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A novel electrochemical method for visual detection of surface inclusions in metallic substrates

I. RUBINSTEIN*

General Electric Corporate Research and Development, P.O. Box 8, Schenectady, New York 12301, USA

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An electrochemical method is presented for fast and non-destructive detection of surface inclusions in metals and alloys. Using electrode modification techniques, the sample surface is coated with a dark layer; the non-conductive inclusions remain uncoated and thus appear bright and highly visible. The new technique is demonstrated on different alloys with simulated and real inclusions.

1. Introduction

Modern engineering materials are increasingly used in applications requiring higher operating temperatures, higher stresses, and more aggressive environments. As a result, there is an increasing need for the use of materials of the highest possible quality. In particular, knowledge of the number, size, and distribution of surface defects is highly desirable, since such defects are important in establishing the fatigue life of a component [1–2].

In the present publication we wish to report an electrochemical method for detection of non-conductive surface inclusions (e.g., oxides, carbides) in metallic components. The method is fast, non-destructive, and simple to apply. It employs electrode modification techniques [3–5], in this case electrochemical coating of the surface with highly-coloured layers. The inclusions, being non-conductive in nature, are not coated, thus becoming highly visible as bright spots on the dark background. Using this technique, inclusions of *c* 30 μm or larger in diameter can readily be identified visually on the surface.

2. Experimental procedure

2.1. *Materials*

Acetonitrile (Fisher, certified ACS), tetrabutylammonium fluoborate ($TBABF_4$; Southwestern Analytical Chemicals, electrometric grade), and heptyl viologen dibromide (Eastman-Kodak), were used as received. Pyrrole (Aldrich Chem. Co.) was distilled and kept under an inert atmosphere. Samples of Inconel-718† and Rene-95† alloys were obtained from General Electric components.

2.2. *Cell and instrumentation*

The galvanostatic polypyrrole deposition was performed in a simple two-electrode cell, with the sample alloy as the working electrode and a planar Pt foil as the counter electrode. For the potentiostatic heptyl viologen deposition, a saturated calomel electrode (SCE) was used in addition. Instrumentation included PAR model 173 Potentiostat/Galvanostat with model 179 Digital Coulometer, PAR model 175 Universal Programmer, and Hewlett-Packard model 7004B *X–Y* Recorder. IR compensation was applied whenever necessary. A Veeco Inst. Co. sputter apparatus was used for Al_2O_3 sputtering, with an Al_2O_3 target under O_2 gas.

2.3. *Sample preparation*

Square pieces of the alloy were finished to the desired surface condition, which was one of the following: A, highly polished, i.e., with 1.0, 0.3, and 0.05 μm alumina powder, consecutively or

* Present address: Department of Plastics Research, Weizmann Institute of Science, Rehovot 76100, Israel.

† Inconel-718 and Rene-95 are Ni-base superalloys.

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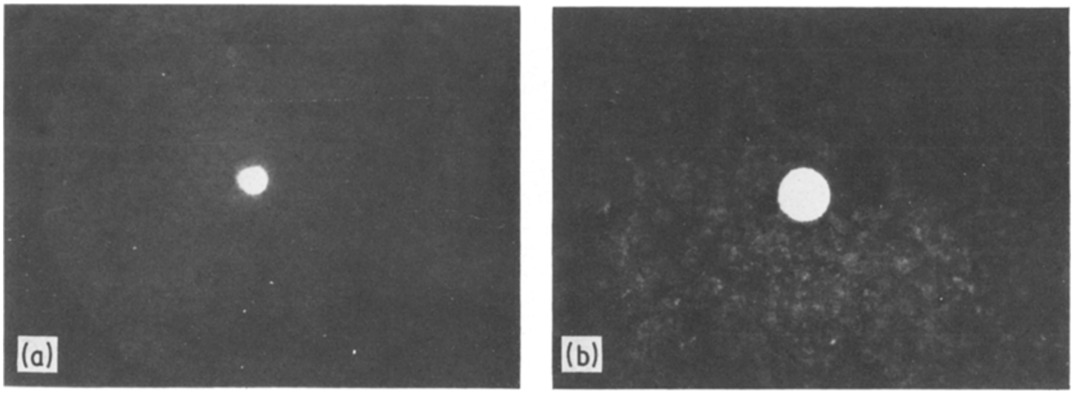

Fig. 1. Optical microscope pictures of Inconel-718 pieces, type A surface finish, (a) coated with polypyrrole film and (b) HV^+Br^- layer. In centre: Sputtered Al_2O_3 inclusions, 30 μm (a) and 60 μm (b) in diameter. (HV^+Br^- photographed *in situ*.)

B, polished with 600-grit silicon carbide paper. The sample was then cleaned with acetone, isopropanol (or trichloroethylene), and distilled water, 10 min each in an ultrasonic bath, and dried. It was then wrapped with Teflon[R]** tape to leave a single exposed surface, and was placed in the electrochemical cell with the working surface parallel to the Pt counter electrode.

3. Results and discussion

3.1. *Coating system*

Very satisfactory results for detection of surface inclusions are obtained by employing polypyrrole deposition. This electrode reaction was first described by Diaz *et al.* [6–8], and later studied [9] and used for protection of semiconductor electrodes toward photocorrosion [10–13]. For the present application, polymerization/deposition was performed by generally following the literature procedure [6–8], in an acetonitrile solution containing 0.25 mol dm^{-3} $TBABF_4$ and 0.25 mol dm^{-3} pyrrole. Application of a constant current of 1.2 mA cm^{-2} for 2.5–3.5 min with the sample as the anode results in deposition of a continuous, adherent, black polypyrrole film on the sample surface. Any natural or simulated inclusion (see below) appears as an uncoated, bright spot on the black background. Coated samples can be rinsed, dried and stored, if desirable.

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3.2. *Coating experiments*

In order to establish the reliability of the method, experiments were carried out on two types of samples:

1. Inconel-718 with simulated inclusion. Artificial oxide inclusions were successfully implanted on the surface of Inconel-718 pieces by sputter-deposition of Al_2O_3. An aluminium mask with small holes was placed on the surface of the substrate during sputtering, to produce six oxide spots ranging in diameter 30–280 μm. The oxide thickness was 15.0 nm, which is within the range of the surface roughness. Sputtered samples were subsequently subjected to the cleaning and coating procedures; typical results are presented in Figs. 1 and 2. The blank sample in Fig. 2 is entirely coated with a black, continuous film, whereas the oxide inclusions are clearly visible on the sputtered piece, down to the smallest size, with high resolution and contrast. The same results are obtained with both type A or type B surface finish.

2. Doped Rene-95 samples. Rene-95 with bulk Al_2O_3 inclusions of known size range were prepared using powder-metallurgy techniques by pre-mixing oxide particles with the alloy powder during processing*. Pieces of doped Rene-95 were polished, cleaned, and coated with polypyrrole, to produce results of the type

* Doped Rene-95 samples were supplied by Dr R. L. Fullman, General Electric Research and Development Center.

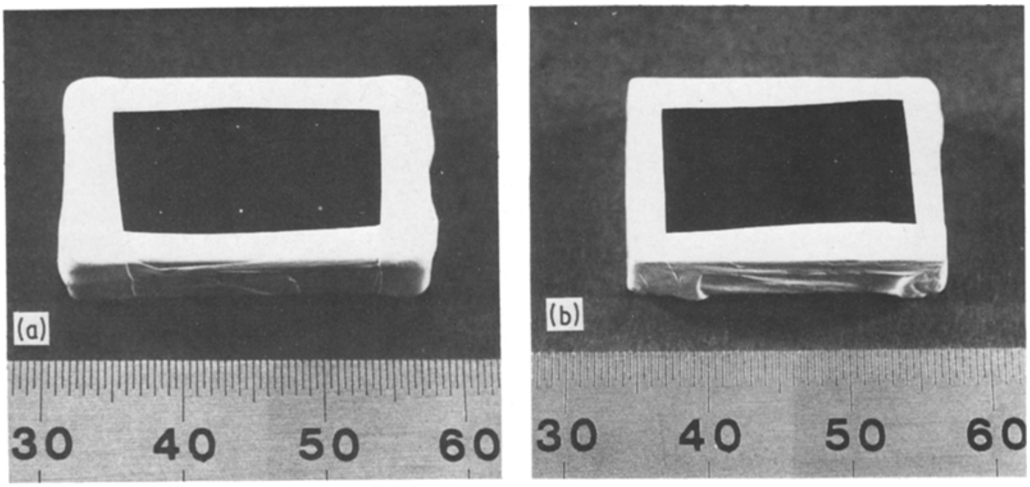

Fig. 2. Polypyrrole-coated Inconel-718 pieces, type A surface finish. (a) With six sputtered Al_2O_3 inclusions. Inclusion diameter, in μm: 280 (lower, right), 200, 120, 90, 60, 30 (upper, left). (b) With no sputtered inclusions. (Scale in mm.)

presented in Fig. 3. Again, the surface inclusions are clearly visible to the naked eye.

3.3. *Alternative systems*

While the best results were obtained with polypyrrole coating, other systems were also examined. For example, good inclusion detection was demonstrated with heptyl viologen (N,N′-diheptyl-4,4′-bipyridinium ion, or HV^{2+}). Upon electrochemical reduction of the 2^+ ion in aqueous KBr solution, a dark-purple layer of the water-insoluble HV^+Br^- is deposited on the electrode surface [14]. In our case, alloy samples were immersed in an aqueous solution of 0.2 mol dm^{-3} KBr and 0.01 mol dm^{-3} HV^{2+} dibromide, and negatively polarized at -0.65 volt (v. SCE) for 10–30 s. Good visibility of the bright surface inclusions on the dark-purple HV^+Br^- background was obtained, as exemplified in Fig. 1. A possible disadvantage of this system, however, is that the coating must be observed *in situ*, since exposing the sample to air causes fast oxidation of the coating and disappearance of the colour.

4. Conclusions

We have demonstrated that high-quality visual detection of non-conductive and small surface

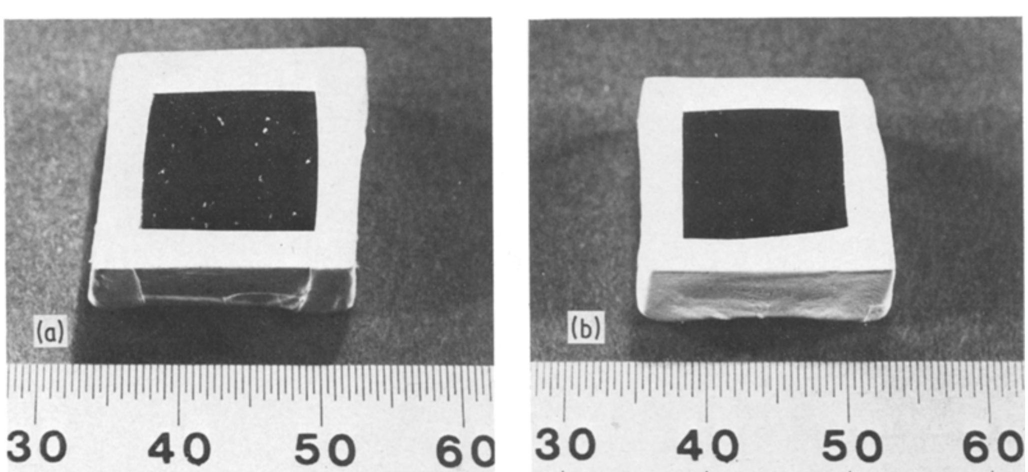

Fig. 3. Polypyrrole-coated doped Rene-95 pieces, type B surface finish. Average inclusion diameter, 270 μm (a); 160 μm (b). (Scale in mm.)

inclusions in metals and alloys can be achieved non-destructively by employing electrochemical techniques. Anodic polymerization of pyrrole results in deposition of a black polypyrrole film on the sample, in which the inclusions appear as highly-visible bright spots. Flaws as small as 30 μm were shown to be readily detectable. The method is fast, reproducible, easy to apply, and can be used with different types of surface finish. It is also highly suitable for automation, using computerized optical detectors.

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