. S. PERAUD, S. PAUTROT, P. VILLECHAISE, P. MAZOT and J. MENDEZ, *Thin Solid Films* **292** (1997) 55.
24. S. PERAUD, P. VILLECHAISE and J. MENDEZ, to be published.
25. J. MENDEZ, P. VILLECHAISE, P. VIOLAN and J. DELAFOND, in "Corrosion Deformation Interaction'92," edited by T. Magnin and J. M. Gras (Les Editions de Physique, 1993) pp. 741–754.

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