PERGAMON

Scripta mater. 43 (2000) 491–496

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

SUPPRESSION OF FATIGUE CRACKING WITH NANOMETER-SCALE MULTILAYERED COATINGS

M.R. Stoudt*[†], R.C. Cammarata[†], and R.E. Ricker*

*Metallurgy Division, National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce, Gaithersburg, MD 20899-8553 [†]Department of Materials Science and Engineering Department, Johns Hopkins University, Baltimore, MD 21218

(Received March 1, 2000)
(Accepted in revised form May 4, 2000)

Keywords: Fatigue; Multilayers; Plating; Surfaces; Crack initiation

Introduction

Fatigue crack initiation in initially smooth samples of homogeneous ductile metals almost always occurs at the free surface as a result of surface roughening and the development of a critical surface morphology (1–3). For face centered cubic (FCC) metals with high stacking fault energies such as Cu, this critical morphology is the result of irreversible dislocation processes occurring during cyclic slip and consists of notches and peaks (intrusions and extrusions) formed at persistent slip bands (PSBs) (2,4). Recognizing that it should be possible to influence fatigue crack initiation by modifying the properties or microstructure of the surface, investigators have examined the influence of various coatings and surface treatments such as shot peening, anodizing, oxidizing, nitriding, boriding, plasma spraying, ion beam mixing, and ion implanting (5–10). While hard coatings prevent surface roughening and crack initiation by the normal roughening mechanism, they usually result in modest improvements because cyclic loading manages to initiate fatigue cracks by another mechanism. For example, Hornbogen and Verpoort (9) examined the influence of boriding, nitriding, and plasma spraying on fatigue crack initiation in austenitic stainless steels and found that while these coatings suppressed surface roughening, fracture of the films resulted in slip localization and rapid initiation of fatigue cracks which actually degraded performance in some cases (9). Alden and Backofen (5) examined thick anodic films on Al and found that they could extend the fatigue life by periodically treating the surface to remove cracks in the films. This review of the literature (1–13) indicates that a surface film should have five properties to maximize fatigue crack initiation resistance: (i) hardness - to prevent surface roughening, (ii) ductility (toughness) - to prevent cracking where PSBs intersect the film, (iii) cyclic work hardenability - to prevent slip localization, (iv) residual compressive stresses - to reduce the magnitude of tensile stresses in the film, and (v) adherence - to stay on the substrate.

The mechanical properties of nanometer-scale multilayered thin film coatings can be modified and adjusted by changing the composition and thickness of the layers (14–16). As a result, multilayered coatings can be developed that are optimized with respect to the properties identified above as being desirable in a coating for fatigue crack initiation resistance. In particular, a multilayer composed of thin layers of two normally ductile FCC metals may have sufficient hardness to block surface slip yet retain sufficient ductility, toughness, and cyclic work hardening capacity, that cracking of the film or other slip localization mechanisms will not prevent this film from suppressing fatigue crack initiation. The

1359-6462/00/$–see front matter. Published by Elsevier Science Ltd.
PII: S1359-6462(00)00449-8

objective of this research was to test this hypothesis by electroplating a Cu-Ni multilayer on smooth pure Cu fatigue samples and comparing the resulting fatigue life to that of bare electropolished Cu samples and Cu samples plated with a monolithic coating of Cu or Ni.

Experimental

For this work, cylindrical rotating beam fatigue specimens with a gage section 7.3 mm in diameter and 9.5 mm long were prepared from extruded, polycrystalline electronic grade Cu (CDA101) rod stock and given a 2-stage heat treatment (2 h at 260 °C, 0.5 h at 650 °C, air cooled) to yield a strain free microstructure with a nominal grain size of 15 $\pm$ 5 μm. The specimens were mechanically polished to a 4000 grit finish and electropolished in 85% ortho-phosphoric acid. The four surface treatments selected for evaluation of the hypothesis were: (i) bare electropolished Cu, (ii) a 5 μm thick monolithic Ni film with a composition and structure as close to that of the Ni layer in the multilayer as possible, (iii) a 5 μm thick monolithic Cu film also approximating the Cu layer in the multilayer, and (iv) a 5 μm thick Cu-Ni multilayer with equal thickness layers and a composition modulation wavelength (bilayer repeat length) of 40 nm.

The multilayer was electrodeposited on bare electropolished Cu samples starting and ending with a Ni layer from a single, nickel sulfamate-based, plating solution of the type described by Moffat and Searson (17,18). In this approach, both layers are plated from the same solution by switching potential from one where only Cu can deposit to another where both Ni and Cu deposit, but with Cu mass transport rate limited such that an almost pure Ni layer is deposited ($\approx$0.5 atomic % Cu). The thickness of the layers is controlled by measuring the current. A special system was designed to enable deposition of uniform high quality multilayers over the entire gage section of relatively large cylindrical fatigue samples (13). Since the Ni layers in the multilayer will contain a small concentration of Cu and possibly Cu dendrites (13,17,18), the monolithic Ni coating was deposited from the same bath as the multilayer. Since the Cu layer will be essentially pure Cu and the deposition of a 5 μm thick Cu layer at the mass transport rate limiting current of the multilayer plating solution would require a very long plating time, the monolithic Cu coating was deposited from a different electrolyte (1.5 mol/L $CuSO_4$). The quality and uniformity of the deposited layers was evaluated by optical microscopy and only layers that reproduced the microstructure of the substrate, including all grain boundaries and twin boundaries, were used for fatigue testing. The layered structure of the multilayers was confirmed by transmission electron microscopy of a layer cut in cross section after plating on a fatigue sample (13).

The fatigue tests were conducted with a commercial rotating beam bending fatigue machine of a type frequently used for fatigue crack initiation studies (19). In this type of test, a cylindrical sample is placed in 4 point bending and rotated subjecting the surface of the sample to a sinusoidally varying, fully reversed, load cycle. After an initial series of fatigue tests was conducted to establish the fatigue life as a function of stress for bare electropolished copper samples with this grain size (13), a single cyclic stress range in the range where crack initiation dominates fatigue life ($\pm$97 MPa) and loading frequency (15 Hz) was selected for testing the hypothesis. Since the range of scatter in the fatigue lives for a surface treatment might be large compared to any improvement, five samples were tested with each surface treatment at the same cyclic stress range and the results were analyzed by creating a probability-life or Weibull plot of the results by estimating the failure probability from the ordered rank of the results and fitting the probabilities to a Weibull cumulative distribution function (20–24).

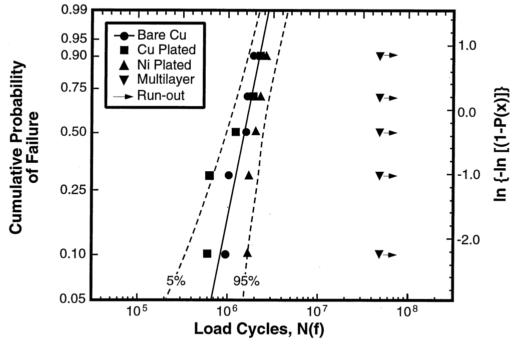

Figure 1. Fatigue results in a Weibull Scale probability-life diagram. The solid line represents a Weibull fit to the bare Cu data and dashed lines represent the confidence interval for fit to the bare Cu data (20–24).

Results

The results of the fatigue experiments are plotted in the probability-life diagram of Figure 1 with the mean of the cycles to failure (N_f) and the standard uncertainty for each condition given in the captions of Figures 2–5. In Figure 1, the solid curve is the Weibull fit to the results for bare Cu and the dashed lines represent the 90% confidence band estimated for bare Cu using the 5 to 95% rank confidence intervals of Little and Jebe (21). Any point inside the interval defined by the two dashed lines is not significantly different from that observed for bare Cu at this confidence level. The monolithic Cu coated samples did tend to fail slightly before the bare Cu samples and the monolithic Ni coated samples tended to last slightly longer than the bare Cu samples. The multilayer coated samples did not fail at this cyclic stress range and a testing time or cycle limit had to be imposed. After examining the mean and standard deviation determined for the other conditions, it was decided that at 5×10^7 load cycles the statistical significance of the results would be unquestionable so this was used as the "run-out" point. While these run-out tests prove that the multilayer improves the fatigue life, it only allows for the observation of the early stages of the fatigue crack initiation mechanism in the multilayer coated system.

Figure 2 is an SEM micrograph of the fatigued surface of one of the bare Cu samples. In this figure, the classic surface morphology of PSBs with notches and peaks as described in the literature for fatigue crack initiation in Cu and other high stacking fault energy FCC materials can be seen (1–3). The surface of a sample coated with a monolithic Cu coating is shown in Figure 3 and while the morphology shown in this figure is not identical to that shown in Figure 2, the differences are due to differences in the

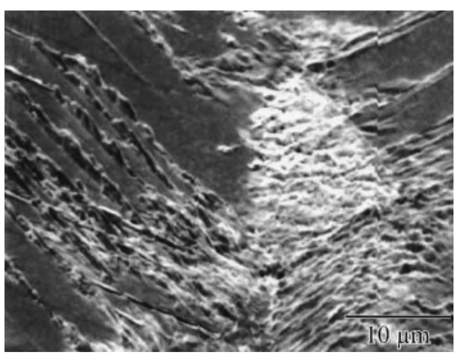

Figure 2. SEM of bare Cu sample after fatigue ($N_f = 1.5\ (\pm 0.5) \times 10^6$ cycles).

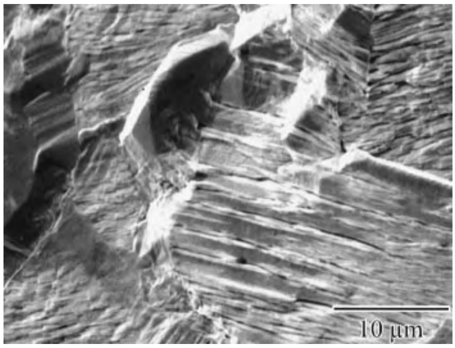

Figure 3. SEM of Cu plated sample after fatigue ($N_f = 1.3\ (\pm 0.7) \times 10^6$ cycles).

crystallographic orientations of the grains shown and not due to any change in the slip behavior. Figure 4 is an SEM micrograph of the surface of a Ni coated sample tested to failure. No evidence of slip could be found in the Ni coatings on these samples. On the other hand, cracking of the Ni layers was observed and the arrow in Figure 4 points to a secondary crack.

Figure 5 is an SEM micrograph of the surface of a multilayer coated sample after fatigue loading to the 5×10^7 load cycles run-out point. There are two significant features shown in this figure. First, there is evidence of slip in the multilayer film, but the quantity and magnitude of the slip steps in the surface are significantly less than those shown in Figures 2 and 3 even though this sample has seen over an order of magnitude more load cycles. Second, there is no evidence of the coating fracture similar to that observed in the Ni coated samples and shown in Figure 4.

Discussion

The fatigue crack initiation mechanism observed for bare Cu in this study is essentially identical to that reported for this material in the literature and the fatigue lives are in the range expected for this grain size (1–3,11). While the monolithic Cu and Ni coatings had no numerically significant influence on the observed fatigue lives, the Cu-Ni multilayer coating resulted in a dramatic improvement in the fatigue lives of the samples. A low stress level where the mean fatigue life would be approximately 10^6 cycles was selected for these experiments because this is where crack initiation resistance is the most significant factor determining fatigue life and where an engineer would design for fatigue crack

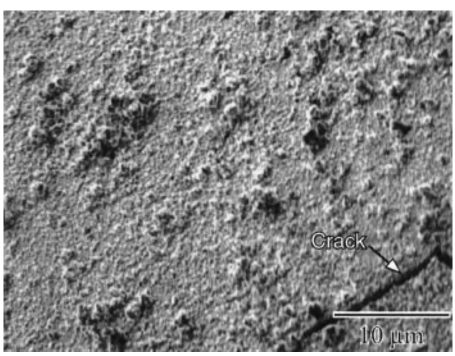

Figure 4. SEM of Ni plated sample after fatigue. ($N_f = 2.0\ (\pm 0.3) \times 10^6$ cycles).

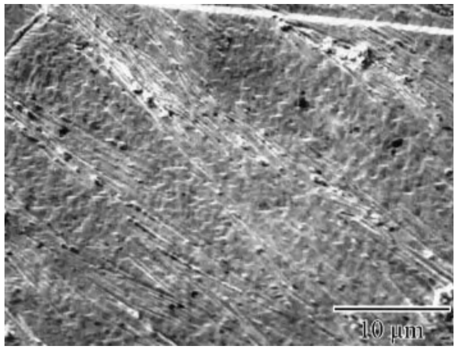

Figure 5. SEM of multilayer plated sample after fatigue. ($N_f > 5 \times 10^7$ cycles).

initiation resistance. Fatigue tests in this cycle regime typically have a large scatter and this is why quantification of the scatter was required, but the magnitude of the improvement provided by the multilayer coating far exceeds that required for significance by any statistical test as indicated by the confidence band in Figure 1 (20–24).

Even though the surface of the multilayer coated sample shown in Figure 5 was subjected to over an order of magnitude more load cycles than the bare Cu sample shown in Figure 2, there is less evidence of slip on the surface of the multilayer. Two types of areas were observed on the surface of the bare Cu samples and both are represented in Figure 2. First, on grains oriented such that multiple slip systems were active, cross slip and work hardening promoted a relatively random and homogeneous slip distribution resulting in a rough surface with a very wavy appearance. On grains oriented such that slip occurred primarily on a single plane, regions essentially free of slip were separated by bands of intense slip activity. These bands contain the deep intrusions which eventually become fatigue cracks. On the multilayer coated samples, a fine distribution of small slip steps was observed as shown in Figure 5. While the multilayer did not completely block slip activity at the surface, it clearly "suppressed" slip activity and it may have promoted a more homogeneous distribution of slip. Since multilayers have yield strengths and hardnesses that exceed their monolithic constituents (14–16), have a modulus which does not deviate significantly from a rule of mixtures (14), and the deposition of a pure Cu layer of the same thickness as the multilayer had no similar effect on slip behavior as illustrated by Figure 3, it is concluded that the hardness of the multilayer is responsible for suppressing slip and preventing fatigue crack nucleation in these samples.

While the hardness of the multilayer is responsible for preventing the normal surface roughening mechanisms of fatigue crack nucleation, numerous investigators have found that applying a hard film and blocking slip at the surface is only successful at preventing fatigue failures if secondary crack initiation mechanisms are also prevented. For example, Hornbogen and Verpoort (9) found that cracking kept their hard brittle films from realizing any significant benefit. Alden and Backofen (5) found that anodic films could extend the fatigue life of Al only if they watched the surface continuously and replaced the film whenever it cracked. Su et al. (25) found that cracking of monolithic and multilayer TiN kept these films from improving the fatigue resistance of a steel. These authors (5,9,25) concluded that the applied load and the stresses imposed by dislocation pile-ups where PSBs intersect the film were sufficient to break these films and nucleate fatigue cracks. In addition, cyclic softening where PSBs intersect a surface film could prevent surface alloying techniques from realizing significant improvements in fatigue resistance (6–8). Several factors could help the Cu-Ni multilayer resist secondary fatigue crack initiation mechanisms. First, since this multilayer is composed of layers of ductile metals, it has enough ductility that brittle fracture should not be a concern. Second, the large number of interfaces in the multilayer form a high surface energy barrier to slip that is not defeated by the passing of dislocations so local cyclic softening should not occur. Third, the interfaces in the multilayer and work hardening should help disperse slip near the surface. And fourth, the residual stresses in the electrodeposited layers may help reduce the magnitude of stresses at critical locations in this microstructure. At this time, the relative significance of each of these is unclear and additional tests are planned to learn more about the role of each factor in helping the multilayer resist fatigue crack nucleation.

Conclusions

The objective of this work was to test the hypothesis that a nanometer-scale multilayered thin film coating composed of two normally ductile FCC metals would significantly extend the fatigue life of a high stacking fault energy FCC metal by suppressing the surface roughening that normally causes fatigue crack initiation in these materials and avoiding the subsequent crack initiation mechanisms that prevent most hard coatings from realizing significant improvements. This hypothesis was tested by electrodepositing a Cu-Ni multilayer on cylindrical Cu fatigue samples which were tested in a rotating beam fatigue testing machine. The results unambiguously demonstrate that the multilayer coating significantly increases the fatigue crack initiation life of a substrate. In addition, since neither of the ductile metals used in the multilayer could induce any significant improvement in fatigue resistance when applied as a single layer with the same total thickness as the multilayer, it is concluded that this improvement is a direct result of the structure and properties of the multilayer.

References

1. T. Thompson, N. Wadsworth, and N. Louat, Phil. Mag. 1, 113 (1956).
2. H. Mughrabi, Scripta Metall. Mater. 26, 1499 (1992).
3. Z. S. Basinski and S. J. Basinski, Scripta Metall. Mater. 26, 1505 (1992).
4. U. Essmann, U. Gösele, and H. Mughrabi, Phil. Mag. A44, 405 (1981).
5. T. H. Alden and W. A. Backofen, Acta Metall. 9, 352 (1961).
6. D. S. Grummon, D. J. Morrison, J. W. Jones, and G. S. Was, Mater. Sci. A. 115, 331 (1989).
7. D. S. Grummon, J. W. Jones, and G. S. Was, Metall. Trans. A. 19, 2775 (1988).
8. D. S. Grummon, J. W. Jones, J. M. Meridon, G. S. Was, and L. Rehn, Phys. Res. B. 19, 227 (1987).
9. E. Hornbogen and C. Verpoort, Advances in Fracture Research, p. 315, Pergamon, Oxford (1982).
10. I. G. Greenfield and A. Purohit, Surface Effects in Crystal Plasticity, p. 609, Noordhoff-Leyden (1977).
11. T. L. Grobstein, S. Sivashankaran, G. Welsch, N. Panigrahi, J. D. McGervey, and J. W. Blue, Mater. Sci. Eng. A138, 191 (1991).
12. R. E. Ricker, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, NY (1983).
13. M. R. Stoudt, Ph.D. Dissertation, John Hopkins University, Baltimore (1999).
14. R. C. Cammarata, Thin Solid Films. 240, 82 (1994).
15. S. A. Barnett and M. Shinn, Annu. Rev. Mater. Sci. 24, 481 (1994).
16. G. S. Was and T. Foecke, Thin Solid Films. 286, 1 (1996).
17. T. P. Moffat, J. Electrochem. Soc. 142, 3767 (1995).
18. P. C. Searson and T. P. Moffat, Crit. Rev. Surf. Chem. 3, 171 (1994).
19. E. J. Czyryca, Metals Handbook, vol. 8, p. 366, ASM International, Metals Park, OH (1985).
20. L. G. Johnson, The Statistical Treatment of Fatigue Experiments, Elsevier, New York (1964).
21. R. E. Little and E. H. Jebe, Statistical Design of Fatigue Experiments, Wiley & Sons, New York (1975).
22. H. A. David, Order Statistics, John Wiley, New York (1981).
23. B. F. Kimball, J. Am. Statist. Assoc. 55, 546 (1960).
24. J. S. White, Technometrics. 11, 373 (1969).
25. Y. L. Su, S. H. Yao, C. S. Wei, W. H. Kao, and C. T. Wu, Thin Solid Films. 338, 177 (1999).